Contribution to the study of Boiling Liquid Expanding Vapor Explosions and their mechanical effects

by

Behrouz Hemmatian

A Doctoral Thesis submitted in partial fulfilment of the requirements for the award of Doctor of Philosophy in Chemical Engineering

Thesis supervisors:

Dr. Joaquim Casal Fàbrega Dr. Eulàlia Planas Cuchi

Universitat Politècnica de Catalunya
Barcelona, Catalonia, Spain

July, 2016

Abstract

Boiling Liquid Expanding Vapor Explosions keep occurring from time to time in process plants, storage areas and transportation by road or rail, often with severe effects. There is no doubt that a better knowledge of their main features will help in decreasing both their frequency and their consequences.

This is the main aim of this thesis: the analysis of the main causes of BLEVEs, the improvement in the prediction of their effects and consequences and, finally, the definition of simple measures to be applied in the management of emergencies associated to these events.

Historical analyses have been performed to determine the prevalence of BLEVEs among all major accidents in fixed plants and in the transportation of hazardous materials, as well as their main causes; the action of fire as domino effect escalation has also been studied, with special attention to the time to failure of a vessel in such a situation.

The different existing methodologies for the estimation of the peak overpressure are presented and compared, and the diverse uncertainty factors affecting the prediction of BLEVE mechanical effects are analyzed.

A new and relatively simple methodology has been proposed to predict the blast effects of these explosions, which allows a quick and accurate estimation. Finally, based on all these analyses, simple emergency management measures are proposed which could reduce significantly the consequences of BLEVEs on people.

Resum

Encara avui, en plantes de procés, àrees d'emmagatzematge o en el transport per carretera o ferrocarril, de tant en tant es continuen produint les explosions anomenades BLEVE (*Boiling Liquid Expanding Vapor Explosion*, en català explosió del vapor en expansió d'un líquid bullent), sovint amb efectes molt severs. No hi ha cap mena de dubte que conèixer millor les principals característiques d'aquestes explosions permetrà reduir-ne tant la seva freqüència com les seves conseqüències.

Aquesta és precisament la principal finalitat d'aquesta tesi: l'anàlisi de les causes principals de les BLEVEs, la millora en la predicció dels seus efectes i conseqüències i, finalment, la definició de mesures que siguin senzilles d'aplicar quan es produeixen emergències associades a aquest tipus d'esdeveniment.

S'han dut a terme anàlisis històriques per a determinar la prevalença de les BLEVEs d'entre tots els accidents greus que es poden produir en instal·lacions fixes i durant el transport de mercaderies perilloses, així com també per a determinar-ne les causes principals. També s'ha analitzat l'acció que exerceix el foc com a element desencadenant d'efecte dominó, fent especial atenció al temps que trigarà un dipòsit en esclatar quan es veu sotmès a la seva acció.

També es presenten i comparen les diverses metodologies existents per a l'estimació del pic de sobrepressió produït en una BLEVE, i s'analitzen els diversos factors d'incertesa que afecten la predicció dels efectes mecànics generats en una BLEVE.

S'ha presentat una metodologia nova i relativament simple per predir els efectes d'aquest tipus d'explosions, que permet fer estimacions ràpides i acurades. Finalment, en base a totes aquestes anàlisis, s'han proposat mesures senzilles per a la gestió d'aquest tipus d'emergències que poden ajudar a reduir significativament les conseqüències de les BLEVEs sobre les persones.

Acknowledgements

The day that I decided to leave home and continue my study abroad, I would never imagined to what extent this way could be combined with sweet experiences for me. In the beginning, the goal of leaving home was to study and become familiar with people from different parts of the world and their cultures. Not only I could achieve the anticipated goals, but also I could gain valuable experiences by knowing different people and their respectful cultures. The role of Barcelona (Catalonia) was important and undeniable. Therefore, I would like to express my gratitude to those who always supported me during these years and helped me to make my wishes come true.

During my stay in Barcelona, I had a great chance to know a kind, honest and responsible gentleman, Professor Joaquim Casal. It was my honor to have him as the supervisor of my PhD thesis. Not only I could learn from him many things related to my studying field, but also he taught me many useful lessons for life. Despite his high academic achievements, he always behaved me with modesty. I would like to send my sincere gratitude to him. I also want to thank my supervisor, Professor Eulàlia Planas. She is a clever and diligent lady who always guided and taught me new concepts in my field of study while doing my PhD. As a leader of CERTEC, she always supported me and managed the team in a way that I always felt as a member of it. I also acknowledge with gratitude Professors Pastor and Arnaldos, who were always kind and ready to help me.

The first challenge in my life was not to travel and live abroad. In fact, the main challenge in my life had started earlier. I could pass that challenge successfully due to the unconditional support and devotion of my dear parents, Hossein and Haedeh. During all the difficult moments, they were a source of hope for me and motivated me to have big wishes. They also supported me every day and every moment while I was living and studying abroad. I would like to express the deepest appreciation to them. Moreover, I extend my sincere thanks to my lovely brother, Behnam, who is my best friend, great supporter and big guide in my life. He was always with me when I needed a friend to talk. Additionally, I thank my dear grandmother, Molouk, who was the source of positive energy for me and was my strength in times I needed motivations and helping hand. Living abroad let me know the value of family more than before, and be proud of having such a precious family.

I had the opportunity to know lovely persons while doing my PhD in Barcelona and UPC. Professor Darbra was one of them. She is a kind lady who always supported and helped me, her character and behavior impressed me. I am thankful for all her supports and kindness. I also owe a gratitude to my lovely friends, Martí Puig, Ariadna Sans and Diana Tarragó for everything they have done for me. They were with me when I really needed help and support. In addition, I would like to thank Miguel Muñoz, Giovanni Ramírez, Oriol Rios, Mario Miguel Valero, Borja Rengel, Christian Mata, Xavier Seguí, Jose

Roberto Gonzalez Dan, Esteban Bernechea, Diana Villafañe, Adriana Miralles Schleder, Alan Guix, Ignacio Montero and all of my friends and colleagues in CERTEC, who helped and supported me during my stay in Barcelona. I should also send my gratitude to Ms. Irene Perez for all her helps and supports. And, finally, I thank UPC for its welcome and support.

Table of contents

Chapter 1. INTRODUCTION

1.1 Risk and industrial activities

There is no doubt that industry –and, more specifically, chemical industry– has implied a significant improvement in human life. It has given us fuels, medicals, paintings, detergents, insecticides, etc. Thanks to all these products, life expectance in industrialized countries has improved continuously in the last decades.

Nevertheless, it is also true that with the industry and its related activities –including process plants, storage areas, transportation of hazardous materials– new risks have also appeared. New severe accidents –the so-called major accidents– have occurred, associated to them: fires, explosions, toxic releases. The consequences of these accidents can reach distances beyond the contour of the industrial plant or far from the transportation path. Even though both the industry and the administration realized this very soon, and regulations were issued and appropriate measures were taken in most industrialized countries, it is a fact that from time to time severe accidents occur. Process industry grew significantly after the Second World War and, with it, the storage and transportation of dangerous goods continuously increased. Due to these factors, the frequency of industrial accidents also increased, especially in developing countries. The effort to improve the safety of industrial activities must therefore continue to decrease, as far as possible, their risk.

It is a fact that the risks to which people are subjected have changed significantly with the industrialization of society: some of them have practically disappeared and some new hazards have appeared.

Everybody understands what “risk” means. However, to analyze it, a strict definition allowing its quantification is required. Among the diverse definitions proposed, this one is nowadays the most widely accepted:

$$Risk = frequency\ of\ an\ event \times magnitude\ of\ its\ consequences$$

A quantitative assessment of risk implies, according to this definition, the knowledge of the frequency with which a given event will occur and the estimation of its consequences on people, environment and equipment if it occurs. Both variables can be predicted but, even if a significant effort has been devoted to this field, this prediction implies still a significant error in some cases. The essential aspects of certain accidents are not sufficiently known and the frequency with which they could happen depends on many circumstances. As a whole, the analysis of the risk associated to a given installation or activity involves nowadays a significant uncertainty. This is why an effort must be done to improve our knowledge on major accidents, on their main features, on their physical effects and consequences and, even, on their expected frequencies.

The aim of this thesis is to contribute to the knowledge of one of the most severe major accidents that, unfortunately, occur from time to time: the BLEVE, a mechanical explosion that often is coupled with a thermal phenomenon, the fireball.

1.2 Major accidents

Industrialization has had a tremendous effect in everyday life. Even if its main aim is to make human life easier and safer, some problems and undesired events can unfortunately happen. These problems sometimes show themselves as steady state polluting situations, sometimes as accidents which can have consequences on people, equipment and environment.

Based on the extent of those accidents, they can have different effects on their surroundings. Specifically, the occurrence of major accidents is possible in chemical plants and also during transferring, transporting and storing of hazardous substances. Some of those accidents have had inevitable effects on people and on the surrounding environment. Moreover, a few of them, because of their specific characteristics and severe consequences, caused fundamental changes in legislation and in safety culture. Major accidents such as those of Flixborough (1974), Seveso (1976), San Juanico (1984) and Bhopal (1984) had an important impact and, as a consequence, a significant effort was done in industrialized countries to improve the safety of certain plants and activities.

The definition and main features of major accidents is discussed here, with a special emphasis on their main effects (thermal radiation, overpressure and dispersion of toxic compounds).

Major accidents can be defined in different ways. An official one is that contained in the Council Directive 2012/18/EU on the control of major-accident hazards involving dangerous substances (also known as the Seveso III Directive):

"*An occurrence such as a major emission, fire, or explosion resulting from uncontrolled developments in the course of the operation of any establishment (this defined as the whole area under the control of an operator where dangerous substances are present in one or more installations, including common or related infrastructures or activities), and leading to serious danger to human health or the environment, immediate or delayed, inside or outside the establishment, and involving one or more dangerous substances*"

Furthermore, Meyer and Reniers (2013) proposed the following definition:

"A major accident (disaster) as an event that is brutal and sudden and of an enormous dimension. It has severe consequences that are accompanied by destruction of goods and/or deaths"

Indeed, the release –instantaneously or over a short period of time– of a significant amount of energy or hazardous materials is closely associated to the occurrence of major accidents. Consequently, thermal (thermal radiation), mechanical (blast and ejection of fragments) and chemical (release of toxic material) effects are the dangerous phenomena following such accidents. These phenomena can have an effect on people, property and environment.

Besides the direct effects, people can be psychologically harmed. Furthermore, equipment and buildings can be badly damaged in the occurrence of a major accident. Additionally, the release of hazardous materials into the soil, water or the atmosphere can imply another impact on the surrounding environment. Finally, a major accident can have an effect on intangible assets (e.g., brand) of the company involved.

The occurrence of such accidents is associated to the release, often instantaneous or in a short time, of a hazardous substance or of energy. If this occurs, the evolution of the risk situation will depend on the meteorological conditions, on the amount of substance released and on the distance to the vulnerable targets. The diverse possibilities have been plotted, in a simplified scheme, in Figure 1-1 (Casal, 2008).

There are various possible scenarios. When a hazardous substance is released, its physical condition (liquid, gas or vapor, particulate solid or two-phase mixture) is an important factor to define the evolution of the event.

The spilled hazardous material can penetrate into the soil if it is in liquid phase; this can imply ground water contamination and soil pollution. This scenario happens in the absence of any concrete layer, when the spilled liquid can contact directly to the soil. On the other hand, contact of the spilled liquid with surface water can cause water pollution. In both cases, if a pool is formed (in the case of a spill on water, when both liquids are immiscible), the evaporation of the substance may happen.

If a released liquid originates a pool, a pool fire can emerge in presence of an ignition point if the material is flammable. The smoke of pool fire is sooty and possibly toxic in the case of a toxic material. Nearby equipment can be affected by intense thermal radiation of the pool fire. When there is no immediate ignition, the formation of a toxic or flammable cloud will be possible. If that flammable cloud meets an ignition point later on, a flash fire will be possible and an explosion can also occur, depending on the amount of material in the cloud and the confinement degree.

The evolution of a toxic or flammable cloud depends on the wind and on the meteorological conditions. A toxic cloud can have potential dangerous effects on people in the affected area. A vapor cloud is also likely to be generated from released material in liquid-vapor state (two-phase flow, usually from the release of a hot and pressurized liquid). Because of the evaporation of liquid droplets, the volume and concentration of the vapor cloud can be increased.

The speed of the material released in gas-vapor state is an important factor for predicting the further scenarios. In the case of low-speed exit, the formation of a cloud is probable. On the other hand, releasing of the material at high speed (often the sonic one) will only cause atmospheric dispersion, due to the strong turbulence of the jet and the associated entrainment of air, which dilutes the release. However, if the substance is flammable, a jet fire can occur, with a strong thermal flux.

Dust or dispersed fine particles have a potential to cause an explosion inside its container or inside a building. Due to the confinement, such explosion can have very severe effects, damaging a significant area. If fine powders are released into the atmosphere, and depending on the prevailing atmospheric conditions, a toxic cloud can be originated (for example, a released of soybean dust can give rise to allergic effects on population, as happened years ago in the Barcelona port).

Finally, a container or vessel –a tank, a reactor, etc.– can explode if the pressure inside it exceeds a certain value (e.g. it exceeds the design pressure of the vessel) or if the container fails by an impact (for example, in the case of a road accident), or the vessel is engulfed by fire and loses its strength as a result of the wall heating. The blast and ejection of the fragments are the possible effects of such explosion (often called a BLEVE). Moreover, if the contained liquid is flammable, the explosion is usually followed by a fireball.

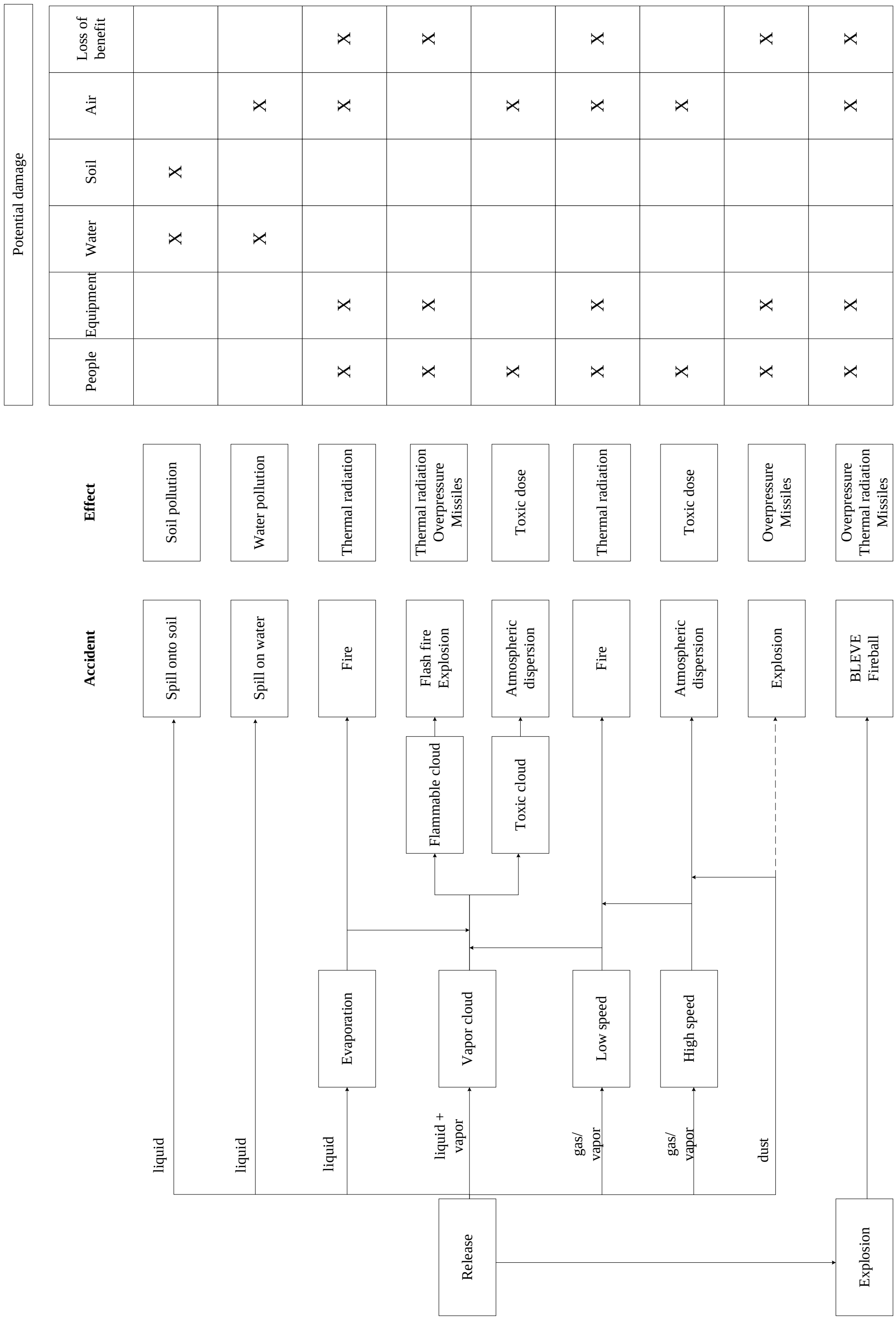


Figure 1-1.Major accidents: simplified schema (modified from Casal (2008)).

These accidents occur from time to time, both in fixed plants and in the transportation of hazardous materials.

1.3 What is a BLEVE?

Even though a BLEVE is a very severe accident, it is still insufficiently known. In this section, the definition of this phenomenon is presented.

BLEVE is the acronym of "Boiling Liquid Expanding Vapor Explosion", proposed by Walls, Marsh and Smith in 1957 to define a certain type of vessel explosion. These authors coined this acronym during their investigation about the explosion of a vessel containing formalin and phenol. They defined this type of explosion as (Abbasi and Abbasi, 2007b):

"The failure of a container occurring at a moment when the contained liquid is at a temperature well above its boiling point at atmospheric pressure".

A BLEVE is therefore a physical explosion, and not at all a chemical one (Abbasi, Pasman, Abbasi, 2010). The effects of BLEVE accidents could be categorized in three groups:

1. blast overpressure
2. fragments ejected
3. fireball (if a flammable substance is involved) and thermal flux.

However, even though this first definition was quite adequate, other definitions were proposed later on by different authors. Some of these definitions have been summarized in Table 1-1 and will be analyzed deeply in Chapter 4.

Table 1-1. BLEVE definitions proposed by different authors

Date	Author	Definition
1957	J.B. Smith, W.S. Marsh and W.L. Walls	The acronym BLEVE was coined in 1957 by three Factory Mutual Research Corporation workers J.B.Smith, W.S.Marsh and W.L.Walls. They had analyzed the likely of failure of a vessel containing an overheated mixture of formalin and phenol, and had believed that the container had suffered a "boiling liquid expanding vapour explosion" (Abbasi et al., 2007b).
1979	R.C. Reid	Reid defined BLEVE as "the sudden loss of containment of a liquid that is at its superheated limit temperature" (Reid, 1979).
1978	W.L. Walls	A failure of a major container into two or more pieces, occurring at the moment in time when the contained liquid is at a temperature well above its boiling point at normal atmospheric pressure (Walls, 1978, 1979).
1991	I.R.M. Leslie and A.M. Birk	The BLEVE is usually associated with a large explosive release of a LPG. The explosive part of the release is caused by a very rapid phase change from liquid to vapor. A BLEVE does not necessarily involve a fireball (Leslie and Birk, 1991).
1993	J.E.S. Venart, G.A. Rutledge, K.	Simple "BLEVE" experiments have revealed the existence of a loss of containment event we call a Boiling Liquid Compressed Bubble

Date	Author	Definition
	Sumathipala and K. Sollows	Explosion,"BLCBE". Such an event is more powerful than the BLEVE and is at an extremum of failure types that range from it to the BLEVE and ultimately down to those which result only in the expulsion of their contents as a flashing two-phase jet. All the events and their interrelationships are obviously very complex and have many interacting dynamic components. The generic features of the BLCBE consist of: 1. Partial failure of the containment vessel. 2. Multiple bubble initiation, and growth in a prenucleated bulk liquid. 3. Rapid two-phase swell, repressurization and coherent collapse of the bubbles formed. 4. Bubble collapse shock pressure failure of the previously damaged vessel. 5. Violent distribution of the compressed two-phase contents as extremely fine evaporating aerosol with significant blast, and 6. If contents are flammable, the potential for a detonation. Obviously, as the contents of such vessels approach the superheat limit, even more powerful events are possible (Venart, Rutledge, Sumathipala, Sollows, 1993).
1996	A.M. Birk and M.H. Cunningham	A BLEVE is a physical explosion that follows the sudden loss of containment of a LPG. When an LPG experiences a sudden pressure drop (due to loss of containment, for example) the bulk of the liquid is sent into a state of superheat. If the degree of superheat is large, it causes violent flashing of the liquid which can be explosive. Generally speaking, a large degree of superheat requires a very rapid pressure drop (Birk and Cunningham, 1996).
2004	E. Planas-Cuchi, J.M. Salla and J. Casal	BLEVEs occur when a tank containing a pressurized liquid is heated, for example, due to a fire. As pressure increases, a condition is reached at which the walls of the container (whose temperature has been increasing, especially in the upper part where the liquid is not in contact with them) can no longer withstand the pressure and the vessel bursts. At the moment of failure, due to the instantaneous depressurization, the temperature of the liquid will be higher than that which would correspond to it according to the saturation curve on the P–T diagram: the liquid will be superheated. If the liquid temperature in the instant of the depressurization is higher than the ‘‘superheat temperature limit’’ (which is different for each substance), a violent and instantaneous flash of a fraction of the liquid will occur and a superheated liquid vapor explosion will take place (Planas Cuchi , Salla , Casal 2004b).
2004	A.C. van den Berg, M.M. van der Voort, J. Weerheijm, and N.H.A. Versloot	A BLEVE, the acronym for boiling liquid expanding vapor explosion, is the consequence of the rupture of a pressure vessel containing a liquefied gas. If the liquid pressure suddenly drops, as a result of a sudden rupture of the vessel, a fraction of the liquid will quickly evaporate. The evaporation process extracts heat from the liquid by which the temperature and the vapor pressure of the liquid fall. The evaporation continues until the liquid temperature has fallen to the boiling temperature at atmospheric pressure and, consequently, the vapor pressure has fallen to atmospheric pressure. The quick phase change from liquid to vapor goes hand in hand with the increase of a large volume. One cubic meter of liquid propane, for instance, gives rise to about 260 cubic meters vapor under atmospheric conditions. The volume of vapor pushes the surrounding

Date	Author	Definition
		air aside, which produces a blast wave. The blast wave may do damage up to a substantial distance in the environment (van den Berg, van der Voort, Weerheijm, Versloot, 2004).
2007	A.M. Birk, C. Davison and M.H. Cunningham	A BLEVE is the explosive release of expanding vapor and boiling liquid when a container holding a LPG fails catastrophically (Birk, Davison, Cunningham 2007).
2010	S. M. Tauseef, T. Abbasi and S. A. Abbasi	If a container with a LPG suffers structural failure –be it due to creep, fatigue, or fire-induced or any other form of failure– it may lead to a sudden depressurization of the container. As a result, the LPG will suddenly be transformed into a fluid, which is superheated with respect to the precipitously lowered pressure. Depending on the nature of the chemical, quantity of superheated liquid present, and the mechanism of the container failure, such a situation can lead to instantaneous and violent vaporization of the contents, causing a boiling liquid expanding vapor explosion, a BLEVE (Tauseef, Abbasi, Abbasi, 2010).
2010	CCPS	BLEVE is defined as a sudden loss of containment of a pressure-liquefied gas existing above its normal atmospheric boiling point at the moment of its failure, which results in rapidly expanding vapor and flashing liquid. The release of energy from these processes (expanding vapor and flashing liquid) creates a pressure wave. A BLEVE requires three key elements: • A liquid that exists above its normal atmospheric pressure boiling point • Containment that causes the pressure on the liquid to be sufficiently high to suppress boiling • A sudden loss of containment to rapidly drop the pressure on the liquid (CCPS, 2010).

Some of these definitions are somewhat restricted, as they impose the condition of reaching the superheat limit temperature or they refer specifically to pressure-liquefied gases.

As a summary of aforementioned definitions, we can conclude that nowadays the following definition could be a more general and correct one, being in practice widely accepted:

"A BLEVE is the explosion of a vessel containing a liquid (or liquid plus vapor) at a temperature significantly above its boiling temperature at atmospheric pressure". (Hemmatian et al., 2016)

1.4 Substances that can originate a BLEVE

There is some confusion on this point, as some people believe that only flammable substances (which can give rise to a fireball) can undergo a BLEVE. But really, practically all liquids, reaching certain storage conditions, can undergo a BLEVE. By looking at the preceding definitions, LPG (Liquefied Petroleum Gas) leads to the instantaneous generation of a gas phase in the event of a sudden pressure drop (depressurization). It should be noted that the pressurized liquefied gases have usually atmospheric boiling temperatures lower than ambient temperature. For instance, light hydrocarbons (such as propane, ethane and butane), refrigerants and ammonia, belong to this group. However, this does not mean that other types of substances which have atmospheric boiling temperatures higher than ambient temperature could not undergo a BLEVE. Indeed, their boiling temperatures will be going beyond the normal atmospheric boiling temperature if they are exposed to thermal heating in a closed vessel. Water and heavy hydrocarbons are some examples of this kind of liquid (Abbasi et al., 2007b; CCPS, 2010). In fact, the explosion of a steam boiler is usually a very strong BLEVE, due to the high enthalpy content of water.

Concerning LNG, there are various views about the BLEVE probability. Venart (2005), an author with a considerable experience in this field, mentioned that an LNG BLEVE is possible even if the probability of occurrence is low. For corroboration of this statement, he presented one LNG accident in Spain which had been reported by Planas-Cuchi et al. (2004a). In contrast, some other researchers like Napier and Roopchand (1986), Bernatik et al. (2011) and Pitblado and Woodward (2011) refuse the credibility of BLEVE accidents with LNG; they believe that an LNG BLEVE is improbable because of the following reasons:

– LNG outer tank and insulation prevent heat transfer from a fire to main tank
– LNG tanks are designed to work at relatively low operating pressures.

However, most of those articles in which were denied the possibility of an LNG BLEVE, accepted the road tanker accident occurred in 2002 (Planas Cuchi et al., 2004a) as a BLEVE phenomenon.

1.5 The significance and prevalence of BLEVEs

Studies in the field of BLEVE phenomenon are essentially based on their effects and the corresponding consequences, which can be very severe. Diverse authors have performed scientific works and published papers in this field. Reid (1979) presented the definition for BLEVE and introduced the possible mechanism for it. Walls (1978, 1979) also worked on this phenomenon and gave his definition for that phenomenon in order to figure out what kind of an accident could be considered as a BLEVE. Later on, Birk et al. (1996; 1996; 2007; 1993; 2009) investigated about that phenomenon by doing interesting experiments and simulations. Their works focused on fired BLEVE and resulting blast. Several authors used their experimental data in order to predict the BLEVE consequences. Abbasi et al. (2007a , 2007b) published a review article about the BLEVE mechanism and its consequences assessment and management, and they defined a framework for superheat limit temperature (T_{sl}). Casal (2008, 2013) and Casal and Salla (2006) studied BLEVE definitions, mechanism, its consequences, and possible approaches for mitigating and managing its risk. They introduced a new approach for predicting BLEVE mechanical energy and resulting blast by using a definition of liquid superheating energy. Additionaly, Salla et al. (2006) proposed a physical explanation for the concept of the superheat limit temperature (T_{sl}). Planas-Cuchi et al. (2004a , 2004b) studied BLEVE mechanical energy by assuming real gas behavior and adiabatic irreversible expansion. They believed that the previous studies in this field were based on thermodynamic assumptions which caused a significant overprediction in the assessment of BLEVE consequences; they also reported and analyzed two LNG BLEVE accidents. CCPS (2010) devoted one chapter to BLEVE phenomenon which contained BLEVE definition and mechanism, as well as the assessment of its consequences. Although these studies have really helped to a better understanding of this phenomenon, unfortunately severe BLEVE accidents still occur, showing that further research is needed.

Analyzing the BLEVE accidents occurred during previous years can help to have a better understanding on the phenomenon and on its main features. In the scientific resources, there are rather few historical studies about this phenomenon. Prugh (1991) presented a brief historical survey, analyzing 49 BLEVE accidents and their general causes (Table 1-2). Abbasi et al. (2007b) analyzed 89 BLEVE accidents occurred in the period 1926 – 2004: fire (36%) and mechanical failure (22%) were the main causes of them; domino effect was found in some cases.

Table 1-2. Results of Prugh historical analysis on the cause of BLEVEs (Prugh, 1991)

Cause	**Number of incidents**	**Percentage (%)**
Exposure to fire	17	34.7
Mechanical damage	11	22.4
Overfilling	10	20.4
Runaway reaction	6	12.2
Overheating	3	6.1
Vapor-space explosion	1	2.1
Mechanical failure	1	2.1
Total	49	100.0

However, these surveys were performed on a relatively reduced number of cases and some of the accidents covered occurred long ago, when the conditions both at industry and in the transportation where different from those found today. A wider historical analysis seemed therefore necessary in order to have a better knowledge of different aspects of BLEVE accidents such as their cause, origin, consequences and frequencies. This is why, as a first step, a set of 167 BLEVEs occurred between 1960 and 2013 have been collected and analyzed. The result of this historical survey are presented in the next sections.

1.6 Occurrence of BLEVEs: a historical survey

The historical analysis of BLEVE accidents is an interesting way to understand them better, as it can give a good overview about this phenomenon and which important factors play a role in it. MHIDAS (Major Hazard Incident Data Service) database (MHIDAS, 2007) was used to obtain the main data in this study. This database covers 14,168 incidents (November 2007 version) recorded from the beginning of the 20th century until 2006 in over 95 countries, and each record is classified according to different fields (e.g. cause, origin) to facilitate automatic processing; it is managed by the UK Health and Safety Executive. Moreover, other databases were also consulted: Analysis, Research and Information on Accidents (ARIA, 2012), created by the French Ministry of Regional Planning and the Environment; Major Accident Reporting System (MARS, 2012), through which EU member states report industrial accidents in a standard format, overseen by the Major Accidents hazards Bureau of the EU Joint Research Centre; and Failure and ACcidents Technical information System (FACTS, 2010), a database for accidents involving hazardous materials created by TNO Industrial and External Safety. The lack of information in some accidents was fulfilled by getting assistance of other available resources like the U.S. Chemical Safety Board, (CSB, 2012), the U. S. National Transport Safety Board (NTSB, 2013) and the National Fire Protection Association (NFPA, 2012).

When collecting a large volume of information by using different databases, the probability of recording repetitious accidents increases. The retrieval of information among large databases is also another difficulty when analyzing the accidents. In this study, Microsoft Access® was used in order to manage and classify the data. By doing so, analyzing and editing of BLEVEs information became easier.

Analyzing different databases for finding information will be confusing without providing relevant keywords or criteria to identify accidents as a BLEVE. The criteria used in this selection have been the following:

- The definition for BLEVE, already mentioned in a preceding section (end of Section 1.3), was used.
- This study has only taken into account accidents occurred after 1st January 1960. This is due to the fact that before this date (more than half a century ago) the type of industry was essentially different from the present one (control, safety, management, etc.) and therefore those accidents would not be much useful nowadays to find common trends and reach sound conclusions.

- This survey considers accidents occurred in process plants, in storage areas or in the transportation of hazardous materials (road, rail and ship). Moreover, it also includes accidents that have occurred because of natural events such as earthquakes or floods.
- Accidents occurred in military premises (ammunition, etc.) or with fireworks have not been considered.

Although the number of BLEVE accidents was reduced when applying the aforementioned criteria, the accuracy and quality of the accidents' sample increased. Finally, a set of 167 BLEVE accidents –the largest sample of BLEVE accidents surveyed until now– were obtained and analyzed. The features of the selected accidents are discussed in the next sections.

1.6.1 Distribution of accidents according to the time and location

The frequencies of the BLEVE accidents during the decades have been plotted in Figure 1-2. The highest frequency belongs to the 70's (29.9%). The occurrence of this type of accidents decreased until the end of 20th century and afterwards a clear trend cannot be observed. A fact that should be mentioned here, and which could have some influences, is the much better access to information on major accidents (BLEVE included) in the last decades; this could contribute to increase the frequency of registered cases.

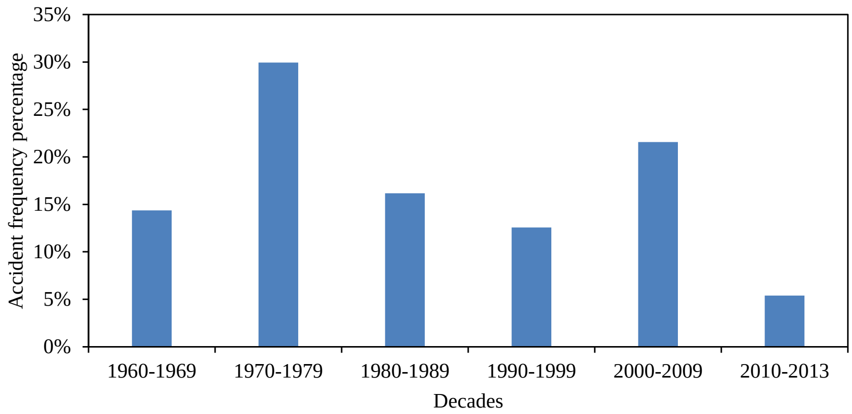


Figure 1-2. Distribution of BLEVEs over the time.

The selected accidents have also been classified by their region. This type of classification was done by considering different factors such as political and development-based criteria. Countries in the world were classified in three independent groups and the accidents were distributed in them:

1. European Union (20.4%),
2. Other developed countries: Australia, Canada, Japan, New Zealand, Switzerland, Norway and the United States (55.4%),

3. Rest of the world (25.1%).

According to these categories, the highest percentage (75.8%) is found in the developed countries. This high percentage should be attributed to the presence of an important number of plants and to the associated transportation and storage infrastructures in these countries. Moreover, in developed countries, due to the existing policies and institutions in the field of safety and environment, more information about the occurred accidents is available.

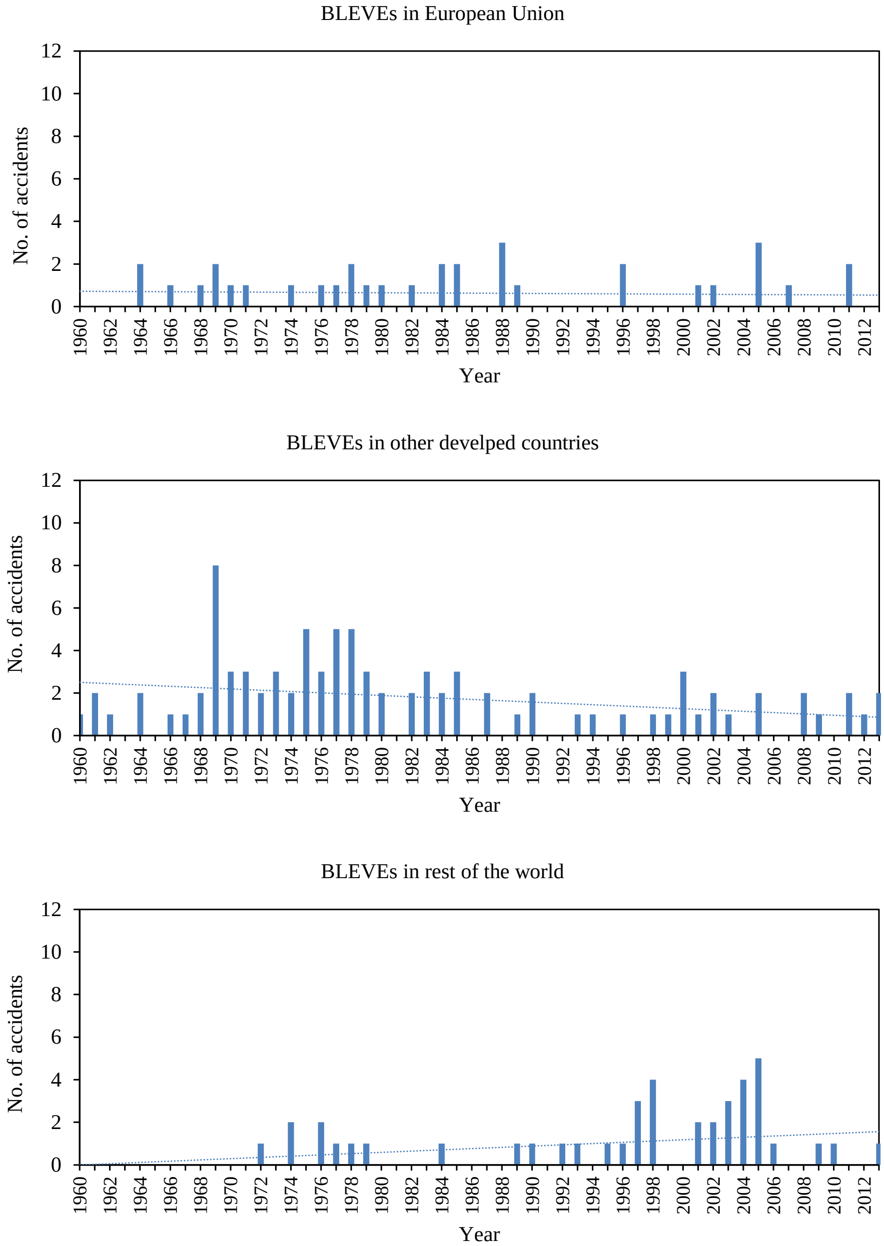


Figure 1-3. Trend of BLEVEs occurrence in different parts of the world.

Figure 1-3 shows the frequencies of BLEVEs as a function of time in the three different regions. It can be seen that the contribution of developing countries has increased in recent years, while it has decreased in developed ones.

1.6.2 Substances involved

As already mentioned, a liquid can undergo a BLEVE if its temperature at the moment of vessel failure is higher than its atmospheric boiling temperature. By this definition, it can be expected that substances with boiling temperature lower than ambient temperature – such as light hydrocarbons– are prone to BLEVE.

Table 1-3 shows the substances involved in the 167 BLEVE accidents here analyzed. 247 substances have been identified, as in some of the accidents more than one substance were simultaneously involved. As it can be seen in this table, LPG was by large the most frequent material, being found in 66% of BLEVEs, followed by vinyl chloride (6%) and oil (6%); LNG took part in 3% of the BLEVE accidents.

Table 1-3. Substances involved in BLEVEs

Substance	**Number of accidents**	**Percentage**
LPG	111	66
Vinyl chloride	10	6
Oil	10	6
Gasoline/Petrol/Diesel/Kerosene	8	5
Ethylene oxide	7	4
Carbon dioxide	6	4
Water	5	3
LNG	5	3
Propylene	4	2
Ammonia	3	2
Chlorine	3	2
Butadiene	3	2
Ethylene	3	2
Toluene diisocyanate	3	2
Sodium hydroxide	3	2
Sulfuric acid	3	2
Other chemical substances	60	36
Total	247	149

It should be noticed that water also appears (3%). Concerning water, the following consideration must be done; probably the number of BLEVEs involving it has been much larger than those registered in databases, even though, as water is not flammable and therefore it does not originate any subsequent fireball, many of such cases had not been registered as BLEVEs.

These substances were also classified according to their hazardousness (Table 1-4). Here again the total percentage exceeded 100% because several substances present more than one hazard (e.g., ammonia is flammable and toxic; carbon dioxide is cold and asphyxiating). Flammable substances were involved in 132% of BLEVEs, followed by toxic substances (44%) and corrosive ones (23%). However, these figures should be considered with certain caution, as the fact that BLEVEs with flammable substances are usually followed by a fireball increases the magnitude of the accident and make them more prone to be included in accident databases.

Table 1-4. Hazard of substances involved in BLEVEs

Hazardousness of substance	**No. of accidents**	**Percentage**
Flammable	221	132
Toxic	73	44
Corrosive	38	23
Oxidizing	22	13
Explosive	18	11
Cold	13	8
Asphyxiating	8	5
Total	393	236

1.6.3 General/specific cause

Understanding the main causes of accidents can be a good mean to prevent further similar accidents. In Table 1-5, MHIDAS database categories for generic causes were used to identify the causes of BLEVE accidents. The total number of causes were larger than the number of BLEVE accidents because in some accidents there were more than one cause. General causes of accidents were not specified in 27 (16.17%) out of 167 cases; the results in Table 1-5 correspond thus to 140 accidents.

Impact failure (47.1%) followed by human factor (30.7%) and external events (29.3%) were the main causes. By comparing these data with those in Table 1-2, the latter (external events) decreased from 34.7% to 29.3%; but the impact failure increased significantly from 22.4% to 47.1%. This could be attributed to an increase in number of transport accidents which will be defined as specific cause of BLEVE accidents in Table 1-6.

Table 1-5. General causes of BLEVEs

General cause	Number of accidents	Overall percentage	EU%	Other developed countries%	Rest of the world%
Impact failure	66	47.1	17.2	68.8	19.4
Human factor	43	30.7	41.4	20.0	48.4
External events	41	29.3	20.7	33.8	25.8
Mechanical failure	39	27.9	44.8	25.0	19.4
Instrument failure	7	5.0	6.9	5.0	3.2
Violent reaction	6	4.3	-	5.0	6.5
Service failure	1	0.7	-	1.3	-
Upset process conditions	1	0.7	3.4	-	-
Total	204	145.7	134.4	158.9	122.7

A detailed analysis was also performed by referring to each region. In European countries, mechanical failure (44.8%) was the most probable cause of BLEVEs, while in other developed countries it was impact failure (68.8%). However, human factor (48.4%) and external events (25.8%) were the main causes of the accidents in the rest of the world. This can be explained by a worse safety training of operators and poor safety culture in these countries.

Each general cause was subdivided into specific causes in Table 1-6. Rail accidents (55%) and road accidents (22%) were the most frequent specific ones in impact failure. Regarding human factor, general maintenance (27%) followed by general operation (16%) were the main frequent ones. Finally, fire (72%) was the main specific cause in external event category.

Table 1-6. Specific causes of BLEVEs

General cause	Specific cause	No. of accidents	%
Impact failure (47.1%)	Rail accident	40	55
	Road accident	16	22
	Other vehicle	11	15
	Heavy object	4	6
	Excavating equipment	1	1
	Ship to ship collision also barges	1	1
Human factor (30.7%)	General maintenance	8	27
	General operation	5	16
	Overfilling	4	13
	Management	3	10
	Procedures	3	10
	Failure to connect or disconnect	2	7
	Design error	2	7
	Draining accident	2	7
	Failure to isolate or drain before uncoupling	1	3
External events (29.3%)	Fire	33	72
	Explosion	7	15
	Temperature extremes	4	9
	Earthquake	2	4
Mechanical failure (27.9%)	Overheating	20	37
	Overpressure	7	14
	Hose	4	7
	Brittle failure	4	7
	Leaking coupling or flange	4	7
	Corrosion	3	5
	Relief valve failure	3	5
	Weld failure	3	5
	Leaking or passing valve	3	5
	Metallurgical failure	2	4
	Fatigue	2	4
Instrument failure (5%)	Indicator	2	40
	Trip	2	40
	Controller	1	20
Violent reaction (4.3%)	Run away reaction	4	80
	Confined explosion	1	20
Service failure (0.7%)	Electricity	1	100
Upset process conditions (0.7%)[1]	-	1	100

[1]For this case MHIDAS does not have any categories

1.6.4 General/specific origin

The general origin of accidents (Table 1-7) gives an interesting information concerning the activities in which the probability of such accidents is higher; the total percentages of accidents are higher than 100 again, because some accidents had different origins. Overall, transport (46.7%) and storage area (23.4%) obviously had dominant percentages than the other groups. Transfer (including loading/unloading operations) has a significant contribution as well. The general origin of accidents was also investigated for the different parts of the world; transport was the main origin: EU (29.4%), other developed countries (56%), and rest of the world (40.5%). It was followed by process plants (20.6%) in European Union and by storage in the other two categories. The origins "Transport" and "Transfer" are specially interesting. When analyzing all accidents (Vilchez et al., 1995), approximate values of 39% for Transport and 8% for Transfer are found. However, for the specific case of BLEVE those percentages increase significantly: up to 47% for Transport and 13% for Transfer (17.6% for EU). Clearly, road/rail accidents and loading/unloading operations have an important influence.

Table 1-7. General origin of BLEVEs

General origin	No. of accidents	Overall percentage	EU, %	Other developed countries, %	Rest of the world, %
Transport	78	46.7	29.4	56.0	40.5
Storage area	39	23.4	17.6	25.3	23.8
Transfer	22	13.2	17.6	11.0	14.3
Process plant	19	11.4	20.6	4.4	19.0
Domestic/commercial premises	10	6.0	11.8	3.3	7.1
Warehouse	3	1.8	2.9	1.1	2.4
Disposal area	2	1.2	2.9	1.1	-
Total	173	103.7	102.8	102.2	107.1

The specific origin of the accidents was also studied. According to the data gathered in Table 1-8, rail tanker (29.9%), road tanker (19.2%) and pressurized storage vessel (18.6%) had the highest percentages.

Table 1-8. Specific origin of BLEVEs

Specific origin	No. of accidents	Percentage
Rail tanker	50	29.9
Road tanker	32	19.2
Pressurized storage vessel	31	18.6
Portable transport container	18	10.8
Fired process equipment	7	4.2
On-plant pipes and associated valves	6	3.6
Heat exchanger	6	3.6
Atmospheric pressure storage tank	5	3.0
Ship	5	3.0
Tank container	4	2.4
Process vessels	3	1.8
Reactor	3	1.8
Hose	2	1.2
Small commercial tank	2	1.2
Pipeline	2	1.2
Barge	1	0.6
Total	177	106.1

1.6.5 Affected population

The affected population is one of the important aspects in safety and risk analysis, and reducing the number of people affected by the BLEVE consequences is the aim of many scientific studies in the field of safety and loss prevention. The affected population can be classified in three groups: fatalities, injuries and evacuees. The results presented here are just for those cases where information was available (in 72% of cases for fatalities, for injuries in 75% and for evacuees in 29%).

In 120 BLEVEs occurred since 1960, about 1280 people were killed; a detailed study was performed on them. The $p - N$ curve is usually used to represent the lethality of accidents (Figure 1-4). In this plot, the number of fatalities (N) is shown on the abscissae and the probability of a BLEVE accident with fatalities equal or greater than N (for $N = 1$, $p = 1$) is illustrated on its ordinate axis. In fact, the accumulated probability of BLEVE accidents can be represented by this illustrative curve as a function of its severity. The accumulated probability was calculated by the least square method. The resulting function was $p = N^b$, with the b value equal to -0.711. This means that the accumulated probability of BLEVE accidents that causes 10 or more deaths is 5.13 times greater than the accumulated probability of BLEVE accidents with 100 or more fatalities.

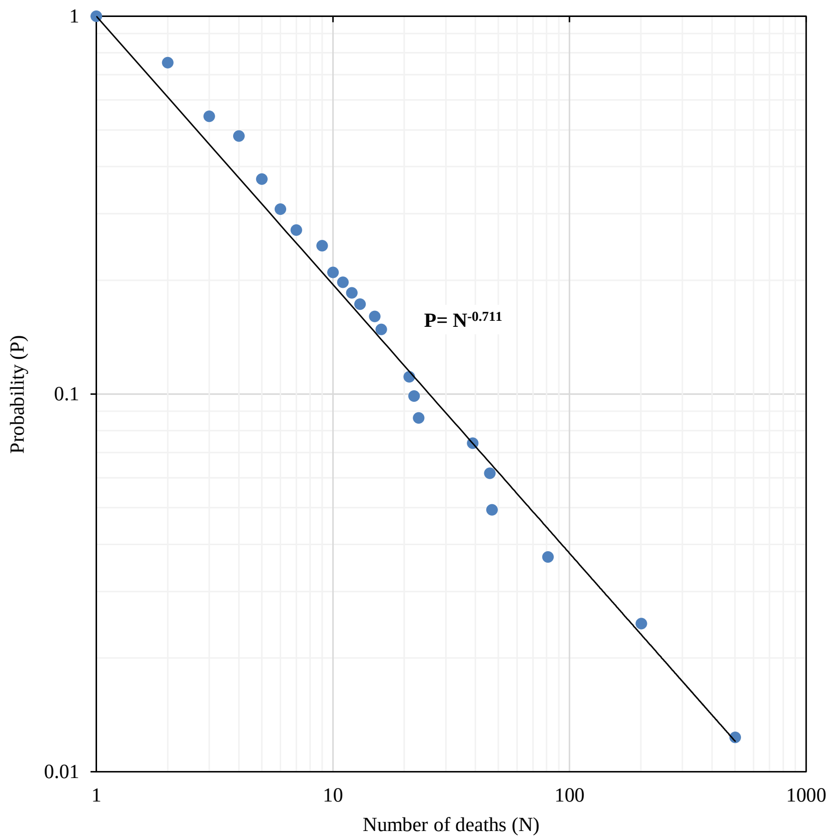


Figure 1-4. Accumulated probability as a function of number of deaths.

The accumulated probability of fatalities versus the number of deaths was also calculated for different parts of the world (Figure 1-5).

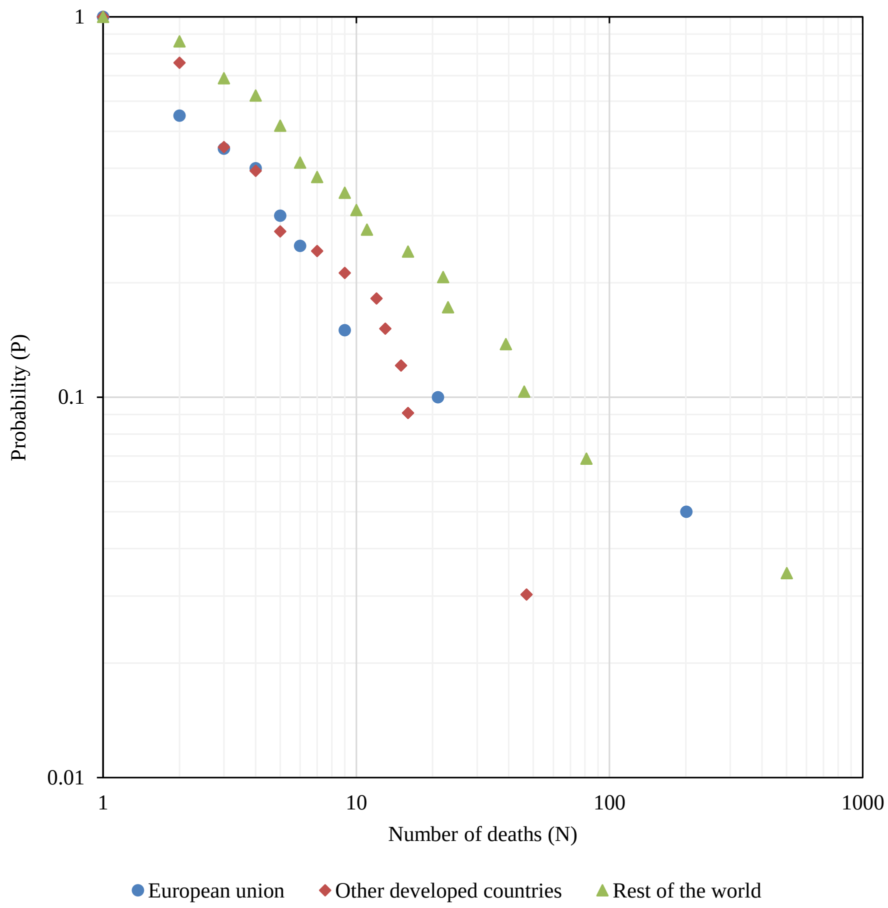


Figure 1-5. p-N curve according to the development degree of the countries.

Despite similar probability of deaths for developed countries, the accumulated probability of number of deaths was higher for the “rest of the world”, specifically for $N > 20$, with a value of $b = -0.544$.

The analysis of the number of injuries in the accidents (Table 1-9) showed that only 25.2% of accidents had no injured 39% of accidents had between 1 and 10 injured; in 30.9% of cases there were between 11 and 100 injured; and only 4.9% had more than 100 injured people.

Table 1-9. BLEVEs Injured

Injured	**No. of accidents**	**Percentage**
No injuries	31	25.2
1-10	48	39.0
11-100	38	30.9
101-1000	5	4.1
>1000	1	0.8
Total	123	100.0

Further analysis (Table 1-10) showed that in 20.8% of BLEVE accidents there were no evacuees, in 27.2% there were between 1 – 100, in 20.8% there were between 101 – 1000, in 20.8% there were between 1001 – 10,000, and in only 10.4% of accidents there were more than 10,000 people evacuated.

Table 1-10. BLEVEs evacuees

Evacuees	**No. of accidents**	**Percentage**
No evacuees	10	20.8
1-10	10	20.8
11-100	3	6.4
101-1000	10	20.8
1001-10,000	10	20.8
>10,000	5	10.4
Total	48	100.0

1.7 Objectives of the thesis

The data presented in this introductory chapter shows that BLEVEs can occur –and, in fact, keep occurring from time to time– in process plants, in storage areas and in the transportation by road and rail. They are a significant major accident, having caused severe consequences on people and on equipment.

However, even if this is a well-known fact, BLEVE is still not enough known. Diverse authors have analyzed it theoretically and a few ones have performed experimental tests; all these efforts have improved certainly the knowledge of this phenomenon, but there are still significant gaps.

There is no doubt that a better knowledge of BLEVE main aspects would help in decreasing its frequency, in improving the management of emergencies and, finally, in reducing its potential effects and consequences.

The main objective of this thesis is therefore to improve the knowledge of BLEVE main features, with a special emphasis in the prediction of its physical effects (blast overpressure). The achievement of this main objective has been planned through the definition of a set of more specific objectives, listed below:

- Analysis of the main causes and consequences of BLEVEs through the historical analysis tool.

- Study of the influence of domino effect (and, specifically, of fire as escalation vector) on BLEVE accidents and their main drivers.
- Comparison of the current existing models to predict BLEVE blast effects.
- Proposal of an improved methodology to predict BLEVE blast effects that allows to be used in a quick but accurate way.
- Proposal of essential emergency management measures, specially in transportation accidents, to avoid or reduce the consequences on people.

Chapter 2. MAJOR ACCIDENTS AND DOMINO EFFECT. THE SIGNIFICANCE OF BLEVES

2.1 Introduction

Recent surveys have emphasized the importance of the domino effect in the occurrence and severity of the major accidents that take place in the process industry and in some closely related activities, such as the transportation of hazardous materials (Abdolhamidzadeh et al., 2010, 2011; Darbra et al., 2010). Escalation criteria have been proposed to assess the near-field effects of fire and explosion (Cozzani et al., 2006). The main features of domino accidents have been recently analyzed by diverse authors in the book "Domino effects in the process industries. Modelling, prevention and managing" (Reniers and Cozzani, 2013). The diverse chapters of this book clearly show the complexity of domino effect accident scenarios and the many ways through which the escalation and propagation of accidents can take place.

Although an increasing interest can be inferred from the publications found in the literature, this subject has been treated by a relatively reduced number of authors. As a result, the main domino effect features and trends are still poorly known.

Domino effect has a special importance concerning the occurrence of BLEVEs, as often these accidents are the secondary step of a domino sequence: for example, a fire which impinges on a vessel which after a certain time collapses. Thus, in this chapter the diverse aspects of domino effect are analyzed, with a specific reference to BLEVE.

Diverse definitions and interpretations about the meaning of the domino effect are available; Reniers (2010) published a list of them. For the purpose of this chapter, the definition proposed by Delvosalle (1998) will be used to select the accidents. According to him, a domino accident can be defined as:

"*a cascade of events in which the consequences of a previous accident are increased both spatially and temporally by the following ones, thus leading to a major accident*".

Domino effect can be analyzed through different approaches. Amongst them, the analysis of past accidents seems to be a powerful tool. Past accidents are in fact the only source of "experimental data" available in this field, data for which a high price has been paid. The analysis of these accidents gives the possibility of knowing diverse aspects of domino effect: the usual events that initiate it, the most frequent sequences, the substances that are more prone to be associated to these accidents, etc. However, such a survey has certain implicit difficulties, the most significant one being the lack of information.

Accidents involving domino effect can be found from the specialized literature, from reports of certain institutions and in appropriate databases. However, often the information thus obtained is not complete; this implies a reduction of the sample size when a statistical treatment must be performed, with the consequent loss of significance of the results.

Several historical surveys have been published on this subject. Bagster and Pitblado (1991) studied the frequency and likelihood of domino accidents in a pioneering work. Kourniotis et al. (2000) performed a survey on a total of 207 accidents, of which 80 involved domino effect; their sequences (ratio of accidents with one or two domino effects) and their consequences on the population were analyzed. Ronza et al. (2003) studied 108 accidents occurred in port areas which involved as well domino effect. With a much more specific approach, Gómez-Mares et al. (2008) published a survey on accidents involving jet fires, 50% of which had been the primary event of a domino effect sequence. Darbra et al. (2010) performed a historical analysis on 225 accidents involving this effect. Shortly after, Abdolhamidzadeh et al. (2011) published another survey on 224 accidents also involving domino sequences.

In these last two papers the main features of the accidents were analyzed: substances involved, origin, primary events, consequences, etc. In Darbra et al. (2010) the accident sequences were studied through the relative probability trees. In Abdolhamidzadeh et al. (2011) a list of the accidents studied was included. The results of these two surveys differed in some aspects, essentially because of the difference in the respective sets of data (geographical location of accidents). Thus, aspects such as the severity of accidents over the years or their frequency as a function of time were different.

Therefore, it seemed of interest to devote a chapter to perform a wider analysis including both sets of data (avoiding repetitions); the two collections were merged and screened, adding also new accidents occurred in the recent years. Accidents occurrence and features in developing countries (in which industry is developing quickly) were analyzed and compared with the situation in the industrialized ones. In addition, a specific analysis of accidents occurred in the period 2000-2013 has been also performed. The whole analysis has given as well some information of the relative significance of BLEVEs among all major accidents.

2.2 Methodology

The survey was performed by using both datasets and other sources of information. Many data were obtained from resources which are mentioned in Chapter 1 such as: MHIDAS database (2007), MARS (2012), FACTS (2010), and ARIA (2012). Moreover, other resources were also consulted, like in the previous chapter, in order to complete the information about some accidents (e.g., CSB (2012), NTSB (2013) and NFPA (2012)). Finally, the information on accidents was collected and centralized in Microsoft Access in order to manage and retrieve easily and avoid duplication of recorded accidents.

In order to identify the different domino accidents from the databases, keywords related to domino effect were selected. Once the accidents were gathered, clear criteria to define if they involved a domino effect were established. In this way, a proper selection of accidents was done. The criteria used in this selection are the following ones:

Domino effect occurs when a first accident in a unit (e.g. an explosion) triggers a second one in another unit (e.g. release and fire in a tank). This is known as a spatial domino accident.

It is also considered a domino effect when a first accident in a unit (e.g. a jet fire from a vessel impinging on the vessel wall) originates a second one (e.g. BLEVE of the vessel) in the same unit. This is known as a temporal domino accident.

In the case that “two” accidents are essentially simultaneous, this is not domino effect. They should be considered practically as the same accident; for example: the explosion in a floating roof tank followed immediately by a fire in the same tank.

This study has only taken into account accidents occurred after 1st January 1961. As commented in Chapter 1, before this date (half a century ago) the type of industry was essentially different from the present one (control, safety, management, etc.) and, therefore, those accidents would not be much useful nowadays to find common trends and reach sound conclusions.

This survey considers accidents occurred in process plants, in storage areas and in the transportation of hazardous materials (road, rail and ship). Moreover, it also includes accidents that have occurred because of natural events such as earthquakes or floods.

Accidents occurred in military premises (ammunition, etc.) or with fireworks have not been considered.

After applying these criteria, the number of selected accidents was reduced considerably; however, the accuracy and quality of the domino accidents’ sample was increased. Finally, a collection of 330 accidents was obtained. This is the largest sample of domino accidents analyzed until now.

2.3 Accident analysis

In this section, the main features of the selected domino accidents are analyzed.

2.3.1 Distribution of accidents according to time and location

Figure 2-1 shows the evolution of the accidents frequency as a function of time. As it can be seen, the 70's is the decade with the highest percentage of accidents (23.9%); after an exceptional decrease in the 90's, the frequency increases again in the first decade of the 21st century to the previous values (this figure is quite similar –although the values are different– to Figure 1-2, as part of the accidents analyzed, are coincident). These values do not show a clear increasing or decreasing trend, but rather a more or less stationary one.

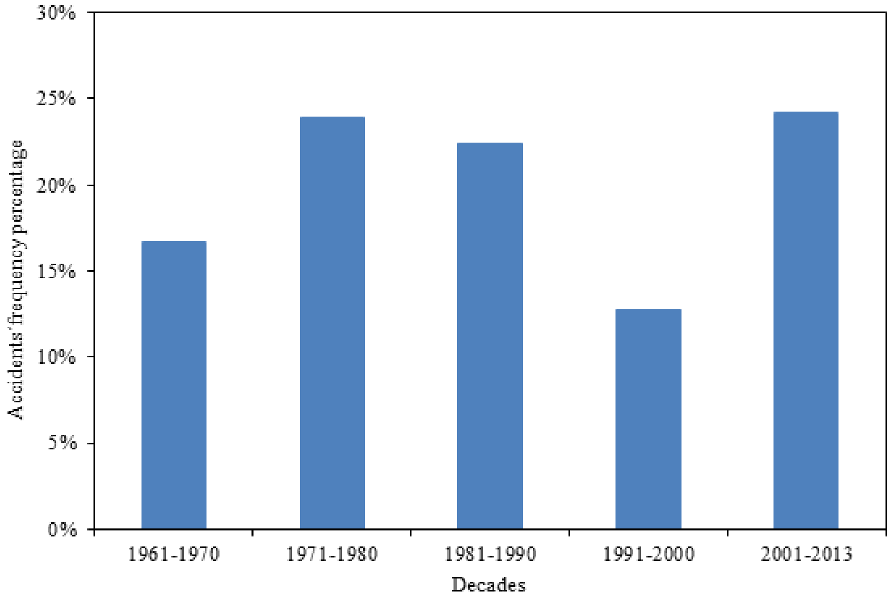


Figure 2-1. Distribution of domino accidents over the time.

The location of the domino accidents was also studied, as the main features of the process industry, as well as legislation and risk-planning policies –which have an effect on the occurrence and severity of accidents– can change from one country to another. Although it is not easy to make such clusters, finally, by applying development-based criteria, the accidents were classified in three main groups depending on the country where they had occurred:

1. European Union (21.8%)
2. Other developed countries: Australia, Canada, Japan, New Zealand, Switzerland, Norway and the United States (54.5%)
3. Rest of the world (23.7%).

As it can be seen in this classification, 76.3% of domino accidents occurred in developed countries. The presence of a high number of plants and the associated transportation and storage infrastructures in these countries accounts for this high percentage; another factor that contributes to this value is the fact that more information on accidents occurred in these countries is available. However, the contribution of developing countries has increased in comparison with a previous study from Darbra et al. (2010): from 19% to 23.7%.

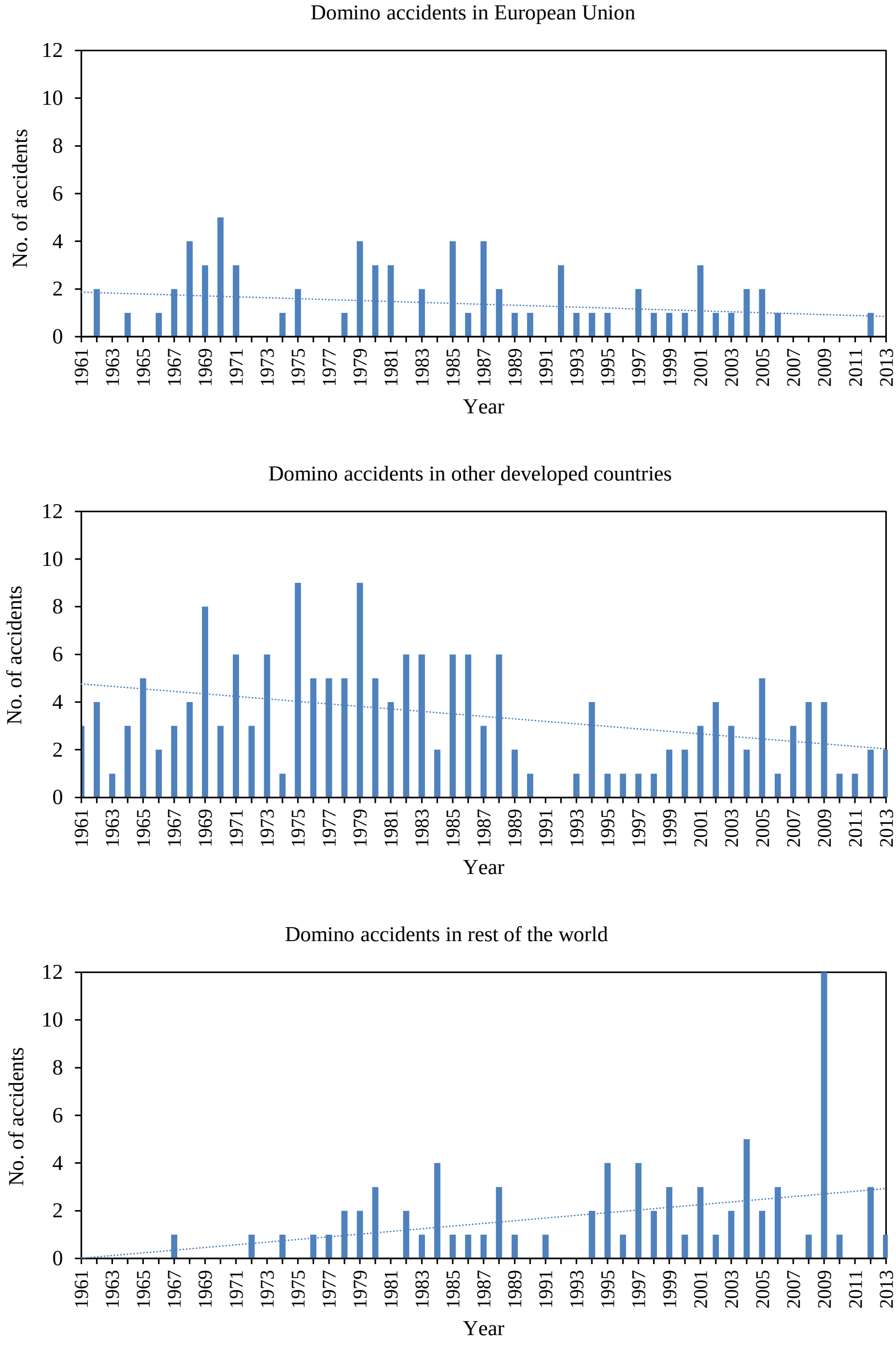


Figure 2-2. Trend of domino accidents in different parts of the world.

Figure 2-2 presents a detailed analysis of the occurrence of domino accidents as a function of time in the different parts of the world. An overall slightly decreasing trend with time can be observed for the EU and other developed countries; this trend can change if shorter periods –for example, one decade– are analyzed. This would agree with the data published by Niemitz (2010) for accidents registered in the MARS database between 1996 and 2004. This trend would show the influence of the existing policies and institutions related to safety and environment in these countries. Instead, a rather increasing trend is observed over the whole analyzed period for the “rest of the world”. This gives a clear indication that a special attention should be paid to the situation in the developing countries, some of which are undergoing a significant increase in their industrial activity sometimes not linked to an increase in the corresponding safety regulations.

2.3.2 Substances involved

Often more than one substance was involved in the accidents (domino effect is usually characterized by affecting different equipment in an accidental sequence). In total, 537 substances were identified in 330 accidents. However, the real number of substances could be higher, as in some accidents only those involved in the primary accident were specifically mentioned, and sentences such as “the fire spread to storage tanks containing chemicals” were occasionally used to describe the secondary accident.

As shown in Table 2-1, LPG was the most common substance, being involved in 22% of domino accidents. It was followed, at a significant distance, by gasoline (10%) and oil (9%); other liquid hydrocarbons were found such as diesel oil/fuel oil and naphtha; hydrocarbons were involved in 55% of accidents.

Table 2-1. Substances involved in domino accidents

Substance	No. of accidents	Percentage
LPG	72	22
Gasoline	33	10
Oil	29	9
Diesel oil/fuel oil	20	6
Naphtha	14	4
Vinyl chloride	13	4
Chlorine	11	3
Natural gas	11	3
Ammonia	10	3
Ethylene oxide	10	3
Other chemical substances	314	95
Total	537	162

Toxic substances were also involved: chlorine and ammonia. The percentages in this table do not total 100 because of the involvement of more than one substance in many accidents.

Concerning the hazardousness of the materials, flammable substances were the most frequent ones, being involved in 142% of the domino accidents. They were followed by toxic substances (55%) and, with a smaller contribution, by corrosive substances (19%). Again, the percentages do not add up to 100.

2.3.3 General/specific causes

Understanding the causes of accidents is a helpful aspect to prevent them from occurring again. Although the information came from a variety of sources, the MHIDAS database categories were used for the generic causes: external events, mechanical failure, human error, impact failure, violent reaction (runaway reaction), instrument failure, upset process conditions and services failure.

Table 2-2 shows the generic causes that initiated a domino accident in the cases included in this analysis. Again, the percentages do not total 100 because some accidents were triggered by more than one generic cause. Mechanical failure (35.2%) and external events (29.4%) were the main causes of the accidents. Human error caused 24.6% of the accidents. These values have increased with respect to those of Darbra et al. (2010) survey: 28.9%, 30.7% and 20.9%, respectively.

Table 2-2. General causes of the domino accidents

General cause	**No. of accidents**	**Overall percentage**	**EU, %**	**Other developed countries, %**	**Rest of the world, %**
Mechanical-failure	103	35.2	38	38	25
External events	86	29.4	18	33	33
Human factor	72	24.6	26	21	33
Impact failure	49	16.7	1	27	7
Violent reaction	25	8.5	13	9	2
Instrument failure	13	4.4	7	4	2
Upset process conditions	9	3.1	4	4	0
Services failure	5	1.7	1	2	2
Total	359	123.6	108	138	104

A more detailed investigation about general causes of the accidents in the different parts of the world showed that mechanical failure was the main cause in European and other developed countries. However, for the particular case of the rest of the world, the main generic causes were human factor and external events (see Table 2-2). Accidents associated to human factor have increased significantly in developing countries (33%) compared with industrialized countries (21% in EU and 26% in other developed countries); this could be probably explained by a worse safety training of operators and a poorer safety culture, as well as to the existence of less severe regulations.

Table 2-3. Specific causes of the domino accidents

General cause	**Specific cause**	**No. of accidents**	**%**
Mechanical failure (35.2%)	Overpressure	14	16.1
	Overheating	13	15.0
	Other metallurgical failure	10	11.5
	Leaking coupling or flange	9	10.3
	Leaking or passing valve	8	9.2
	Hose	6	6.9
	Corrosion	4	4.6
	Fatigue	4	4.6
	Leaking gland or seal	4	4.6
	Relief valve failure	4	4.6
	Weld failure	4	4.6
	Brittle failure	3	3.4
	Use of incompatible materials	2	2.3
	Overloading	2	2.3
External events (29.4%)	Fire	49	49.0
	Explosion	28	28.0
	Lightning	14	14.0
	Extreme temperatures	3	3.0
	Earthquake	2	2.0
	Sabotage	2	2.0
	Flooding	2	2.0
Human factor (24.6%)	General maintenance	16	21.1
	General operation	15	19.7
	Overfilling	12	15.8
	Design error	10	13.2
	Procedures	8	10.5
	Management	7	9.2
	Draining accident	3	3.9

	Failure to isolate or drain before uncoupling	2	2.6
	Accidental venting	2	2.6
	Failure to connect or disconnect	1	1.3
Impact failure (16.7%)	Rail accident	33	70.3
	Other vehicle	6	12.8
	Heavy object	5	10.6
	Road accident	1	2.1
	Ship to land collision	1	2.1
	Ship to ship collision	1	2.1
Violent reaction (8.5%)	Runaway reaction	11	57.9
	Confined explosion	8	42.1
Instrument failure (4.4%)	Controller	6	50.0
	Indicator	3	25.0
	Trip	3	25.0
Upset process conditions (3.1%)[1]	-	-	-
Services failure (1.7%)	Electricity	4	80.0
	Water supply	1	20.0

[1]For this cause MHIDAS does not have any categories

Each general cause includes the contribution of different specific causes, which are shown in Table 2-3. Within the mechanical failure causes, overpressure (16.1%) and overheating (15%) were the most frequent ones, followed by metallurgical failure (11.5%) and leaking coupling/flange (10.3%). Regarding to specific causes of external events, accidents (essentially fire and explosion) in other plants were the most frequent types. Finally, when considering human factor as generic cause, maintenance was the main specific cause (21.1%).

2.3.4 Origin

The MHIDAS categories are used in Table 2-4 to define the origin of accidents. Again, the number of general origins can be higher than the total number of domino accidents because some accidents may have two origins at the same time. The main origin of the accidents is process plants (38.5 %); this percentage has increased clearly from the 28% found by Darbra et al. (2010). Storage areas have been the origin of the accidents in 33% of the cases. This could be explained by the high degree of confinement found in some process plants and by the presence of tanks containing hazardous materials in storage areas.

Table 2-4. General origin of domino accidents

General origin	No. of accidents	Overall percentage	EU, %	Other developed countries, %	Rest of the world, %
Process	127	38.5	44.4	37.8	34.6
Storage	109	33.0	31.9	32.8	34.6
Transport	53	16.1	6.9	20.6	14.1
Transfer	35	10.6	12.5	10.0	10.3
Warehouse	15	4.5	0.0	0.0	7.7
Domestic or commercial premises	11	3.3	4.2	2.8	3.8
Waste storage or disposal areas	1	0.3	5.6	2.8	1.3
Total	351	106.3	105.5	106.8	106.4

An interesting contribution is that of “transfer” which, as found already in other surveys (for example, the extensive one performed by Vilchez et al. (Vílchez, Sevilla, Montiel, Casal, 1995), represents still the origin of an important percentage of the accidents (10.6%). Even if it is well known that loading/unloading operations are especially dangerous and measures are often applied to prevent these accidents, these operations continue being the source of a relatively high number of dangerous events.

When analyzing the origin in different parts of the world, process plants remain being the main one in the more industrialized countries (44.4% in EU, 37.8% in other developed countries). However, in the rest of the world, storage areas are at the same level than process (both 34.6%). This can be explained due to the fact that in developing countries there are more storage areas than process plants.

The specific origin can also give a good understanding about domino accidents besides the general one. In 18 cases the specific origin was not specified. According to Table 2-5, atmospheric pressure storage vessels (18.6%), portable transport containers and rail tankers (both 13.5%) had the highest percentages as for specific origin.

Table 2-5. Specific origin of domino accidents

Specific origin	No. of accidents	Percentage
Atmospheric pressure storage vessels	58	18.6
Portable transport containers	42	13.5
Rail tanker (tank cars)	42	13.5
Process vessels	32	10.3
On-plant pipes and associated valves	30	9.6
Pressurised storage vessels	28	9.0
Reactor	19	6.1
Tank container	19	6.1
Ship	13	4.2
Pump	11	3.5
Pipeline	10	3.2
Road tanker	8	2.6
Heat exchanger	7	2.2
Barge	4	1.3
Solid storage	3	1.0
Hose	3	1.0
Fired process equipment	3	1.0
Equipment for moving solid material	1	0.3
Small commercial tank	1	0.3
Total	334	107.3

2.3.5 Affected population

The population affected by major accidents is an important priority in many safety studies. According to accident consequences, affected population can be divided in three categories: number of fatalities, number of injuries and number of evacuees. The results presented here are just for those cases where information was available (in 70.3% of cases for fatalities, for injuries in 68% and for evacuees in 32%).

The lethality of accidents has been represented by means of the $p - N$ curve (Figure 2-3) as in the previous chapter. Its slope indicates how the probability of an accident is reduced as a function of its severity. The least square method was used to calculate the probability. The b value of the curve $p = N^b$was found to be -0.814; this means that the probability of an accident involving a domino effect that causes 10 or more deaths is 6.5 times greater than the probability of a domino accident that causes 100 or more deaths. This number is in good agreement with the previous study from Vilchez et al. (1995) for all accidents, in which the value $b = -0.84$ was found. There were two exceptional accidents in Mexico and Iran, respectively, with a great number of fatalities, which have been plotted in Figure 2-3 but have been excluded from the least square calculation since they are outside the trend (confidence interval).

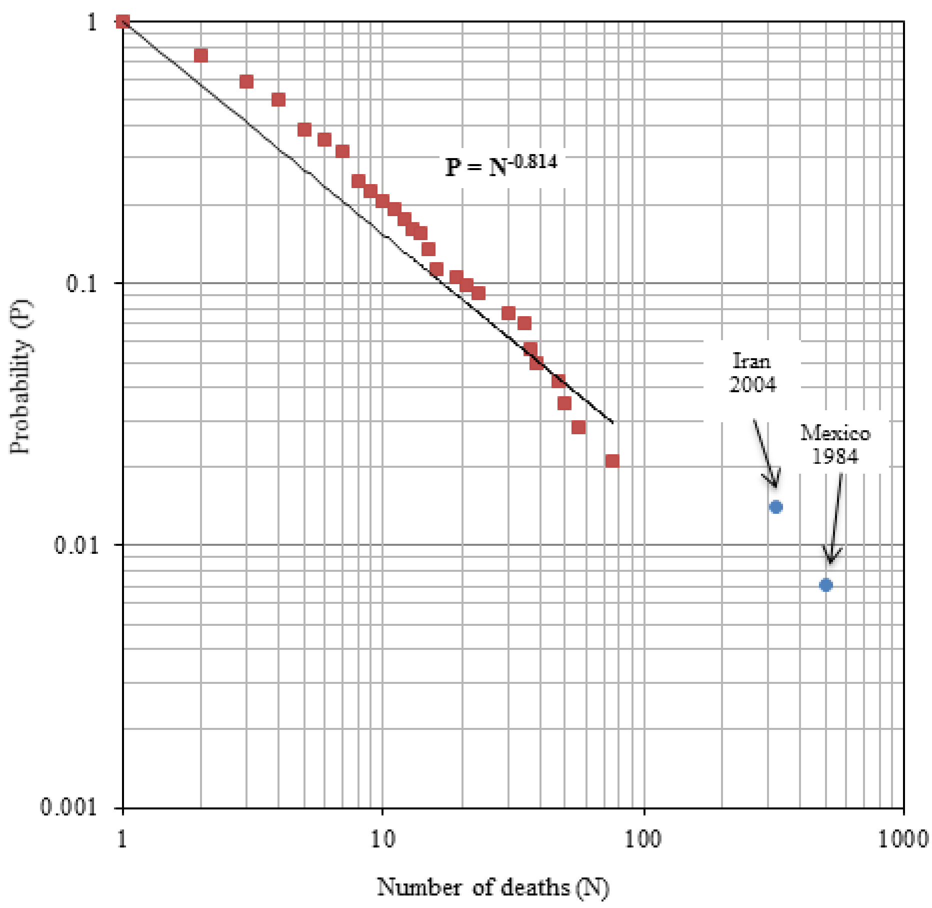


Figure 2-3. Accumulated probability as a function of the number of deaths for domino accidents.

In Figure 2-4, the probability of fatalities in different parts of the world has been plotted versus the number of deaths. The probability of death was similar for all the countries for the less severe accidents; however, for $N > 20$ this probability was significantly higher for the "rest of the world", with a value of $b = -0.65$. It is clear from this plot that the consequences of a severe accident, in terms of lethality, are more important in the developing countries; for example, the probability of having an accident with at least 35 fatalities in a developing country (P_R) is 0.4 times larger than in developed countries (P_D). This should be attributed, at least partly, to the quite different land use planning regulation measures, much less restrictive in the developing countries.

The number of injured people in domino accidents was also studied. There were no injured people in 23.5% of the accidents; 39.4% of accidents had between 1 and 10 injuries; in 31.9% of cases there were between 11 and 100, and only 5.2% had more than 100 injured people.

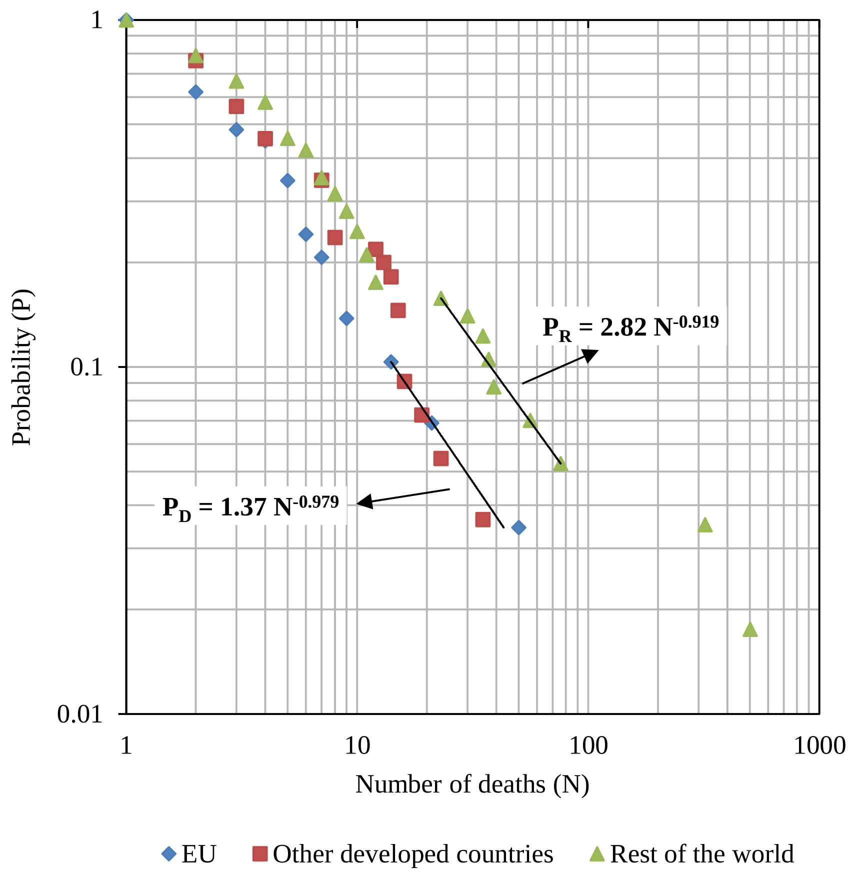


Figure 2-4. p-N curves according to the development degree of the countries for domino accidents.

Further analysis showed that in 16.8% of domino accidents there were no evacuees, in 26.2% there were between 1–100, in 25.2% there were between 101–1000, in 27.1% there were between 1001–10,000, and in only 4.7% of accidents there were more than 10,000 people evacuated.

2.3.6 Domino sequences

A practical way to analyze the domino accident sequences is the relative probability event tree (Darbra et al., 2010), in which each sequence is represented as a branch and its relative probability of occurrence can be easily calculated by a statistical treatment.

The primary events considered were only "explosion" and "fire". "Gas cloud" was not included as a primary event because, when it occurred, it was considered to be an explosion (if it originated mechanical effects) or a fire (if it was just a flash fire), or a toxic cloud which would not cause any secondary event. Figure 2-5 shows the resulting event tree. The number of accidents and the relative probability of occurrence (in square brackets) are included in each branch. The relative probability was calculated by dividing the number of accidents at each level to the number of accidents at its previous level. The overall probability value of each accident's sequence was presented at the end of each branch.

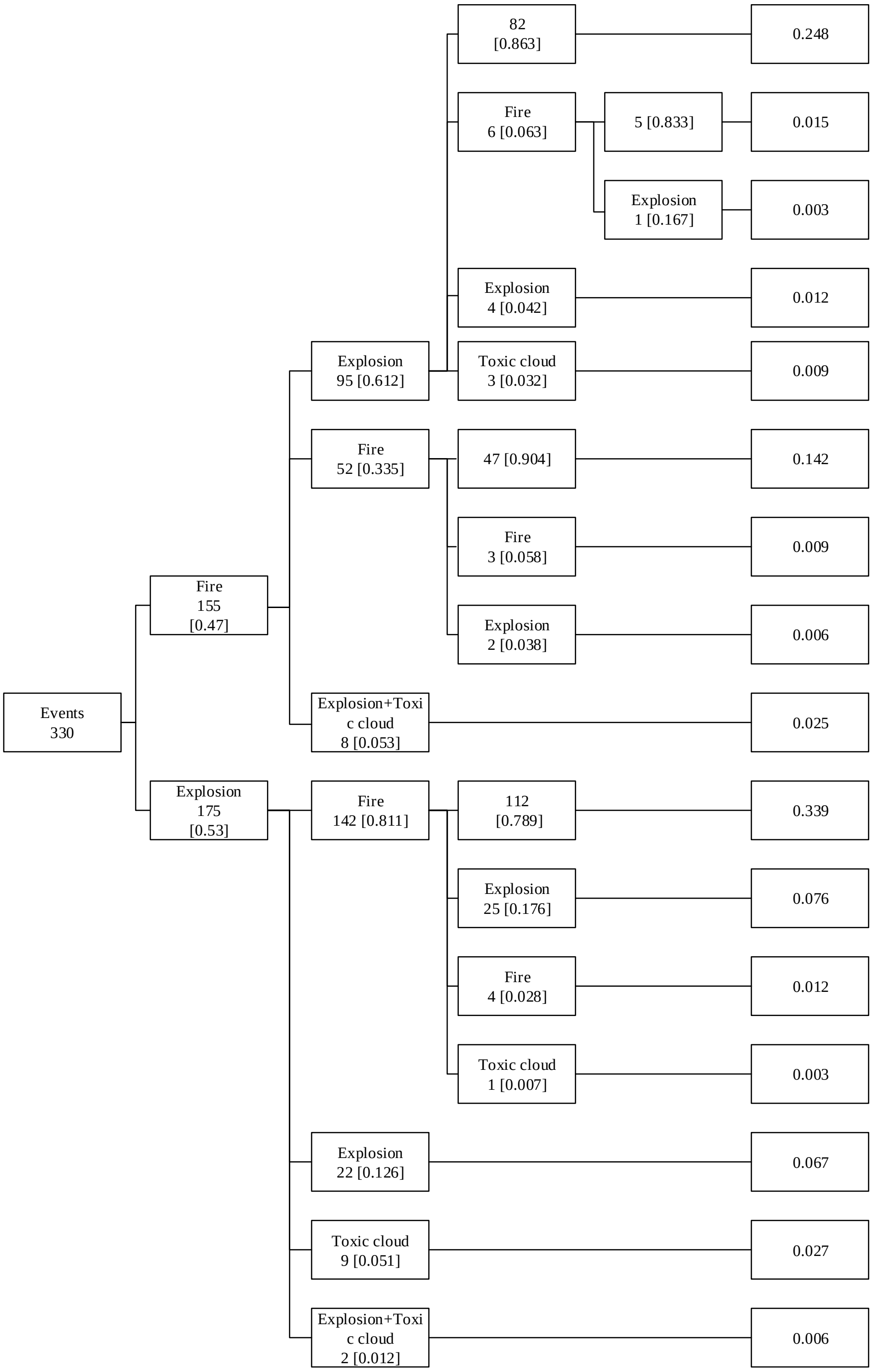


Figure 2-5. Relative probability tree showing the diverse domino effect sequences.

The domino accidents that only include primary and secondary events are called "two-step" domino accidents; if there are at least three events in the sequence, they are called "three-step" domino accidents. Of the 330 domino accidents, treated in this study, 53% started by an explosion and the rest of them (47%) were initiated by a fire.

In 155 cases (47%) the domino sequence started with fire as a primary event; the secondary events were explosion (61.2%), fire (33.5%) and explosion plus toxic cloud (5.3%). The most common three-step sequence was fire→explosion→fire.

Most first step explosions originated a fire as a secondary event (81.1% of cases). In the rest of the cases, another explosion followed the first one (12.6%), or a toxic cloud (5.1%) or both phenomena (1.2%). 30 accidents reached a third step: explosion→fire→explosion (25 cases), explosion→fire→fire (4 cases) and explosion→fire→toxic cloud (one case).

Among the 330 domino accidents analyzed, 282 accidents included primary and secondary events ("two-step"), and 48 of these included in addition a "third step". The only "four-step" domino sequence found was fire→explosion→fire→explosion.

The ratio between "two-step" and "three-step" accidents has been found to be 6; this value is similar to that found in a previous study (Darbra et al., 2010) with a partly coincident set of data. However, it differs from the values obtained in other surveys: Kourniotis et al. (2000) found 2.4 in a set of 80 accidents, and Abdolhamidzadeh et al. (2009) obtained 2.2 in a set of 73 accidents; this difference could be attributed to the fact that these two last sets of data were rather reduced and, probably, obtained from more specific sources.

2.4 Accidents occurred in the 21st century

A special effort has been devoted to the analysis of those accidents occurred recently, i.e., in the first years of the 21st century (2000-2013), since they are the most representative of the current process industry situation and the hazmat transportation, even if the sample is significantly more reduced. As MHIDAS database was not available from 2007, an effort was made to gather more accidents from other sources; this could have introduced a certain bias in this specific sample of data. 84 accidents were submitted to the same treatment described in the previous sections in order to allow the comparison of both periods.

2.4.1 Distribution according to location

When the geographical distribution is analyzed 14.3% correspond to the EU, 44% to "other developed countries" and 41.7% to the rest of the world; this distribution is different from the one found in the general study (Table 2-6). Comparing the two sets of results, it can be concluded that in the developed countries (EU and other developed countries) the frequency of domino accidents has decreased, whereas in the rest of countries there exists an increasing trend.

Table 2-6. Comparison of domino accidents between general study and 21st century

	General study, %	21st century, %
EU	21.8	14.3
Other developed countries	54.5	44.0
Rest of the world	23.7	41.7

This should be considered, once more, as a clear indication that the developing countries have an enlarging problem with their chemical industry activities (furthermore, in some of these countries, the number and size of process plants is increasing), a stronger control being required.

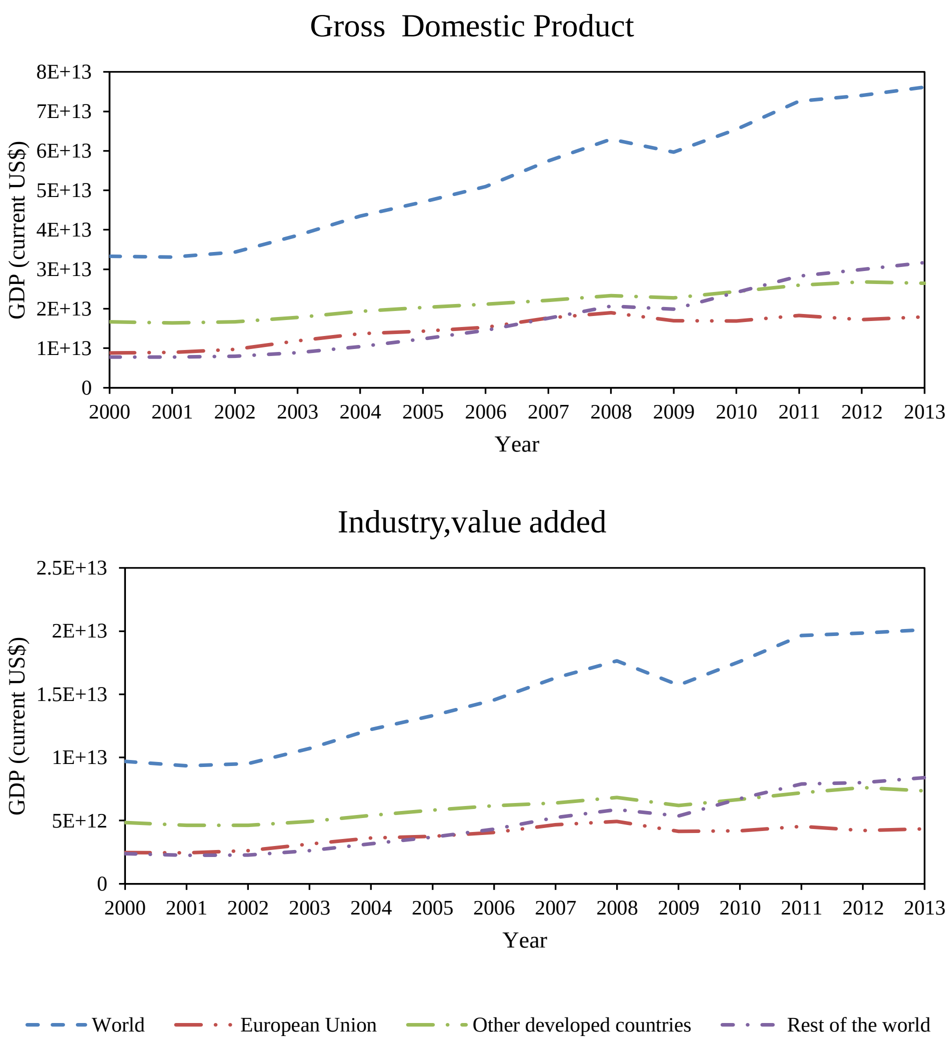


Figure 2-6. GDP and value added by industry in different parts of the world (The World Bank Data, 2015).

The Gross Domestic Product (GDP) (current US$)[1] and the value added by industry are shown for different parts of the world (Figure 2-6). Increasing trend of GDP is observed for the rest of the world. Moreover, the results show that the value added by industry in the rest of the world has a higher amount. It proves the greater rate of industrialization in those countries.

2.4.2 Substances involved and their hazards

No significant changes have been really detected in this category. LPG (14.3%) and oil (11.9%) –together with gasoline– keep being the most common substances involved in domino accidents. Hydrocarbons had a slightly higher contribution in the general study (61%, Table 2-1) than in this new set of data (53.7%). As for the type of hazard, flammable and toxic substances keep being the most frequent ones, followed by explosive and corrosive.

2.4.3 General and specific causes

Table 2-7 shows the main general causes; as in the general study, there are significant contributions also from mechanical failure and human factor, having the latter increased with respect to the overall set of data from 24.6% to 35%.

Table 2-7. General causes of domino accidents in 21st century

General cause	No. of accidents	Percentage
Mechanical-failure	19	40
Human factor	17	35
External events	10	21
Impact failure	5	10
Instrument failure	1	2
Services failure	1	2
Total	53	110

[1] GDP at purchaser's prices is the sum of gross value added by all resident producers in the economy plus any product taxes and minus any subsidies not included in the value of the products. It is calculated without making deductions for depreciation of fabricated assets or for depletion and degradation of natural resources.

Concerning the specific causes, and even though the sample is now much more reduced, overpressure keeps being the most frequent one in the “mechanical failure” category, and general maintenance is also the first specific cause inside “human error”.

2.4.4 General origin

The general origin of accidents in this century is illustrated in Figure 2-7, being the most significant contributions those of process plants, with an increase from 38.5% (in the general survey) to 51.2%. If the geographical distribution is analyzed, this increase is found in all three geographical categories, whereas in storage areas this frequency decreased. It should be noted that no accidents in transfer are found in the EU, while a 10.8% and 2.9% are found in “other developed countries” and “in the rest of the world”, respectively.

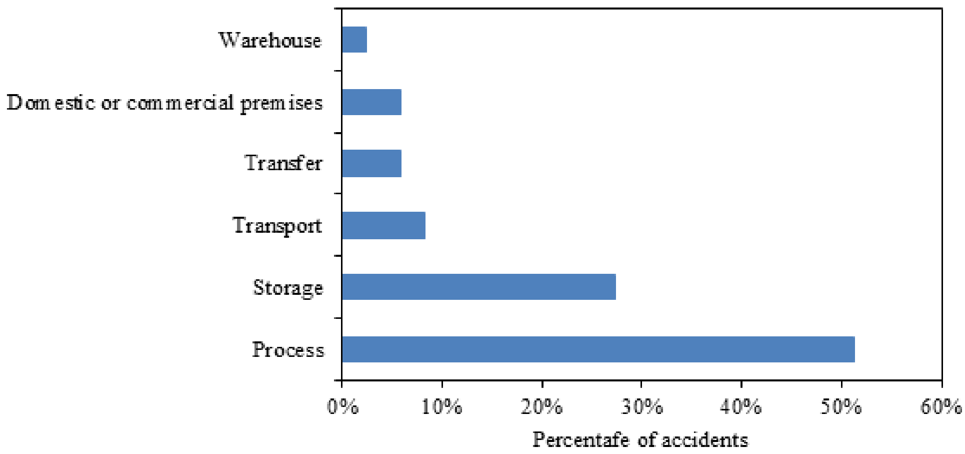


Figure 2-7. General origin of domino accidents in 21st century.

2.4.5 Affected population

The accumulated probability of domino accidents for the number of fatalities in the 21st century has also been studied. In the $p - N$ plot, the new b value is now -0.827. This number is slightly lower than the value previously obtained (-0.814) for the whole set of data, although the difference is not significant.

2.5 Discussion

Domino effect occurs with a certain frequency due to the fact that many process and storage plants are rather compact, with short distances between equipment. This means that, in the event of, for example, a fire, the possibility of flame impingement on a reservoir or a pipe is very high, with the subsequent failure, loss of containment and occurrence of an additional accident scenario. Thus, the domino effect can be very important because of its ability to significantly increase the severity of an accident through an escalation phenomenon. This is why the interest in studying it has increased in recent years.

The present study, performed on a set of 330 cases, has allowed the characterization of some interesting aspects of domino effect; as the cases studied were limited to relatively recent years (from 1961 up to 2013), this characterization must be considered as updated and valid for the current industry.

Most of the accidents (76.3%) occurred in the industrialized countries, what is quite logical taking into account that it is in these countries where the higher number of process industries are located. However, in the 21st century the contribution of developing countries has increased from 23.7% to 41.7%.

The survey has shown that most accidents occurred in process plants (38.5%) and storage areas (33%); the contribution of process plants has increased in the new century up to 51%. Taking into consideration the whole set of accidents, in the industrialized countries the frequency in process plants is higher than in the developing countries, in which storage areas have an important contribution; this is probably due to the fact that in these countries storage facilities are more common than process plants. A relatively low frequency was found in transportation (16.1%); this is a significant –and logical– difference when comparing with “all” major accidents (Vílchez et al., 1995). Instead, the occurrence in loading/unloading (11%) is quite similar. Explosion and fire keep being the initiating accident of the domino sequence, as shown by previous surveys.

The substances more frequently involved were the flammable ones: LPG, gasoline, oil, naphtha, with a rather reduced contribution of toxic materials (chlorine, ammonia); flammable materials were present in 142% of cases and toxic ones in 55% (percentages do not total 100 because diverse materials were often involved in the same accident). Consequently, the main initiating events were explosion (53% of cases) and fire (47%).

In the industrialized countries an important effort has been devoted to improving the safety of plants and operations. This seems to have given good results: the frequency of accidents occurrence shows a slight decreasing trend as a function of time for the European Union and the group of the here called “other developed countries”. Instead, the frequency of accidents in developing countries shows a slightly increasing trend for the whole period analyzed.

The most important causes of the domino accidents were mechanical failure, external events and human factor, increasing the latter from 24.6% to 35% when analyzing the accidents occurred in the 21st century. In addition, the influence of human factor is higher in the developing countries. These two findings suggest that actions need to be taken to improve this situation. Concerning mechanical failure, overpressure is the main specific cause. The importance of pressure relief systems should be emphasized, Kreder and Berwanger (1995) and Berwanger et al. (2000) found that approximately 40% of process equipment has at least one deficiency in its pressure relief systems. This deficiency can be originated from absent and/or undersized pressure relief devices or improperly installed pressure relief devices.

The consequences on the population were analyzed through the $p-N$ plot, which has shown that the probability of domino accidents with higher number of fatalities is higher for the developing countries; again, a better regulation of land use planning could be useful to decrease the impact of these accidents. As for the material damages and losses, no enough data could be gathered to analyze it quantitatively, although it is evident that the domino effect increases significantly the severity of the accident.

Finally, an interesting aspect is the domino sequences, which were analyzed by applying the relative probability event tree. 53% of the accidents started by an explosion and the rest of them (47%) were initiated by a fire. The secondary events were fire (194 cases), explosion (127 cases; in 10 case, a toxic cloud was also involved) and toxic cloud (only 9 cases). The ratio between "two-step" and "three-step" accidents has been found to be 6. There was only one four-step sequence case (fire→explosion→fire→explosion)

The domino effect occurs in many major accidents, increasing significantly both their complexity and their final effects and consequences. Although in recent years the interest on it has increased, less attention has been paid to domino effect as compared to other aspects of industrial accidents; this is the reason why its main features are still insufficiently known.

The results obtained from a historical survey may vary significantly according to the origin of the data analyzed. Thus, it is important to classify the data into adequate categories, such as, for example, industrialized countries and developing countries. A good example of this is the variation of the frequency of domino accidents as a function of time: for the EU and other developed countries the overall trend is slightly decreasing, whereas the developing countries show a certain increasing frequency over the last decades. Another aspect in which a significant difference has been detected is the severity of the accidents, especially for the most severe ones (more than twenty fatalities), which is again worse in these countries; land use planning is probably one of the aspects that can be associated to this situation. And, as a third significant difference, accidents originated by human factor are significantly more frequent in the developing countries. This could be explained by a poor safety culture and training in these countries.

Concerning the situation in the 21st century, a practically stationary frequency has been observed when accidents in the more industrialized countries are analyzed; this would confirm the fact –already observed in other surveys– that the traditionally increasing frequency of occurrence has changed to another trend (stable or slightly decreasing) in the developed countries. However, in the developing countries an increase in the frequency is observed.

A main conclusion which can be inferred from this survey is that the efforts devoted in the industrialized countries to improve the safety of both process plants and transportation of hazardous materials are clearly giving good results, both from the point of view of the frequency and the severity of the accidents. It is evident that a similar effort should be applied urgently in the developing countries, where the situation is unfortunately different and, furthermore, in some of them the chemical industry is growing significantly.

Finally, a set of recommendations can be issued from this survey.

- Accidents occurred in "transfer" operations continue having a constant and important occurrence. Equipment safety devices and methods of loading/unloading should be improved, as well as the specific training provided to the operators.
- Overpressure is the main specific cause of accidents originated by mechanical pressure. Design, installation and maintenance of safety relief devices should be stressed.
- Human factor keeps having a very important influence in domino accidents, even in the new century. This incidence is clearly higher in the developing countries; therefore, the training of the operators, both in maintenance and plant operation, should be significantly improved.
- The frequency of severe (more than twenty fatalities) accidents is higher in the developing countries; there can be probably an influence of land use planning regulations, which should be improved.
- Taking into account both primary and secondary events, fire is the accident with the highest contribution to domino effect. Therefore, the importance of fire protection and firefighting systems should be stressed.
- The frequency of domino effect accidents has lightly decreased in the EU and other developed countries, whereas there is an increasing trend in the developing countries. This indicates once more the importance of safety culture measures and land use planning, which should be more and more important in those countries in which chemical industry is experiencing a significant growth.
- When the BLEVE accidents were searched in the analyzed sample, 58 cases were found. 43 of them occurred as a consequence of a fire and 15 as the first event of a domino sequence; all of them originated a further accident. This implies the 18% of the whole sample.
- The fact that 74% of these BLEVEs were originated by a fire supported the previous belief that fire was the main cause of most BLEVEs. This is a very important aspect; if really it can be proved that this is true, then this would be a good reason to further strengthen and improve the thermal protection of those vessels which are prone to undergo such an accident. Therefore, an additional effort was done to improve the collection of data to analyze this subject in detail; next chapter has been devoted to this.

Chapter 3. FIRE AS A FIRST STEP OF DOMINO EFFECT IN BLEVES

3.1 Introduction

As seen in Chapter 2, the first event in a domino effect sequence is usually an explosion or a fire; these two accidents have approximately the same contribution when large sets of cases are analyzed. However, in the specific case of BLEVEs the situation changes significantly, fire having a much more significant role.

If a vessel containing a pressurized liquid is subjected to the effects of a fire, there is a certain possibility that, depending on the circumstances, it explodes after a time. This can happen even if the vessel is equipped with active or passive protection, and with pressure relief valves; and it can occur almost immediately or after more than one hour from the starting of the fire.

In this chapter the incidence of fire as a primary event leading to a BLEVE is analyzed, as well as the domino effect sequences found in such accidental scenario.

3.2 Effects of fire on a vessel

When a vessel is subjected to a fire, its effects will depend on the type of fire, especially on the thermal flux released, and on whether the equipment is exposed only to thermal radiation or there is flames impingement. As for the consequences, they will depend on the duration of the fire and on the equipment features: design (shape, wall thickness), filling degree and existence of protective measures.

3.2.1 Pool and tank fires

Pool and tank fires can last long time; if their thermal radiation reaches another relatively close equipment, unless this is adequately protected –both thermal insulation and water deluge can be a good protection in this situation– the conditions for failure could be reached.

In this type of fires, the combustion is rather bad due to poor air entrainment as the flow velocity in the flames is usually less than 10 m s^{-1} (Johnson and Cowley, 1992). Flames are composed of relatively bright zones, with a high concentration of incandescent soot, and other zones covered by black smoke; both zones contribute to thermal radiation, bright zones having the highest emissive power (E). For the non-luminous (smoke covered) zones, Muñoz et al. (2004), working with gasoline and diesel oil, found a value of $E_{soot} = 40$ kW m^{-2}, independent of the pool diameter and of the type of fuel. For the luminous, bright zones, they found E_{lum} values ranging between 80 and 120 kW m^{-2}, depending on the pool diameter and the type of fuel. The fraction of the fire surface covered by the luminous flame depends on the type of fuel, although an approximate value of 0.4 can be assumed; this would imply an approximate value for the whole fire surface of $E = 60$ kW m^{-2}. Moorhouse and Pritchard (1982) suggested that with large pool fires of hydrocarbons, excluding liquefied gases, E is unlikely to exceed this value. Other values have also been proposed: API 521 (Standard, 2007) suggests 80 – 100 kW m^{-2}; Nizner and Eyre (1983) obtained surface emissive powers of 35 kW m^{-2} for kerosene, 48 kW m^{-2} for LPG and 153 kW m^{-2} for LNG.

However, the radiation intensity decreases quickly as the distance from the flame surface increases, and the heat load on a given equipment will usually be much lower than these values.

If there is flame engulfment of an equipment, heat transfer will be the sum of two contributions, radiation and convection. Different values have been proposed: heat fluxes in the range of 95 – 130 kW m^{-2} have been measured for kerosene (Moodie et al., 1988), 80 – 150 kW m^{-2} for JP-4 (Schneider and Kent, 1989), 100 – 180 kW m^{-2} as a general range for liquid hydrocarbons and 150 – 250 kW m^{-2} for LPG pool fires (Johnson et al., 1992; Roberts et al., 2004). This can lead to rather high temperature increase rates of the vessel wall above the liquid level.

If there is flame impingement, deluge systems require high flow rates; adequate thermal insulation can give a good protection.

3.2.2 Jet fires

Jet fires thermal characteristics depend on the fuel and on the outlet velocity. Low pressure releases of liquid or two-phase mixtures give low velocity flames and bad combustion, a situation relatively close to that of a pool fire. If the velocity is high, air entrainment is important and this improves the combustion; however, with two-phase flow, the flame is still sooty and bright and the radiation mechanism dominates. Instead, with sonic gas flow –gas jet fires are often sonic and very turbulent– the combustion is very good and the flame is almost transparent, convection being much more important than radiation. This behavior has an important influence on the value of the flame surface emissive power; for propane, Palacios et al. (2012) obtained values of approximately $E = 80$ kW m^{-2} for gas jets and $E = 230$ kW m^{-2} for two-phase flow jet fires.

The thermal radiation intensity decreases significantly with the distance, but if there is impingement of the flames on a surface, very high heat fluxes occur. Impinging on a solid surface modifies significantly the shape of the flame, increasing the area of contact with the equipment. Accurate values cannot be predicted and a wide range of heat fluxes has been proposed; the following ones can be assumed (Casal, 2008):

- natural gas: 50 – 300 kW m^{-2}; average: 200 kW m^{-2}
- propane gas, sonic: 300 kW m^{-2}
- propane, two-phase flow: 150 – 220 kW m^{-2}
- propane, two-phase flow, low velocity: 150 kW m^{-2}.

If these heat fluxes impinge on a non-wetted wall, the temperature increase is so quick that the vessel can fail in a very short time.

3.2.3 Fireballs

The thermal radiation intensity from a fireball can be very strong at short distances. Flames surface emissive power depends on the fuel and is usually significantly higher than that of a pool fire, as practically all the fireball surface is covered by bright flames. Moorhouse and Pritchard (1982) suggested a range of 150 – 300 kW m^{-2}, although it can be as high as 350 kW m^{-2} for LPG. As the duration is short, protected equipment subjected to it will not fail; unprotected equipment could fail in some cases, but the probability is rather low due to the short exposure time. If there is flame impingement, heat fluxes can be in the range 200 – 350 kW m^{-2} (Lees, 1996; Mannan, 2014). In this case, water deluge systems are not efficient due to the turbulence of flames, but fireproofing layers are efficient; again, the contact time will be generally very short as the fireball will rise from the ground level, and the probability of failure must be considered rather low.

3.2.4 Flash fires

The contact time with the equipment is so short that the probability of originating a domino effect is usually negligible and should only be considered for the case of floating-roof tanks (Cozzani et al., 2006).

A summary of the approximate ranges of heat fluxes and surface emissive power for the diverse types of fire can be seen in Table 3-1.

Table 3-1. Approximate ranges of heat fluxes and surface emissive power

Type of fire	***E*, kW m^{-2}**	**Flame engulfment/impingement heat flux, kW m^{-2}**
Pool, tank	Hydrocarbons: 40 – 100	80 – 180
	LNG: 150 – 200	180 – 260
	LPG:50 – 120	150 – 250
Jet (LPG)	Two-phase: 230	150 – 220
	Gas: 80	200 – 350
Fireball	150 – 350	--
Flash fire	LNG, LPG: 125 – 280	--

3.3 Heating rate of vessel wall

When a vessel undergoes the effects of a fire, the situation can change dramatically depending on two circumstances: i) the vessel wall has or not a thermal insulation layer; ii) the vessel wall is in contact with a liquid or with a vapor or a gas.

The existence of a passive protection –a thermal insulation layer– should in principle imply that the vessel wall temperature will not increase up to dangerous values. However, if this protection does not exist or –as often happens– it has been destroyed by a mechanical action (erosion by a turbulent jet, the impact by a fragment from an explosion, a traffic accident in the case of a road or rail tanker), the wall is directly exposed to the fire effects.

In such circumstances, the situation can again significantly change depending on whether the wall is wetted by the liquid contained in the vessel or it is in contact with the vapor above the liquid level.

If the wall is wetted by liquid, its temperature will be close to that of the liquid and thus it will be protected and will not lose strength. However, if the wall is above the liquid level, i.e. it is in contact with the vapor, cooling by convection will be very poor and its temperature will increase rather quickly. The wall heat-up will be especially important if the vessel is engulfed by the flames.

Figure 3-1 shows the evolution of wall temperature for an empty vessel located on a pool fire (Planas Cuchi et al., 1996). With the initial development of the fire, the wall temperature increases quickly (3.5 ºC s^{-1} for the hexane pool, 5.8 ºC s^{-1} for the kerosene pool); in a second stage, with a fully developed fire, fire-induced wind reduced somewhat the wall heating rate: 1.3 ºC s^{-1} for the hexane pool, 3.6 ºC s^{-1} for the kerosene pool. In all cases the rate at which the temperature rises is very high, implying that in very short time the wall can be heated in such a way that, due to the weakening of the material, it will not stand the inside pressure.

The pressure inside the vessel will increase due to the fire heating of the wall surface wetted by the liquid, the heating rate depending on the liquid level and the vessel geometry, and these factors affect the pressure rise (Landucci et al., 2013). For example, a rail tank car filled to 94%, engulfed in a hydrocarbon pool fire, was pressurized up to the safety relief valve set pressure in approximately 2 minutes (Townsend et al.,1974).

However, even if the pressure relief valve opens, it could not prevent the vessel explosion if the vapor space wall has been heated up to too high temperatures; of course, if the valve action delays the explosion, the mass involved in it will be smaller and the effects will be less severe.

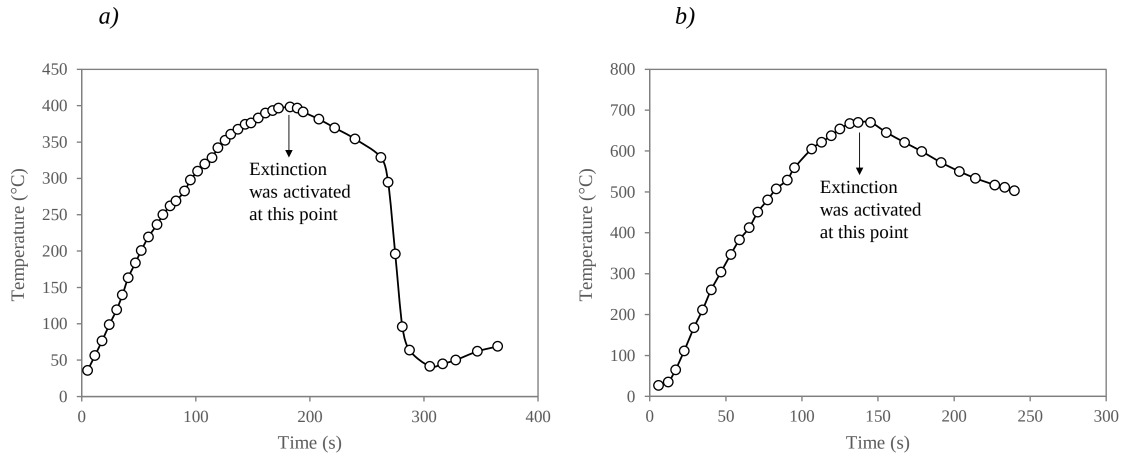


Figure 3-1. Temperature evolution as a function of time in a non-wetted wall of a vessel engulfed in a pool fire: a) pool fire of hexane, 4 m^2, lower lateral wall; b) pool fire of kerosene, 12 m^2, lower lateral wall (Planas Cuchi et al., 1996).

The aforementioned heating rates can be significantly higher if there is impingement of the flames from a highly turbulent jet fire, as in this case the heat flux will be much more important.

3.4 BLEVEs and domino effect sequences

In Chapter 1, a historical analysis was performed on 167 accidents involving a BLEVE event. The same set of data used in Chapter 1 was used here and the analysis of these cases allowed the identification of those accidents in which a domino effect sequence occurred. In 40 accidents, a BLEVE occurred as a single accident whereas in 127 cases a domino sequence was found and the corresponding information was statistically treated.

Table 3-2. General origin of BLEVE accidents with domino effect

General origin	No. of accidents	Overall percentage
Transport	60	47
Storage area	39	31
Transfer	22	17
Process plant	12	9
Domestic/commercial premises	6	5
Other	4	3
Total	143	112

Table 3-2 shows the type of plant or activity in which these 127 accidents occurred; the overall number of accidents (143) is larger than that of real accidents because some of them can be included in two different origins (for example, “transfer” and “storage area”). Practically half of the accidents occurred during transportation, followed by storage, transfer and process plants. It is interesting to note again the high contribution of transfer operations (22 accidents), as noted in Chapter 2.

Table 3-3. Specific origin of BLEVE accidents with domino effect

Specific origin	No. of accidents	Percentage
Rail tanker	40	31
Pressurized storage vessel	24	19
Road tanker	22	17
Portable transport containers	17	13
On plant pipes and associated valves	6	5
Atmospheric pressure storage vessels	5	4
Heat exchangers	4	3
Reactor	3	2
Ship	3	2
Hose	3	2
Other	8	7
Total	135	105

As for the specific origin (Table 3-3), rail tankers were the most common, followed by pressurized storage vessel and road tanker. Here again there are some misleading data; for example, in Table 3-2, 60 accidents correspond to "transport", while in Table 3-3 rail and road tanker plus ship accidents sum 65. This is due to the coincidence of both "transfer" and "transport" in several accidents in the MHIDAS database, which criterion has been kept here.

The substances involved in the accidents have been summarized in Table 3-4. The resulting overall number of accidents (199) is again much larger than that of real accidents because in many of them diverse substances were involved (e.g., in a train accident occurred in 2000 in Louisiana, dichloropropane, toluene diisocyanate, sodium hydroxide, ethylene oxide, acrylic acid and methyl chloride were involved). LPG was clearly the most frequent substance, followed by oil and other hydrocarbons; only four cases were found in which LNG was involved.

Table 3-4. Substances involved in BLEVE accidents with domino effect

Substance	**No. of accidents**	**Percentage**
LPG	90	71
Oil/Gasoline/Petrol/Diesel/Kerosene	14	12
Vinyl chloride	10	8
Ethylene oxide	7	6
LNG	4	3
Propylene	4	3
Other chemical substances	70	56
Total	199	159

As for the general cause of the accidents (Table 3-5), in practically two over five of them it was due to an impact; this cause was found mainly in transportation (typical accidents occurred in road and rail transportation). This was followed by other external events, mechanical failure and human factor, respectively.

Figure 3-2 shows the significance of fire in the BLEVE sequences. In 88 cases (69%) a fire was the first step, while in 33 cases the first event was directly a BLEVE. A typical scenario was a road or rail accident with a release of a flammable substance, quickly ignited; the flames travelled back to the release source, leading to a jet fire which, after a certain time, provoked the explosion of the vessel. In such cases, the existence of a jet fire impinging on the vessel wall is highly probable. If all domino effect steps in the analyzed sequences are considered, then 97 fires and 57 explosions leading to another event are found. Here again the larger contribution of fire as compared to that of explosion is evident.

Table 3-5. General causes of BLEVE accidents with domino effect

General cause	No. of accidents	Percentage
Impact failure	52	47
External events	39	35
Human factor	31	28
Mechanical failure	30	28
Instrument failure	5	5
Violent reaction	5	5
Services failure	1	1
Total	163	148

The explosion following the fire was in most cases the closing event of the sequence, although in a few ones it led to another explosion or to another fire. In those accidents in which the accidental sequence started with a BLEVE, this could lead to a fire (in most cases) or to another explosion. Of course, the complexity of the possible sequences depends on the plant arrangement or on the number of rail tankers involved in the accident.

As a whole, the sequence fire→explosion was found in 97 cases in the event tree, while explosion→another event, occurred only in 57 cases. It should also be noted that in a few, very unusual cases, the vessel can fail without exploding but releasing a large jet fire (Demichela et al., 2004).

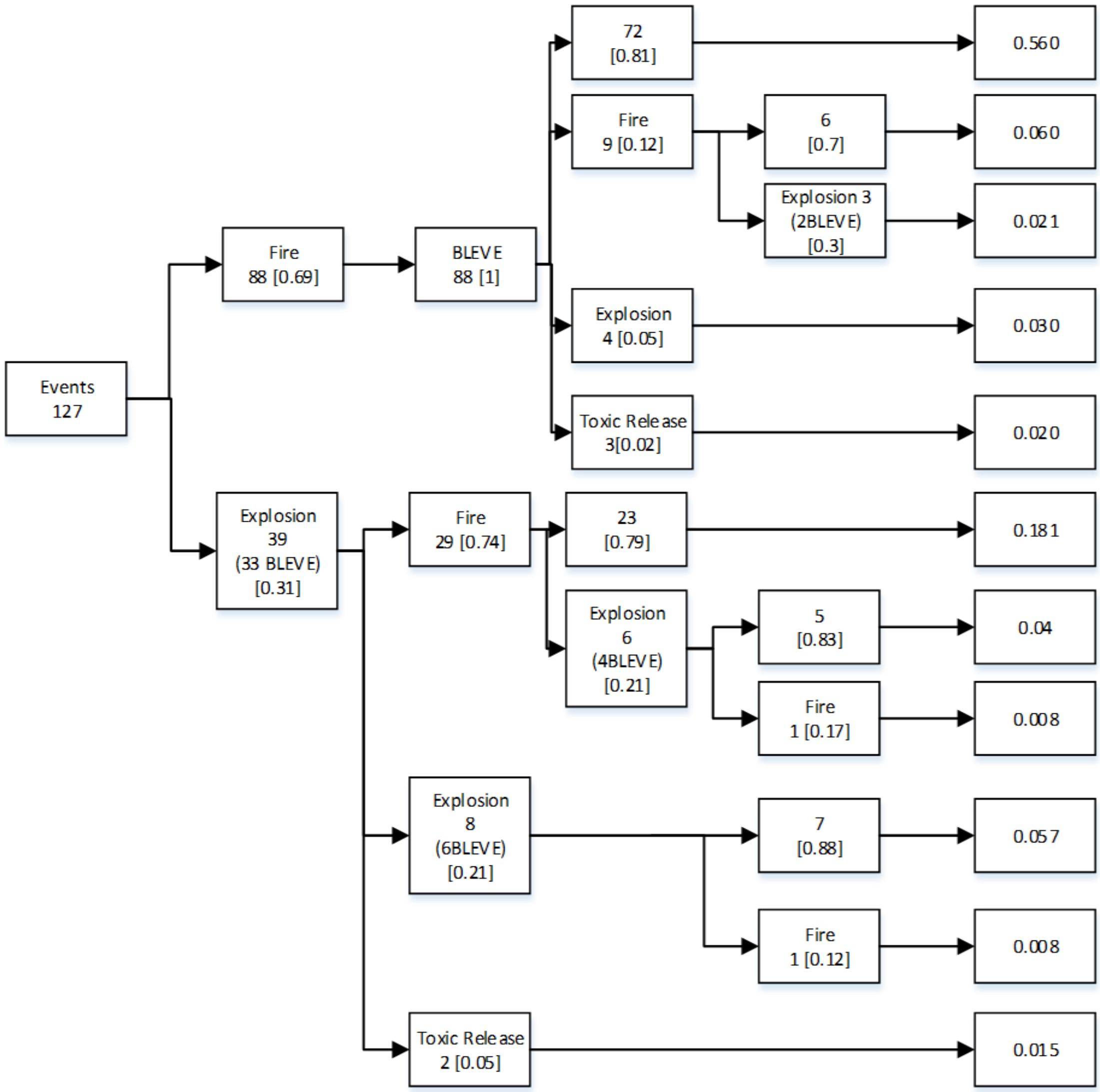


Figure 3-2. Domino effect sequences in BLEVE accidents.

3.5 Time to failure

When an equipment is subjected to the effects of a fire, the time to failure (TTF) is a very important aspect from the point of view of emergency management. Thirty years ago it was generally believed that when a pressurized vessel was subjected to direct contact with flames –a situation that could originate an explosion– about 25 – 30 minutes were available to try to solve the situation; after that time, the explosion could occur at any moment and therefore firefighters should move away. This false belief took the life of many people. It is now well known that in the aforementioned situation, depending on the circumstances, the explosion can occur after a few minutes from the start of the fire action, or even after a shorter time. In the San Juanico accident (Mexico, 1984), the first BLEVEs occurred 70 seconds after the first jet fires appeared; in the accident occurred in Nijmegen

(The Netherlands) in 1978, a tanker of LPG exploded at a filling station just 3 minutes after fire started underneath during unloading. However, the time to failure can be significantly higher: in the accident occurred in Zarzalico (Spain, 2011), an LNG road tanker was exposed to a very strong fire during approximately seventy minutes before the explosion occurred (Planas et al., 2015). Table 3-6 gives the time to failure for a series of accidents involving fire→BLEVE domino sequences (MHIDAS, 2007).

Diverse circumstances can have a significant influence on the value of the time to failure:

1. Whether the flames impinge on the vessel wall below the liquid level (tank wall being therefore refrigerated by the liquid) or above it; in this later case, if there is no passive protection, wall temperature will increase significantly and its tensile strength will decrease, what can eventually lead to the vessel burst in a relatively short time.
2. The existence of a protection system. Active or passive protection can be very useful to avoid or, at least, delay the failure of equipment undergoing thermal radiation or flames impingement.

Water deluge can be efficient to protect equipment subjected to pool fires effects, both for radiation exposure or flames impingement, as they are able to maintain a water film on the equipment surface (Table 3-7). With high momentum jet fires, however, a water deluge system should not be considered a good protection if there is flame impingement, as the high velocity of the jet will probably penetrate the water film and the dry surface will be in contact with the flames (Badri et al., 2013). Fixed water monitors could be effective delivering a high flow rate of water just to the flames impingement zone (Bradley, 2012).

Table 3-6. Time to failure for different cases (fixed plants and transportation)

	Date	Place	Sequence	Material	Time to failure
Fixed plants accidents	1984	Mexico	VCE→Jet fire→BLEVE→Fire	LPG sphere	70 s
	1978	Netherlands	Fire→BLEVE	LPG	3 min
	1961	USA	Fire→BLEVE→Fire	LPG cylinder	10 min
	1974	USA	Fire→BLEVE	LPG	13 min
	1982	USA	Fire→BLEVEs	LPG	15 min
	1978	USA	Fire→BLEVE	Isobutane, propane, propylene, butane	20 min, series of explosions
	2006	Italy	Fire→BLEVE	LPG cylinder	25 min
	1972	USA	Fire→BLEVE	LPG	40 min

	2011	Japan	Fire→BLEVE	LPG sphere	1 h
	1966	France	Fire→BLEVE→Fire→Expl.	LPG sphere	1.5 h
Transport accidents	1980	USA	Fire→BLEVE	Petrol road tanker	3 min
	1970	USA	Fire→BLEVEs	LPG rail cars	First car in 5 min, 6 rail cars in 40 min
	1970	USA	Fire→BLEVEs	LPG	15 min
	1987	Australia	Fire→BLEVE	LPG rail tanker	15 min
	1974	Spain	Fire→BLEVE	Ethylene cryogenic trailer	20 min
	1989	USA	Fire→BLEVE→Fire	Peroxide, polyethylene rail cars	Peroxide car in 20 min; polyethylene car in 6 h
	2002	Spain	Fire→BLEVE	LNG road tanker	20 min
	1972	USA	FIRE→BLEVE	Propylene road tanker	25 min
	1973	USA	Fire→BLEVE	LPG rail car	30 min
	1970	France	Fire→BLEVE	Propane tank car	40 min
	1971	USA	Fire→BLEVE	220 m^3 Vinyl chloride rail tanker	40 min
	1968	USA	Fire→BLEVE→Toxic release	Ethylene oxide	45 min
	2011	Spain	Fire→BLEVE	LNG road tanker	70 min
	1976	USA	Fire→BLEVE	Propane, isobutane rail tankers	First, explosion of propane tank; 1.5 h later, explosion of isobutane tank

However, water deluge systems and water monitors have some practical disadvantages, amongst which the large overall water requirement and corrosion/maintenance problems can be cited as the most important ones. Furthermore, they are restricted to fixed plants.

Table 3-7. Water application rates from API 2510A (Bradley, 2012)

Exposure to radiant heat (no flame impingement)	5 L min^{-1} m^{-2}
Flame impingement (pool fire)	5 – 12.5 L min^{-1} m^{-2}
Flame impingement (jet fire)	1000 – 2000 L min^{-1}

Therefore, passive fire protection is often used, both for vessels and for structural supports, when the danger of jet fires is considered. A fireproofing layer can delay or even avoid the equipment failure. Townsend et al. (1974) performed tests with full-scale rail tank cars containing propane, engulfed in a pool fire. In the case of an unprotected tank car equipped with a pressure relief valve (PRV), initially filled in a 94%, the tank underwent a powerful BLEVE after 24 min (content at the moment of failure: 40%); another tank car, also with a PRV, filled in an 85% and protected with a 3 mm layer of intumescent paint, experienced a BLEVE (content at the moment of failure: 3%) after 93 min. Therefore, fireproofing can increase the TTF, thus allowing the application of emergency measures such as evacuation, and PRV will decrease the amount of material involved in the explosion and in the subsequent (if the material is flammable) fireball. However, if the insulating protection is damaged (by erosion, or by a mechanical impact as often happens in the case of traffic accidents), the temperature of the unprotected element can increase quickly to dangerous values.

As a general approach, correlations have been proposed to estimate the time to failure for pressurized vessels (Landucci et al., 2009), even though they should be used only as indicative approaches and their predictions can be modified by specific circumstances.

3.6 Discussion

The historical analysis has shown that when the first event triggering the domino effect sequence is analyzed for a large set of accidents, fires and explosions have approximately the same contribution; even if fires are more frequent than explosions, the higher reach of explosion effects increases their contribution to domino effect. The same proportion is found when all domino effect steps in the diverse sequences are considered.

However, in the case of BLEVE accidents, fire is the prevailing first event, being found in approximately 70% of cases; when all domino effect steps in the diverse sequences are considered, the fire/explosion proportion is 1.7/1. Approximately half of the accidents associated to the fire→BLEVE sequence occurred in transportation.

If there is flame engulfment or impingement, a BLEVE can occur at any moment from the start of the fire, the time to failure ranging between one minute and more than one hour, depending on the circumstances.

From the point of view of emergency management, such a situation should therefore be considered as very dangerous; people should be evacuated immediately and firefighters should withdraw to a safe distance.

The existence of fireproofing and safety relief valves can contribute –but do not guarantee, especially in the case of mechanical impact– to increase the time to failure; furthermore, safety valves reduce the amount of material involved in the explosion and in an eventual fireball in the case of flammable materials. These passive protection measures are important, especially in the case of jet fires impingement.

Chapter 4. PREDICTION OF BLEVE BLAST: COMPARATIVE ANALYSIS OF THE DIVERSE METHODOLOGIES

4.1 Introduction

The effects of a BLEVE are blast and ejection of fragments. However, flammable substances are often involved in BLEVE accidents; in such cases, the explosion is usually followed by a fireball, which consequences can be very severe. Instead, if the involved material is not flammable (as, for example, water in the case of a steam boiler explosion), there will be no thermal effects.

The common method to predict the most important effects produced by a BLEVE, i.e. the peak overpressure and positive impulse of the blast wave, consist in determining the total mechanical energy released by the explosion. Then, by assuming that a certain percentage of this energy is converted into pressure wave, the peak overpressure can be estimated by the method of the TNT equivalent mass, Sachs scaled distance curve or other similar characteristic curves.

There is not a unique way to calculate the mechanical energy released in a BLEVE, and, several models can be found in the literature. The differences among them rely, basically, on the thermodynamic assumptions on which they are based. Very few attempts have been made to compare results given by the diverse models with experimental data available (Abbasi et al., 2007b; Bubbico and Marchini, 2008; Crowl, 1991; Laboureur et al., 2014; Ogle et al., 2012) and, mostly, the comparison has been made in terms of the peak overpressure generated.

Different authors studied thermodynamic approaches in order to calculate and compare the expansion energy and its resulting overpressures for different fluids in BLEVE accidents. According to those studies, methodologies based on real gas behavior and adiabatic irreversible expansion assumption (Planas Cuchi et al., 2004b; Casal et al., 2006) seem to give a better approximation for the resulting overpressure. However, methodologies based on the assumption of ideal gas behavior and isentropic expansion (Prugh, 1991) have been often applied in a conservative approach. Some questions still remain about the contribution of the different phases (gas and liquid) existing in the vessel to the generation of overpressure.

Therefore, a detailed and comprehensive analysis is required to compare all the methodologies, with their different thermodynamic assumptions, in order to have a better understanding about these different approaches and to try to clarify which are the "best" models. As it will be shown later on, most of the analyses published by the different authors considered only some of the proposed approaches and none of them considered all the published methodologies for their treatment. In this chapter, a comparative analysis of the diverse models used for the calculation of the mechanical energy and, from this value, the peak overpressure, is performed. Data available in the literature and corresponding to diverse experimental tests of BLEVEs with propane and butane vessels have been used.

4.1.1 The superheating limit temperature (Reid's theory)

As a previous step, it is necessary to clarify some aspects concerning a theory that has been very popular among specialist working in this field, and which could create some confusion.

Reid (1979) defined BLEVE as "*the sudden loss of containment of a liquid that is at or above its superheating temperature limit*". He considered that the temperature of the liquid contained in the vessel had to reach the so-called superheat limit temperature (T_{sl}) for the occurrence of a BLEVE explosion. If this limit temperature was not reached just before the depressurization, there would be an explosion, certainly, but it would not be a BLEVE, being much less severe than a BLEVE. According to Reid's definition, there is a mechanical unstable condition whenever $(\partial P/\partial V)_T \geq 0$. At this condition ($T > T_{sl}$), a liquid vaporizes spontaneously and explosively in the event of a sudden depressurization, with a very strong homogeneous nucleation in the whole mass of superheated liquid which gives rise to a practically instantaneous flashing of liquid. According to this theory, it would be this extraordinary nucleation and flash vaporization what would make BLEVEs so severe. Instead, if the temperature of the liquid at the moment of vessel failure is below T_{sl}, the explosion –much less severe– will not be a BLEVE and the overpressure wave will be much less stronger.

Figure 4-1 shows the vapor saturation curve and superheat limit loci, according to Reid's theory. Let us suppose a liquid, with a given T_{sl} value of the superheat limit temperature, in a closed vessel which is being heated. Its pressure and temperature will increase following the P-T equilibrium line. If at a certain moment, at situation A, the vessel fails (T being below T_{sl}), the depressurization will follow the AB line and the explosion will not be a BLEVE. However, if during the depressurization the "superheat limit curve" (sometimes called spinodal line) is reached, as, for example, following the CD line, the explosion will be a BLEVE.

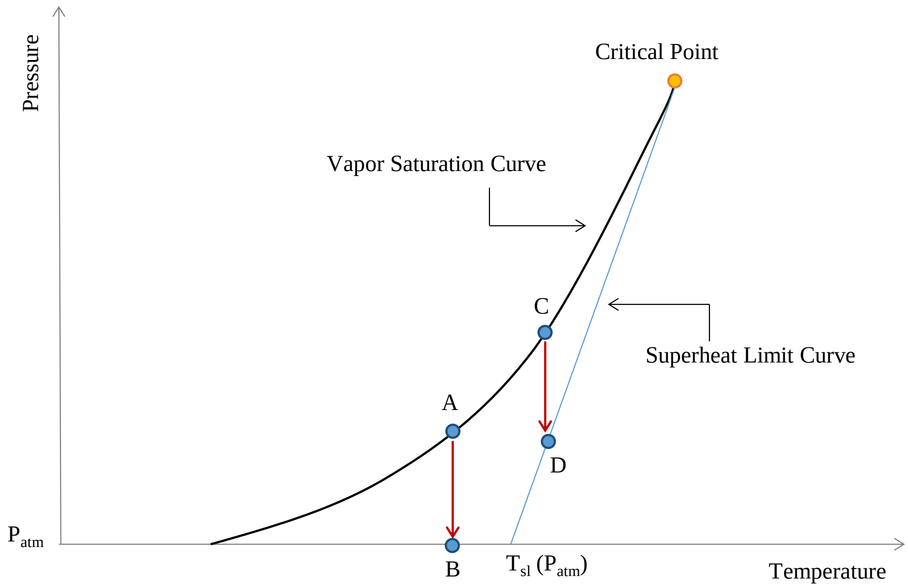


Figure 4-1. Vapor saturation curve and superheat limit line according to Reid theory.

Based on $(\partial P/\partial V)_T = 0$, Salla et al. (2006) calculated T_{sl} for various substances. In this case, they used the Redlich-Kwong (RK) and Van der Waals (VdW) equations of state (EOS). There is a difference of about 30 K between the results obtained from these two EOS. Other authors (Reid, 1983; Sigales, 1990; CCPS, 1994) have proposed several simplified equations to calculate T_{sl}, that are summarized and presented here:

$$T_{sl-T_c} = 0.895 \cdot T_c \tag{4.1}$$

$$T_{sl-T_0} = 0.822 \cdot T_c + 0.105 \cdot T_0 \tag{4.2}$$

$$T_{sl-P_0} = T_c \left(0.11 \cdot \left(\frac{P_0}{P_c}\right) + 0.89\right) \tag{4.3}$$

Salla et al. (2006) also calculated T_{sl} by using the aforementioned equations. They used RK and VdW equations of state together with equations (4.1), (4.2) and (4.3). The results obtained were closer to the T_{sl} values obtained with RK EOS than those from VdW EOS. They concluded that there was a significant uncertainty into the final T_{sl} values if the methods were based on the thermodynamic stability approach, depending on which equation of state was used. Finally, these authors introduced a new approach for the T_{sl-E}

concept. According to their definition, the superheat limit temperature corresponds to a situation in which the energy transferred between the cooling liquid and the vaporizing liquid fractions is at its maximum (leading therefore to a minimum amount of energy in the remaining liquid). The main advantage of this approach is that it only depends on the properties of the substance involved and it does not require using an equation of state . Table 4-1 summarizes the values obtained for T_{sl} according to the diverse methods proposed for some of the substances typically involved in BLEVE accidents.

Table 4-1. Superheat limit temperature obtained from the various methods (Salla et al., 2006)

	$T_{sl-RK}(K)$	$T_{sl-VdW}(K)$	$T_{sl-T_c}(K)$	$T_{sl-T_0}(K)$	$T_{sl-P_0}(K)$	$T_{sl-E}(K)$
Propane	332.0	313.5	331.0	328.3	330.1	315.3
n-Butane	381.5	360.0	380.6	378.3	379.8	348.8
Methane	170.9	161.5	170.6	168.4	170.1	174.7
Ethylene	253.3	239.0	252.7	250.0	252.0	257.2
Ammonia	363.1	343.0	362.9	358.6	361.3	375.2
CO_2	272.5	257.0	272.2	270.5	271.1	280.2
Chlorine	372.2	353.0	373.1	367.9	371.6	375.2
Water	573.0	547.0	579.3	571.4	576.4	606.4

However, nowadays the Reid theory on the superheat limit temperature is not taken into account when analyzing real vessel explosions. Reid's theory could probably be applied at laboratory scale, with small vessels, clean and smooth vessel surface, homogeneous heating, homogeneous liquid temperature (liquid mixing), etc. Instead, at large, real scale, with strong local heating effects and significant temperature differences, the explosion does not follow it. In fact, none of the methods proposed in the literature to calculate the overpressure from a BLEVE takes it into account. This can be checked very easily: if Reid's theory would apply, when calculating ΔP as a function of vessel temperature, a clear discontinuity should appear at T_{sl}, with an abrupt increment of the released energy (overpressure generation energy) and of the peak overpressure.

To illustrate this point, a specific case was defined as an example: a 45 m^3 vessel which is heated up from ambient temperature (300 K) and initially filled up to 50% with liquefied propane. The mechanical energy of the contained fluid was calculated by applying different mathematical models based on different thermodynamic assumptions (analyzed later in this chapter). The results are shown in Figure 4-2. Based on Reid theory, there should be an abrupt change at T_{sl}. However, the data plotted in this figure show that there is not any sudden change in the mechanical energy predicted by anyone of the different models applied.

This is one of the reasons why nowadays Reid's theory is not taken into account in risk analysis, even though it can be useful for a better understanding of BLEVE mechanism.

Birk et al. (2007, 1993) and Leslie and Birk (1991) performed vast experimental investigations about the BLEVE phenomenon. In contrast with Reid's definition, these authors stated that a BLEVE can be expected not only at or above the superheat limit temperature, but also below this temperature. According to their definition, the catastrophic failure of an LPG container leads to violent flashing if the liquid is at superheated condition (i.e. at a temperature higher than its boiling temperature at atmospheric pressure); however, the severity of BLEVEs that happen at their superheat limit temperature is higher than those which occur at lower temperatures.

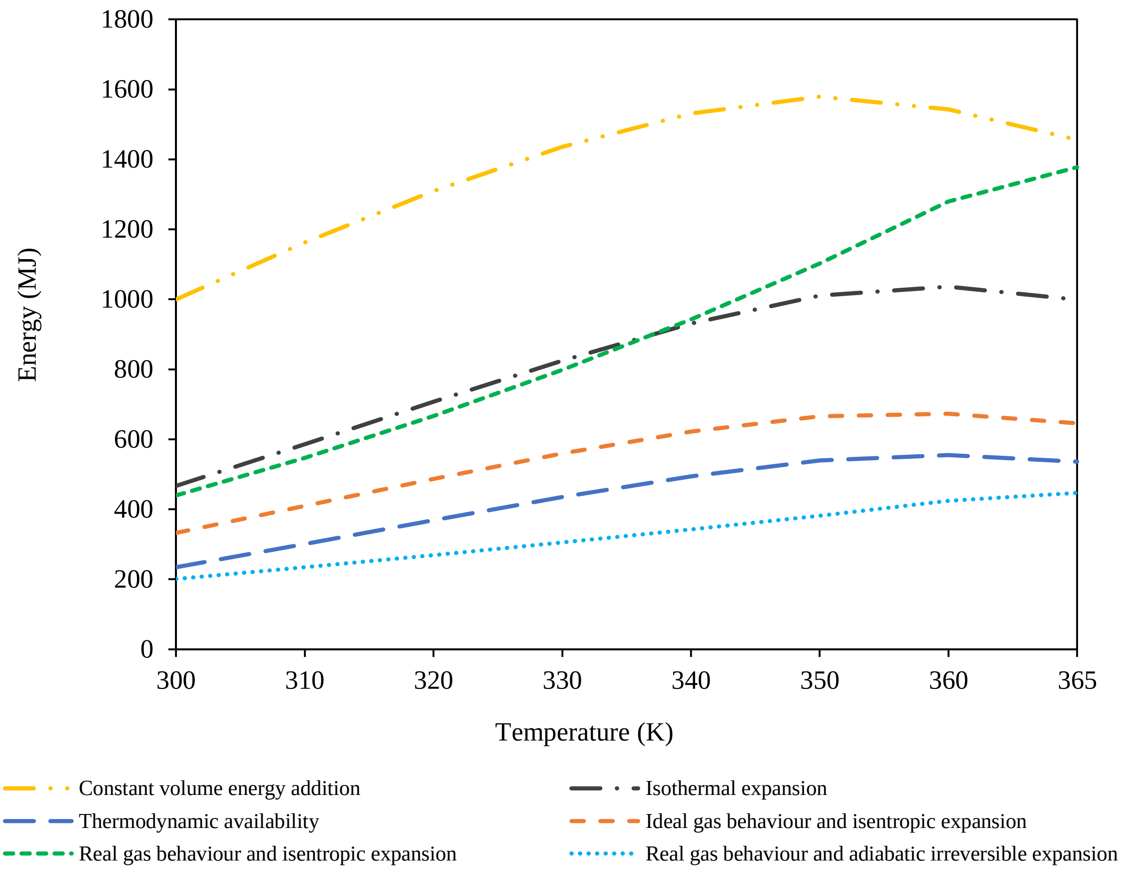


Figure 4-2. Mechanical energy as a function of temperature (including T_{sl}) for propane, according to different mathematical models.

The degree of superheating, which depends on the temperature and pressure inside the vessel just before the rupture, plays an important role in the flashing of liquid and in the generation of the subsequent pressure wave. Figure 4-3 illustrates the degrees of superheat for ammonia, and butane.

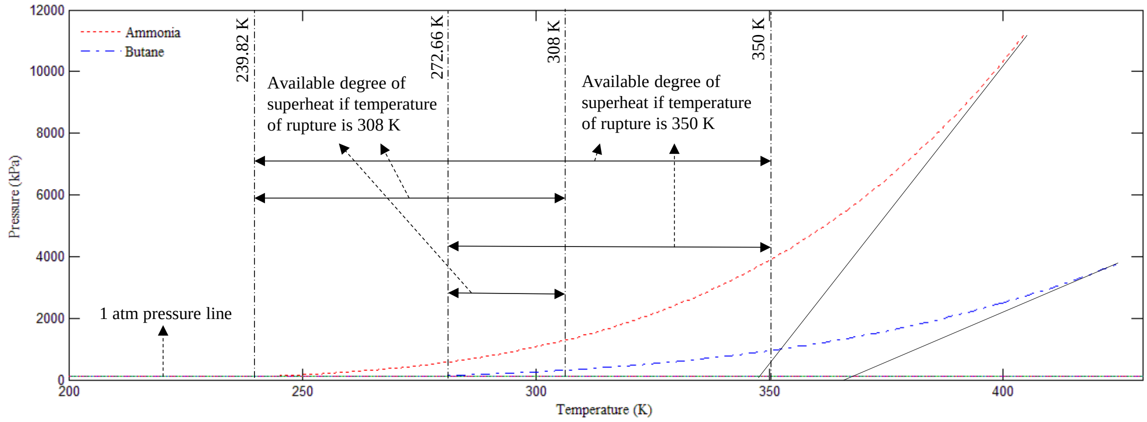


Figure 4-3. Superheating degrees and superheat limit loci for ammonia and butane at P-T graph (Abbasi et al., 2007b).

In fact, the severity increases with the liquid temperature, as the amount of energy contained in it (liquid enthalpy) increases. Indeed, Birk and coauthors have shown that the so-called homogeneous nucleation is not a prerequisite for BLEVE accidents. In some circumstances, a BLEVE can happen both at a temperature near the ambient one or –more often– at a temperature well above it. These explosions are called by some authors cold/weak and hot/strong BLEVEs if they are close or far above the ambient temperature, respectively.

4.2 Review of methods

4.2.1 Methods for evaluating the energy released in the explosion

In the catastrophic failure of a vessel containing a superheated liquid, the expansion of the preexisting vapor at the rupture moment plus the partial flashing of the liquid to vapor give the available mechanical energy. Some part of that energy is the source of overpressure wave. In order to calculate the mechanical energy, different thermodynamic assumptions have been considered. These assumptions have been summarized here:

- Constant volume energy addition (Brode, 1959)
- Real gas behavior and isentropic expansion (CCPS, 2010)
- Isothermal expansion (Smith et al., 1996)
- Ideal gas behavior and isentropic expansion (Prugh, 1991)

- Thermodynamic availability (Crowl, 1991, 1992)
- Real gas behavior and adiabatic irreversible expansion (Planas Cuchi et al., 2004b)
- Liquid superheating energy (Casal and Salla, 2006).

By reducing the pressure of the contained superheated liquid to the atmospheric one, a fraction of liquid flashes to vapor. The volumetric amount of flashed liquid can be obtained by knowing the flashing fraction, which can be calculated as:

$$f = 1 - exp\left[-2.63 \cdot \frac{C_{PL,Tb}}{\Delta h_{v,Tb}} \cdot \left(1 - \left[\frac{T_c - T}{T_c - T_b}\right]^{0.38}\right) \cdot (T_c - T_b)\right] \quad (4.4)$$

And the volume of flashed superheated liquid is:

$$V_f = L \cdot f \cdot \left(\frac{\rho_L}{\rho_V}\right) \quad (4.5)$$

So, the total volume of vapor contributing to generate the explosion energy while reducing the pressure to the atmospheric one is the summation of the preexisting volume of vapor inside the vessel before the explosion and the volumetric fraction of flashed liquid:

$$V^* = V + V_f \quad (4.6)$$

Constant volume energy addition

The energy which is needed to increase the pressure of gas/vapor from ambient condition to the one just before the explosion state provides the energy of explosion (Brode, 1959). According to this assumption, the pressurization process happens at constant volume. Thus:

$$E^* = \frac{(P - P_0) \cdot V^*}{(\gamma - 1)} \quad (4.7)$$

Real gas behavior and isentropic expansion

Real gas behavior and isentropic assumption are considered for the vapor expansion during the explosion. The difference between internal energies just before the explosion and atmospheric (just after the explosion) states provides the energy of explosion:

$$E = \Delta U = m_{L0} \cdot u_{L0} + m_{V0} \cdot u_{V0} - m_L \cdot u_L - m_V \cdot u_V \tag{4.8}$$

The liquid and vapor masses at the final state are:

$$m_{V0} = x_L \cdot m_L + x_V \cdot m_V \tag{4.9}$$

$$m_{L0} = (1 - x_L) \cdot m_L + (1 - x_V) \cdot m_V \tag{4.10}$$

And the fractions of liquid and vapor can be expressed as:

$$x_L = \frac{S_L - S_{L0}}{S_{V0} - S_{L0}} \tag{4.11}$$

$$x_V = \frac{S_V - S_{L0}}{S_{V0} - S_{L0}} \tag{4.12}$$

Isothermal expansion

Depressurization happens abruptly at the explosion moment; so, it can be assumed that the temperature of the contained fluid does not have the chance to decrease; thus, considering that an isothermal process takes place, the energy of explosion will then be:

$$W = R \cdot T \cdot \ln\left(\frac{P}{P_0}\right) \tag{4.13}$$

By substituting the number of vapor moles and adding V^*, from Eq. (4.13) the following expression of the energy released can be obtained:

$$E^{*} = P \cdot V^{*}. \ln\left(\frac{P}{P_0}\right) \tag{4.14}$$

Ideal gas behavior and isentropic expansion

This approach considers that the expansion of the vapor is adiabatic and reversible (isentropic); the ideal gas law is thus followed. Then, the energy released by explosion can be expressed as:

$$E^{*} = \frac{P \cdot V^{*}}{R \cdot T} \cdot \left[1 - \left(\frac{P_0}{P}\right)^{\frac{\gamma-1}{\gamma}}\right] \tag{4.15}$$

Thermodynamic availability

The concept of thermodynamic availability (exergy) was used by Crowl (1991, 1992) to calculate the energy of explosion. In this method, the actual potential of a system to do work is estimated as the energy of explosion by considering ideal gas behavior. The batch availability for this case is:

$$\Delta B = -R \cdot T_0 \left[ln\left(\frac{p}{P_0}\right) - \left(1 - \left(\frac{P}{P_0}\right)\right)\right] \tag{4.16}$$

However, in BLEVE explosions, the temperature of the superheated fluid inside the vessel is usually higher than the ambient temperature because, in many cases, the vessel has been heated by external fire. So, the batch availability formula can be converted to:

$$\Delta B = C_{pv} \cdot (T_{p_0} - T) - C_{pv} \cdot T_0 \cdot ln\left(\frac{T_{p_0}}{T}\right) - R \cdot T_0 \cdot ln\left(\frac{P}{P_0}\right) - R \cdot T \cdot \left(\frac{P_0}{P} - 1\right) \tag{4.17}$$

Equations (4.16) and (4.17) give the useful energy per mole of gas contained in the vessel. To calculate the total amount of gas or vapor involved in the explosion process from these equations, the following expression should be used:

$$E^{*} = \left(\frac{P \cdot V^{*}}{R \cdot T}\right) \cdot \Delta B \tag{4.18}$$

Real gas behavior and adiabatic irreversible expansion

Planas-Cuchi et al. (2004b) assumed that the expansion associated to the explosion is an adiabatic irreversible process; they also considered real gas behavior. These assumptions seem to be closer to the real situation than those corresponding to an isentropic process (an explosion is supposed to create a high amount of entropy). At adiabatic conditions, it can be assumed that the work is equal to the change in the internal energy of the vessel content:

$$-P \cdot \Delta V = \Delta U \tag{4.19}$$

This equation can be solved analytically in order to find the vapor fraction at the final state (equation (4.22)):

$$P \cdot \Delta V = P \cdot [(v_{V0} - v_{L0}) \cdot m_T \cdot x + m_T \cdot v_{L0} - V_T] \tag{4.20}$$

$$-\Delta U = (u_{L0} - u_{V0}) \cdot m_T \cdot x - m_T \cdot u_{L0} + U \tag{4.21}$$

$$x = \frac{m_T \cdot P \cdot v_{L0} - V_T \cdot P + m_T \cdot u_{L0} - U}{[(u_{L0} - u_{V0}) - (v_{V0} - v_{L0}) \cdot P] \cdot m_T} \tag{4.22}$$

Liquid superheating energy

Casal and Salla (2006) assumed that the expansion work of the superheat flashing liquid is the essential contribution in BLEVE overpressure. Even if the constant values (k in Eq. (4.24)) finally used in this method were obtained from all the energy released in the explosion, Eq. (4.24) uses only the mass of liquid in the vessel at the moment of explosion. They assumed an adiabatic process; therefore, the excess stored heat inside the superheated liquid would cover the expansion work which leads to blast wave. The authors defined the "Superheating Energy" as:

$$SE = h_L - h_{L0} \tag{4.23}$$

They demonstrated that, for an isentropic process (assuming that 50% of the energy released was devoted to braking the vessel and ejecting the fragments; see last paragraph of this section), 14% of SE would be invested in creating blast if a reversible process was assumed (what they did not consider acceptable). If, instead, an irreversible (much more realistic) process is assumed, only 5% of SE originates blast; these percentages were introduced through a constant k:

$$E_w = k \cdot m_L \cdot SE \tag{4.24}$$

However, in this thesis, in order to make possible the comparative analysis, k values will be lightly changed, assuming that only 40% (instead of 50%) of the energy participates in resulting BLEVE blast. So, we have:

$k = 0.11$ for isentropic process

$k = 0.04$ for irreversible process

In this study, the irreversible process is considered for the comparative analysis.

Most of the aforementioned methods are able to calculate the maximum amount of energy available that can be released in a BLEVE. However, not all this energy is converted to blast overpressure. Actually, some fraction of the energy is used to break the vessel and eject the fragments (this has been already included in the method proposed by Casal and Salla (2006)). The mechanical properties of materials that constitute the vessel, play here an important role. Approximately 80% and 40% of the energy is considered to generate overpressure in fragile and ductile failures, respectively. The rest of the energy is used for breaking the vessel and ejecting the fragments. This consideration introduces a certain additional (and practically unavoidable) uncertainty when calculating the blast.

4.2.2 From energy released to overpressure wave

Once the energy invested in creating the blast wave is known, it is necessary to estimate the value of the peak overpressure generated.

There are several methods to do this. One which is simple, even though it should be essentially applied to unconfined explosions, is that based on the equivalent TNT mass. The blast energy of TNT is usually considered as $\Delta H_{TNT} = 4680$ kJ·kg^{-1}. Once the equivalent mass of TNT has been calculated (equation (4.25)), the TNT scaled distance can be determined:

$$m_{TNT} = \frac{\beta \cdot E^*}{\Delta H_{TNT}} \tag{4.25}$$

$$\overline{R} = \frac{r_0}{(m_{TNT})^{1/3}} \tag{4.26}$$

Here, β (the fraction of the total mechanical energy converted into pressure wave) will be considered to be 0.4 (i.e., 40%) for all calculations as a ductile failure is assumed.

Another possibility is to use the Sachs scaled distance (based, as well as the TNT scaled distance, on the Hopkinson law), calculated from the following expression:

$$R_s = r_0 \cdot \left(\frac{P_0}{2 \cdot \beta \cdot E^*}\right)^{1/3} \tag{4.27}$$

Figure 4-4 shows the curves to be used for both aforementioned methods. In the case of superheating energy method, E_w should be substituted directly instead of $\beta \cdot E^*$ in equations (4.25) and (4.27).

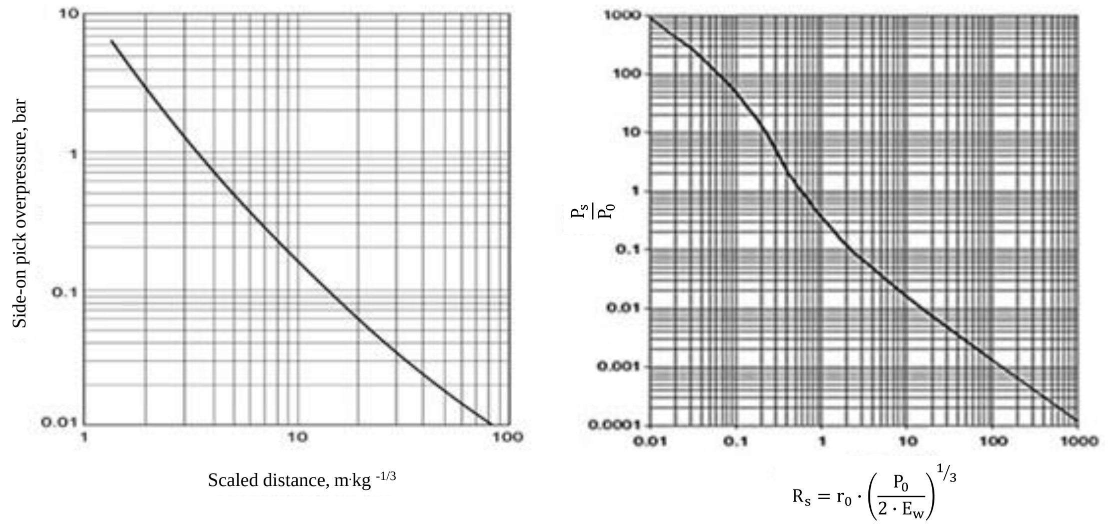


Figure 4-4. Pressure vs. Scaled distance curve: TNT equivalent mass method (left) (CCPS, 1994); Sachs method (right) (Laboureur et al., 2014).

4.3 Review of comparative analyses

A few authors have performed a comparative analysis of some of the aforementioned methodologies (Table 4-2). In the following paragraphs, their analyses and conclusions are commented.

Crowl (1992) conducted a research by using thermodynamic availability, in order to calculate the maximum explosion energy of expansion gas contained in a vessel. Crowl (2010) compared the results obtained in this way with those from three other methods, those based on isothermal, isentropic expansion and constant volume energy addition assumptions. According to their analysis, the isothermal method is more conservative than the other three methods, and that assuming isentropic expansion is the one which predicts the lowest value because it considers the final temperature much lower than the surroundings one. The following conclusion was deduced by them for the value of the energy of expansion obtained from the diverse approaches:

Isothermal approach > constant volume energy addition approach > thermodynamic availability approach > isentropic approach.

Table 4-2. Thermodynamic assumption considered in different studies

	Thermodynamic assumptions*					
Study	**CV**	**RIE**	**IE**	**IIE**	**TA**	**RAIE**
Abbasi, 2007		✓		✓		✓
Bubbico and Marchini, 2008	✓	✓			✓	✓
Crowl,2010	✓		✓	✓	✓	
Ogle, 2012		✓		✓		✓
Laboureur, 2014		✓		✓		✓

*CV = Constant volume energy addition; RIE = Real gas behavior and isentropic expansion; IE = Isothermal expansion; IIE = Ideal gas behavior isentropic expansion; TA = Thermodynamic availability; RAIE = Real gas behavior adiabatic irreversible expansion

Ogle et al. (2012) followed the work of Crowl (1992), calculating the maximum energy which could be released by a BLEVE. They applied this method to different fluids and compared the results with those obtained from other methodologies (ideal gas behavior and isentropic expansion (Prugh, 1991), real gas behavior and isentropic expansion (CCPS, 2010) and real gas behavior and adiabatic irreversible expansion (Planas Cuchi et al., 2004b). The energy of expansion calculated by thermodynamic availability method was much larger than predicted by the other methods, and the real gas behavior and adiabatic irreversible expansion ones gave the lowest energy; the other two methods gave similar values, except when approaching the critical temperature. However, the relative magnitude changed for each fluid.

Abbasi et al. (2007b) performed also a review study of several of these methodologies. According to their results, if the burst energy of a vessel filled with propane was equal to 1 kJ as per the method based on ideal gas and isentropic expansion assumption (e.g. Prugh (1991)), then it would be about 1.1 kJ and as per the method based on real gas behavior and isentropic expansion (e.g. CCPS (2010)) and 0.4 kJ as per the method based on real gas behavior and adiabatic irreversible expansion (Planas Cuchi et al., 2004b); their comparative study shows that this last method (Planas Cuchi et al., 2004b) is less conservative than the other ones and probably much closer to the real value.

Bubbico and Marchini (2008) studied an accident involving the explosion of a vessel filled with propane. They applied different methods to calculate the explosion energy and compared the corresponding calculated overpressures with the value obtained from the analysis of the real case at two different distances. Comparing the estimated results with the real case, they observed that the methodologies based on real gas behavior and adiabatic irreversible expansion assumption gave the closest values; they noted that the constant volume energy addition or isentropic expansion assumptions, even if far from the real phenomenon, may be convenient for conservative calculations.

Finally, Laboureur et al. (2014) performed also a comparative study. They classified the experimental data into three different groups in terms of TNT equivalent mass: large scale (m_{TNT} >1 kg_{TNT}); mid-scale (m_{TNT} = 1 kg_{TNT}); small-scale (m_{TNT} < 1 kg_{TNT}). The methodologies based on real gas behavior and adiabatic irreversible expansion assumption (Casal and Salla, 2006; Planas Cuchi et al., 2004b) gave the best fit in all cases. These authors commented as well that the methodologies based on ideal gas behavior and isentropic expansion assumption (e.g. Prugh (1991)) could be used in a rather conservative approach, even though what their results give really should be considered in fact the theoretical upper limit of the energy released.

4.4 BLEVE mechanical energy: a comparative study of the prediction from the different methodologies

To study the effects predicted by the diverse models previously commented, a scenario was defined for a 45 m^3 vessel filled up to a 20%, 50%, and 80% of its total volume with different substances (the ones most commonly found in BLEVE accidents according to the data from the previous chapters). It was assumed that the vessel was heated up by an external thermal source and that it could break at any temperature up to the critical one; therefore, the released energy was calculated for all these temperatures. NIST Reference Fluid Properties (Version 9.1; Lemmon et al., 2007) was used for the thermodynamic calculations. Figure 4-5, Figure 4-6, and Figure 4-7 summarize the results obtained. The liquid superheating energy method (Casal and Salla, 2006) was not shown in this set of calculations because this method does not give overall energy released, but just the energy invested in creating the overpressure wave; however, it will be considered and included in the subsequent comparative study.

Based on Figure 4-5, Figure 4-6, and Figure 4-7, the results show that the methods based on real gas behavior and adiabatic irreversible expansion give the lowest values for all the substances, with a good agreement with the results of some of the previously mentioned studies (Bubbico and Marchini, 2008; Labourier et al., 2014).

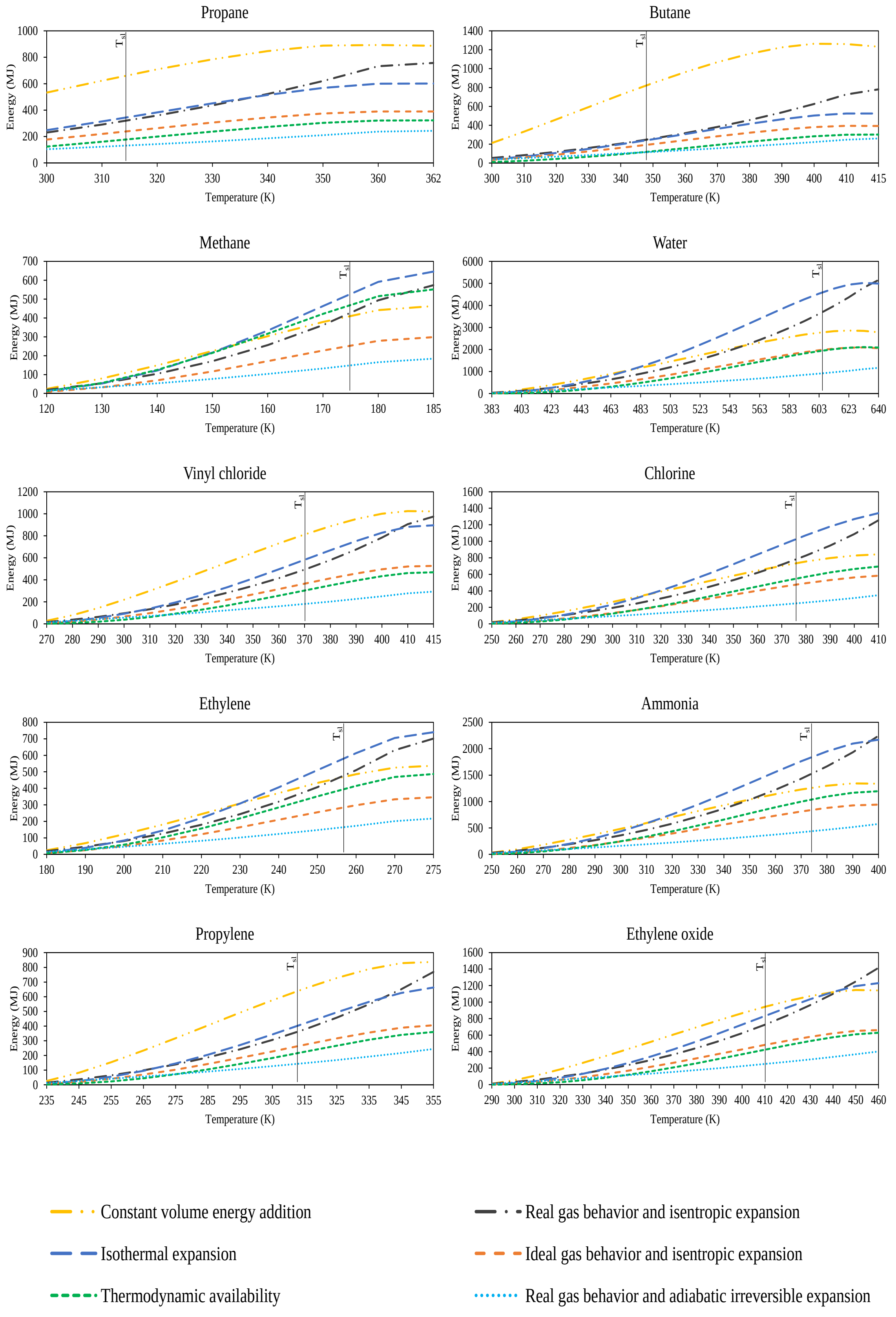


Figure 4-5. Mechanical energy released by the explosion at different temperatures and 20% initial filling level (just before the explosion), based on the diverse thermodynamic assumptions for 10 different substances.

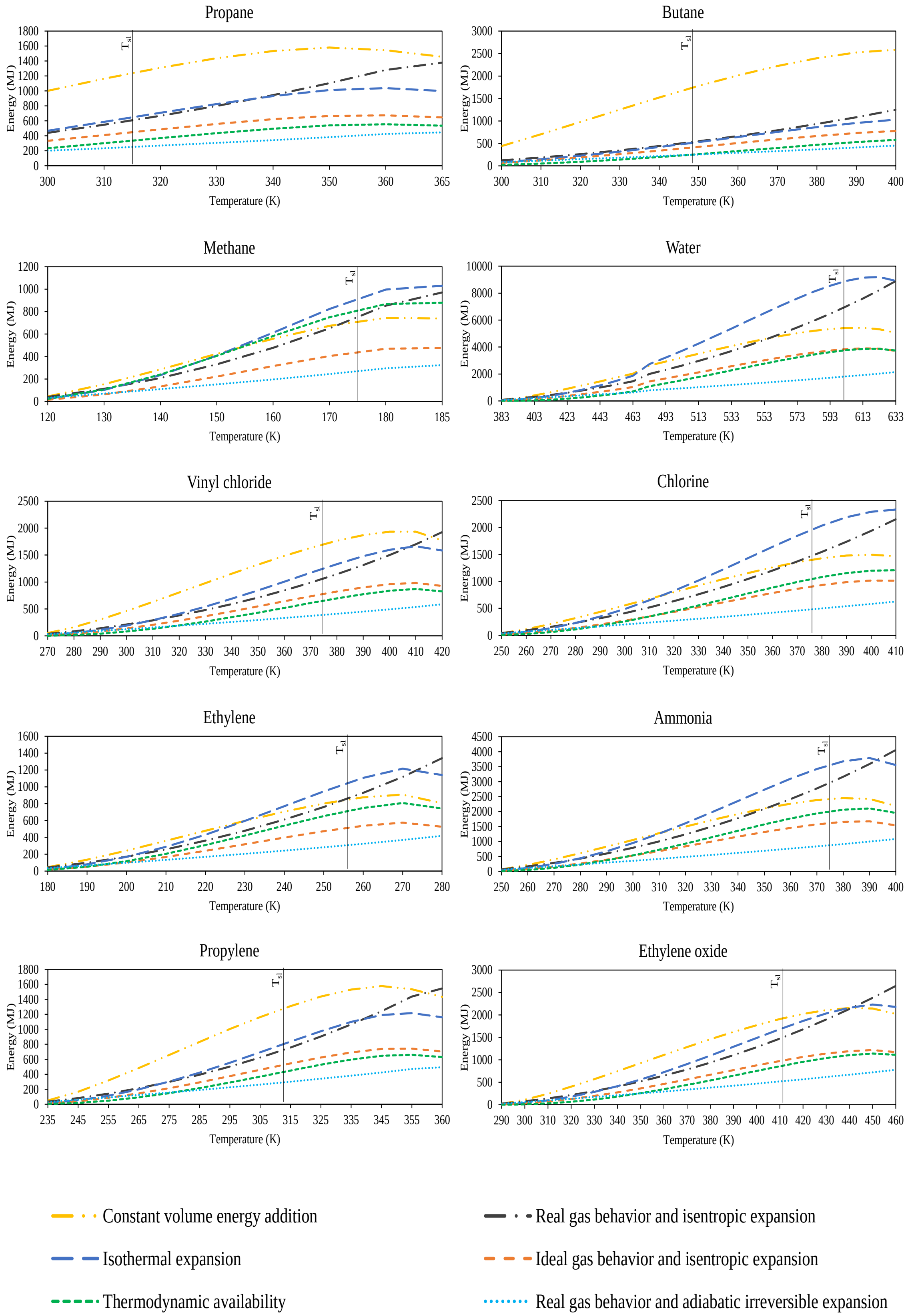


Figure 4-6.Mechanical energy released by the explosion at different temperatures and 50% initial filling level (just before the explosion), based on the diverse thermodynamic assumptions for 10 different substances.

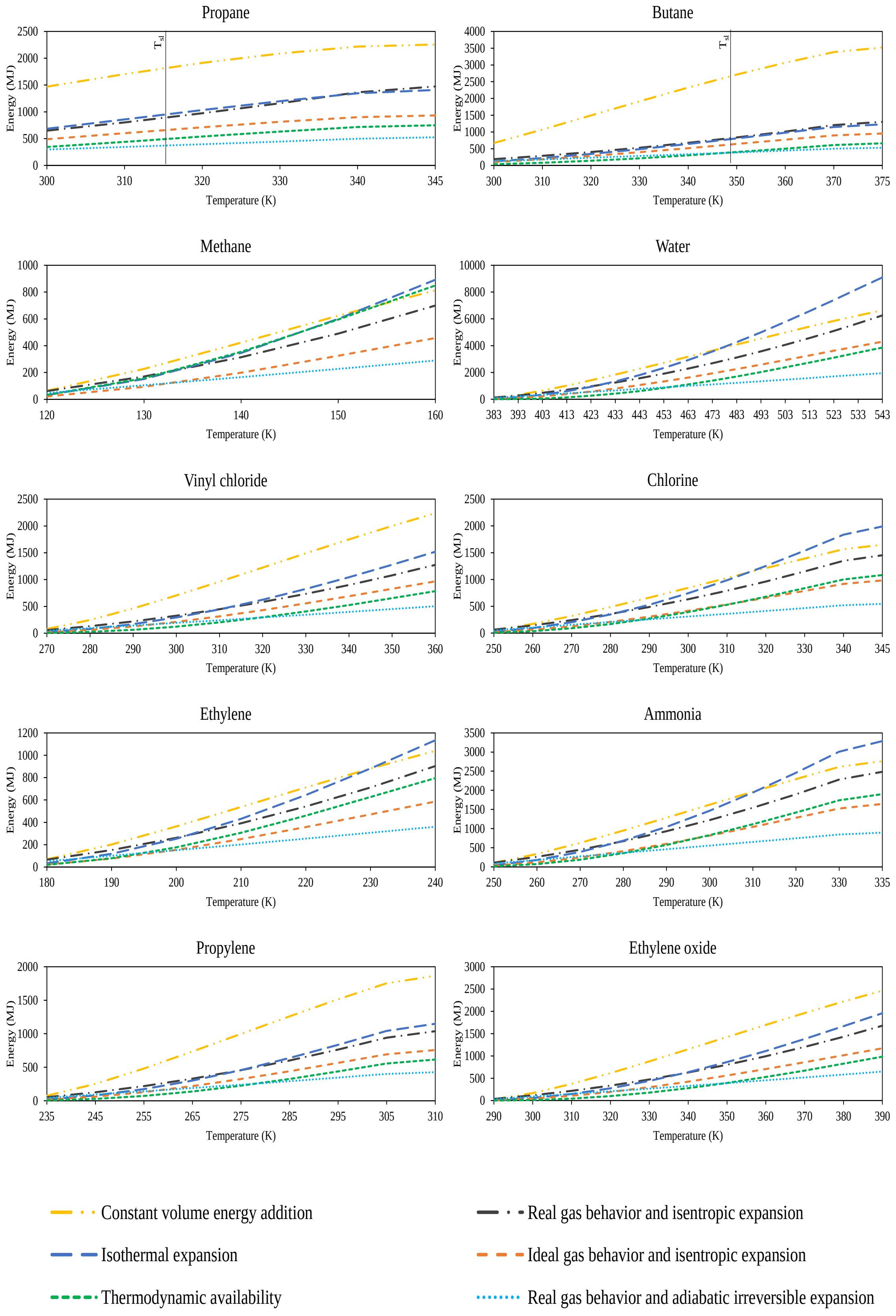


Figure 4-7.Mechanical energy released by the explosion at different temperatures and 80% initial filling level (just before the explosion), based on the diverse thermodynamic assumptions for 10 different substances.

As for the method based on constant volume energy addition, it gives the largest values in the cases of propane, butane, vinyl chloride, propylene, and ethylene oxide, which have higher molecular weight than the rest of substances in this study. Finally, the method based on isothermal expansion gives the largest amount for the rest of substances (methane, water, chlorine, ethylene, and ammonia). The only exception is chlorine, even if it has a high molecular weight. This behavior can be related to its low and constant specific heat capacity at constant volume (C_v) as a function of temperature. Figure 4-8 shows this difference. The method based on thermodynamic availability gives similar results than the one based on isothermal expansion. However, the former method has lower energy value at the same condition than the latter one, because it considers the second law of thermodynamic for the energy lost.

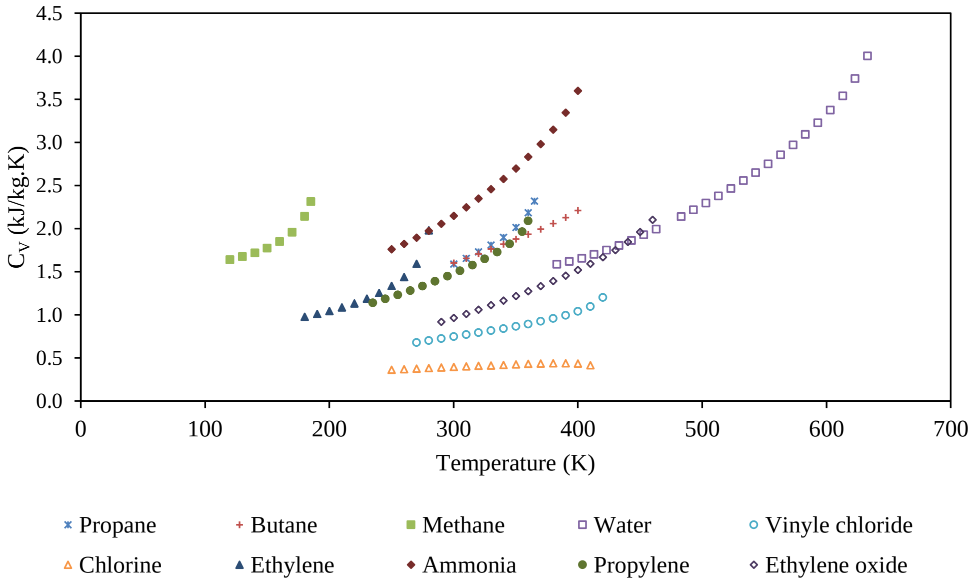
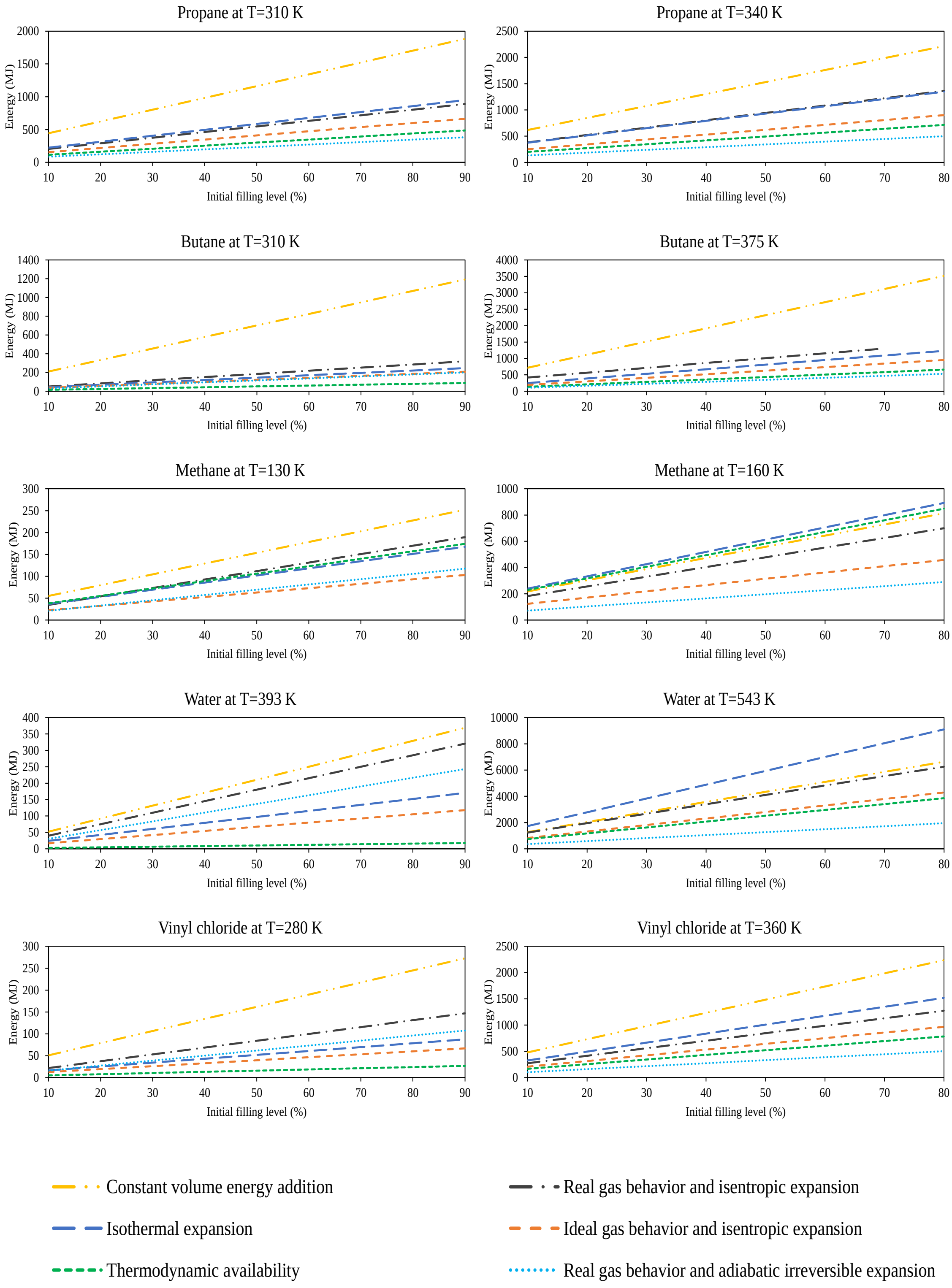


Figure 4-8. Specific heat constants at constant volume for different substances.

Finally, the methods based on real gas behaviour and adiabatic irreversible expansion show a much smaller change as a function of temperature than the other ones.

All aforementioned methods have the same behavior as a function of different filling levels for various substances. During the heating of a vessel, two simultaneous phenomena occur: expansion and evaporation of the contained liquid. If in a vessel there is initially a high level of liquid, this level will increase because of heating and subsequent expansion. In some specific situations, the vessel could become fully filled with the liquid; in such a case, further heating would imply the failure of the vessel due to the increase of pressure, the liquid being an incompressible fluid. This situation which occurred in Els Alfacs accident (Casal, 2008). Concerning the variation of the energy released as a function of vessel temperature just before the explosion, the methods based on real gas behavior and adiabatic irreversible expansion show an essentially linear behavior for all the substances. This linearity is also observed at temperatures close to the critical point and is found at different filling levels.

The calculated energy at different initial filling levels for a constant temperature are shown in Figure 4-9.


Propane at T=310 K
Propane at T=340 K
Butane at T=310 K
Butane at T=375 K
Methane at T=130 K
Methane at T=160 K
Water at T=393 K
Water at T=543 K
Vinyl chloride at T=280 K
Vinyl chloride at T=360 K
Energy (MJ)
Initial filling level (%)
Constant volume energy addition
Real gas behavior and isentropic expansion
Isothermal expansion
Ideal gas behavior and isentropic expansion
Thermodynamic availability
Real gas behavior and adiabatic irreversible expansion

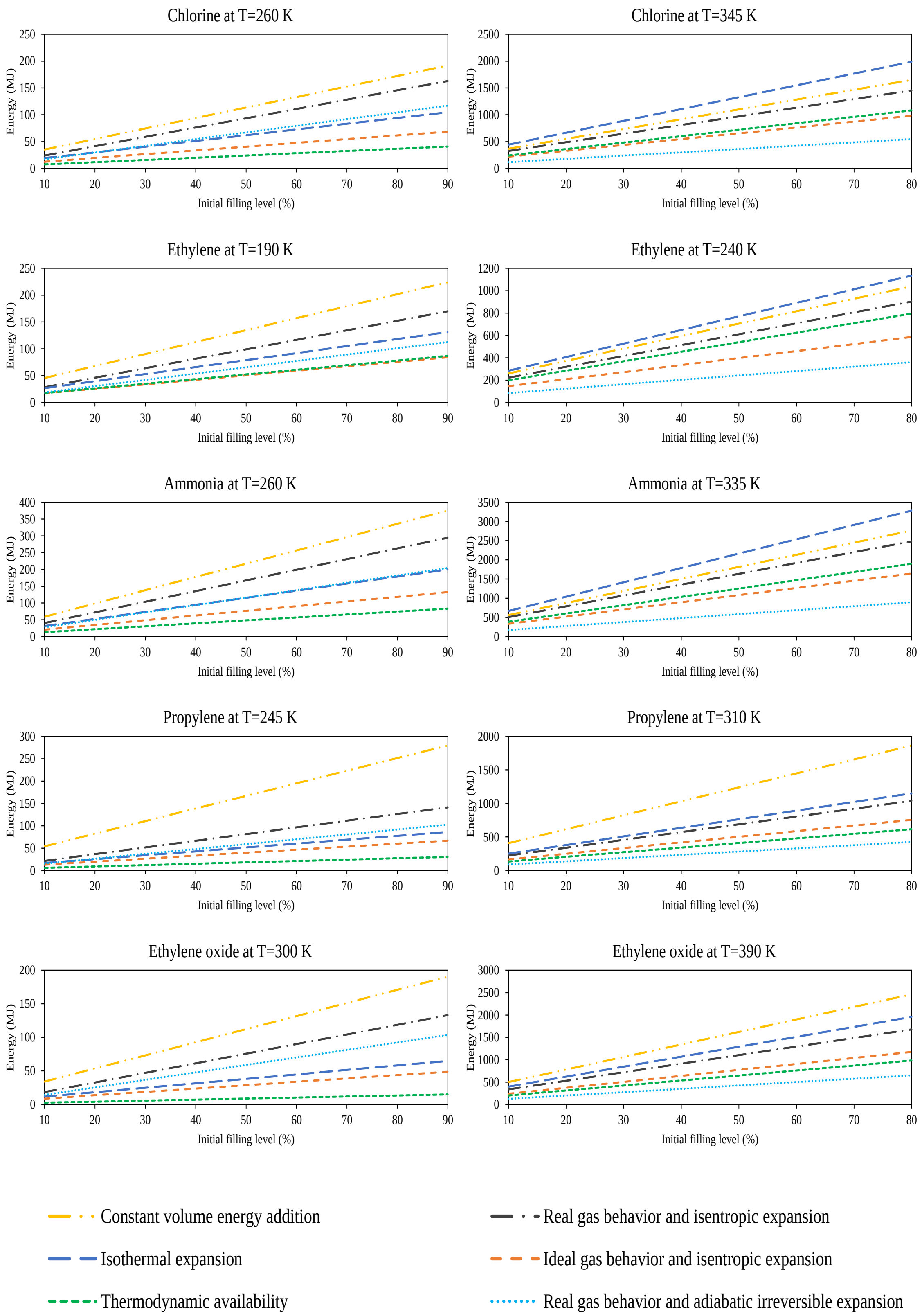


Figure 4-9. Mechanical energy released by the explosion at different initial filling levels and constant temperatures , based on the diverse thermodynamic assumptions.

At high temperatures, the constant volume energy addition gives larger values for the substances with a bigger molecular weight. The chlorine is again an exception due to its specific heat at constant volume.

On the other hand, methods based on isothermal expansion, thermodynamic availability, and ideal gas behavior and isentropic expansion give smaller values at lower temperatures. The difference between isothermal expansion and thermodynamic availability is that the second law of thermodynamics is considered in thermodynamic availability; because of that, the methods based on thermodynamic availability assumption give lower amount than the methods based on isothermal expansion. As for the method based on the isothermal expansion, its prediction varies with temperature, giving higher values at higher temperatures. Finally, the method assuming ideal gas behavior and isentropic assumption gives smaller values.

4.5 BLEVE experimental data

Two sets of BLEVE experiments from literature were used in order to check the performance of the different models previously commented. Johnson et al. (1990) and Birk et al. (2006, 2007) conducted some interesting and complex experimental tests.

Birk et al. used 2 m3 vessels which contained liquid propane. The vessels were engulfed by a set of jet-fires and the overpressures at various distances were measured (P_s), both in the axial and transversal directions; another reported parameter was the vessel failure pressure (P_{rup}). A summary of these experimental results are shown in Table 4-3.

Johnson et al. performed a series of tests with butane and propane (Table 4-4). They used electric immersion heaters for heating up the vessels; a polymeric heat insulator covered the vessels to reduce heat losses. Detonation of a short length of linear shaped high explosive charge provoked the failure of the tanks. Only in one of the tests (J6), the experimental fluid was changed from butane to propane without changing the vessel capacity. These authors also performed one experiment by increasing the volume of the container (10.796 m^3) and keeping the same amount of butane (2000 kg) such as in another test (J5). In another experiment (J3), they reduced the amount of butane to 1000 kg in the same vessel volume than in another experiment.

Table 4-3. Birk's experiments with propane in a 2 m³ vessel

Test	Filling level (%)	P_{rup} (kPa)	r_0 (m)	P_s (kPa)
B1	17	1863	10/20/30(E)/30(S)/40(E)/40(S)	6.65/3.5/3.11/4.19/2.11/2.73
B2	35	1846	10/20/30/40(E)/40(S)	3.97/3.78/2.29/1.48/2.13
B3	13	1699	10/20/40(E)/40(S)	5.29/2.75/1.72/1.83
B4	21	1894	10/40	5.02/1.675
B5	12	1573	10/20/30/40	4.13/2.58/1.58/1.31
B6	51	1803	10/20/30(E)/30(S)/40(E)/40(S)	13.11/8.95/6.03/2.99/3.37/4.06
B7	52	1563	10/20/30/40	4.563/3.4/1.93/1.58
B8	53	1813	10/20/30(E)/30(S)/40(E)/40(S)	4.15/2.99/2.99/2.29/2.6/0.64
B9	61	1858	10/20/30/40	5.44/5.05/3.59/2.7

S: Transversal direction
E: Axial direction

Table 4-4. Johnson's experiments

Test	Filling level (%)	Fluid	m_L(kg)	V(m^3)	P_{rup} (kPa)	r_0 (m)	P_s (kPa)
J1	75	Butane	2000	5.7	1460	25/100/150	6.2/1.3/1.1
J2	76	Butane	2000	5.7	1510	25/50/100/150	6.3/3.9/0.9/0.6
J3	38	Butane	1000	5.7	1520	25/50/100/150	5/2.8/1.2/0.8
J4	68	Butane	2000	5.7	770	25/50/100/150	1/0.5/0.17/0.15
J5	40	Butane	2000	10.8	1510	25/50/100/150	8.2/3.4/1.4/0.7
J6	77	Propane	2000	5.7	1520	25/50/100/150	2.3/1.2/0.3/0.3
J7	76	Butane	2000	5.7	1520	25/50/100	7/3.4/1.3

4.6 Comparative analysis

Here we consider again a constant β factor –fraction of energy released converted into a pressure wave– equal to 40% ($\beta = 0.4$) (Planas-Cuchi et al. 2004b), even if different values had been proposed in the diverse methods (in fact, most authors have considered 100% ($\beta = 1$) in a quite conservative and non-real approach). A constant value was used to obtain a better comparison of the various thermodynamic assumptions corresponding to the diverse methods. The two methods shown in Figure 4-4 (TNT equivalent mass and Sachs method) have been used to estimate the overpressure at the different distances needed. Figure 4-10 depicts the procedure.

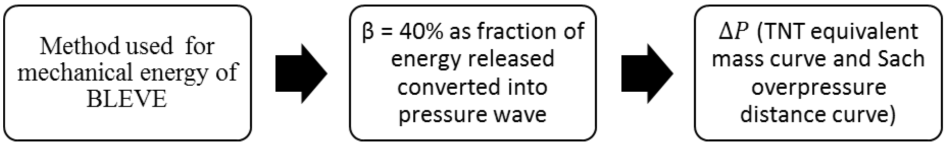


Figure 4-10. Scheme of the methodology used to calculate overpressure at a certain distance, from the total mechanical energy .

The values of the released mechanical energy of the explosion corresponding to the tests performed by Johnson et al. have been summarized in Figure 4-11. As it can be observed, the methods based on real gas behavior and adiabatic irreversible expansion give the lowest mechanical energy. The method based on constant volume energy addition has the largest value as observed in the previous section.

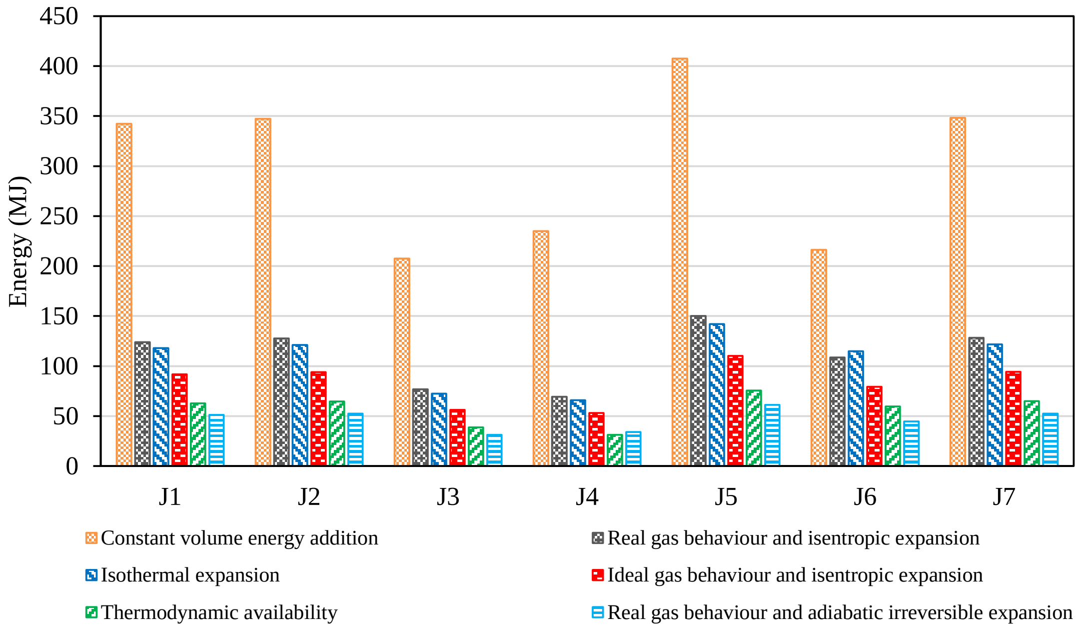


Figure 4-11. Calculated mechanical energy according to the different assumptions for the experiments of Johnson et al. (1990)

Next, the m_{TNT} was estimated from the calculated mechanical energy, assuming β=0.4. Figure 4-12 shows the calculated m_{TNT} values. In this figure and in the following ones the prediction from the superheating energy method has also been included.

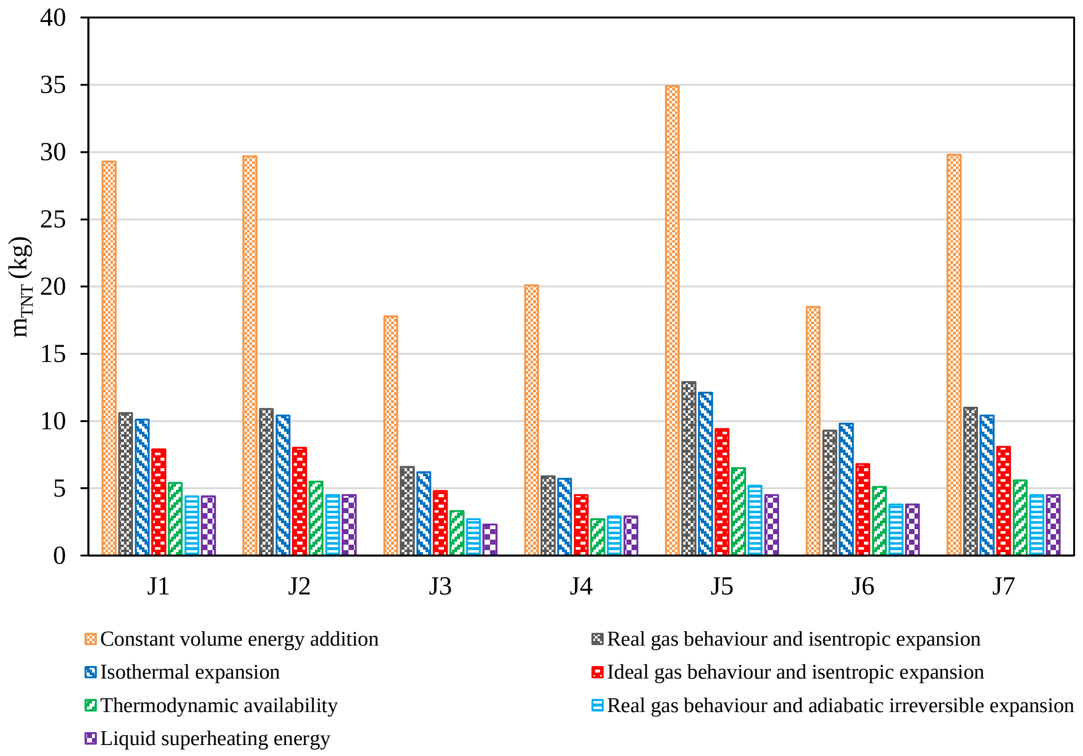


Figure 4-12. Calculated m_{TNT} for Johnson's experiments conditions, according to the different methods.

There is not a big change between the different methods when comparing these results with those in the Figure 4-11; a special case is that of the liquid superheating energy methodology, in which a quite different coefficient must be applied. Therefore, the methods based on the real gas behavior and adiabatic irreversible expansion (including that of superheating energy) give the smallest values, while the one based on constant volume energy addition gives the largest ones.

The diverse predictions for the overpressure at a distance of 25 m have been depicted in Figure 4-13, together with Johnson experimental values. The same behavior as for m_{TNT} is observed here. In most of the tests, the experimental value obtained by Johnson et al. is closer to the predictions from the methods proposed by Casal and Salla (2006), Planas-Cuchi et al. (2004b) and Crowl (1992), which give relatively similar values, and far from the values predicted by the other four methods.

An atypical result is observed in the case of experiments number J4 and J6, which clearly has an experimental value much lower than those predicted by all methods. Laboureur et al. (2014) found similar large deviations in their calculations. This seems to indicate that something strange could have occurred with these two tests.

By using Sachs scaled distance curve, the trend of calculated overpressure is logically similar to the results obtained by TNT equivalent mass curve. However, as it is shown, the value for overpressure obtained by Sachs scaled distance is about 50% lower than the obtained by using TNT equivalent mass method.

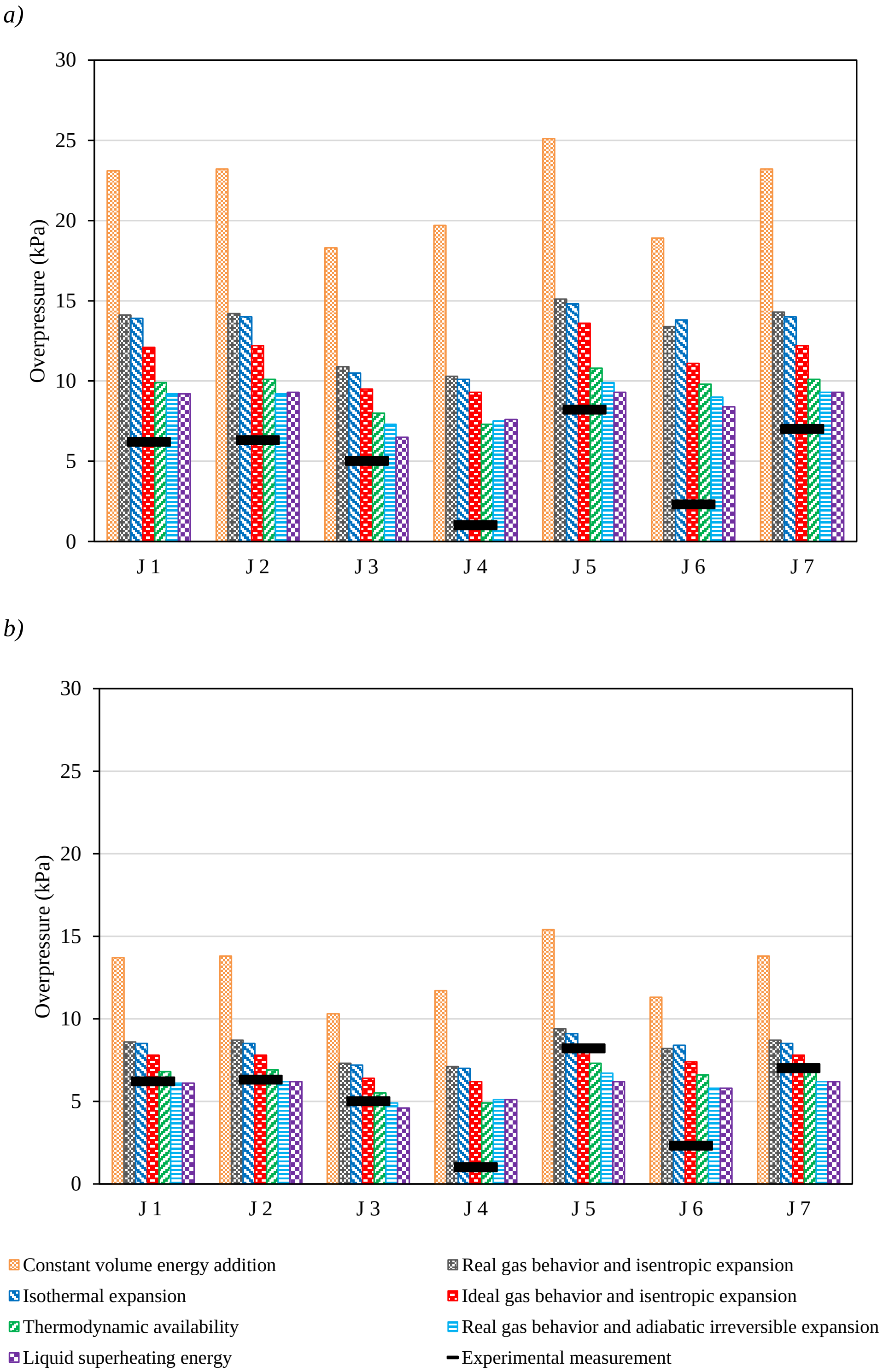


Figure 4-13. Calculated overpressure at a distance of 25 m for Johnson's experiments conditions a) TNT equivalent mass method; b) Sachs method.

Concerning the nine tests performed by Birk et al. (2007), the mechanical energy predicted by the diverse methods has been summarized in Figure 4-14 for each test. The results show again that the methods based on real gas behavior and adiabatic irreversible expansion (Planas et al, 2004) and thermodynamic availability (Crowl,1991,1992) have the smallest values, while the method based on constant volume energy addition (Brode, 1959) has the largest one.

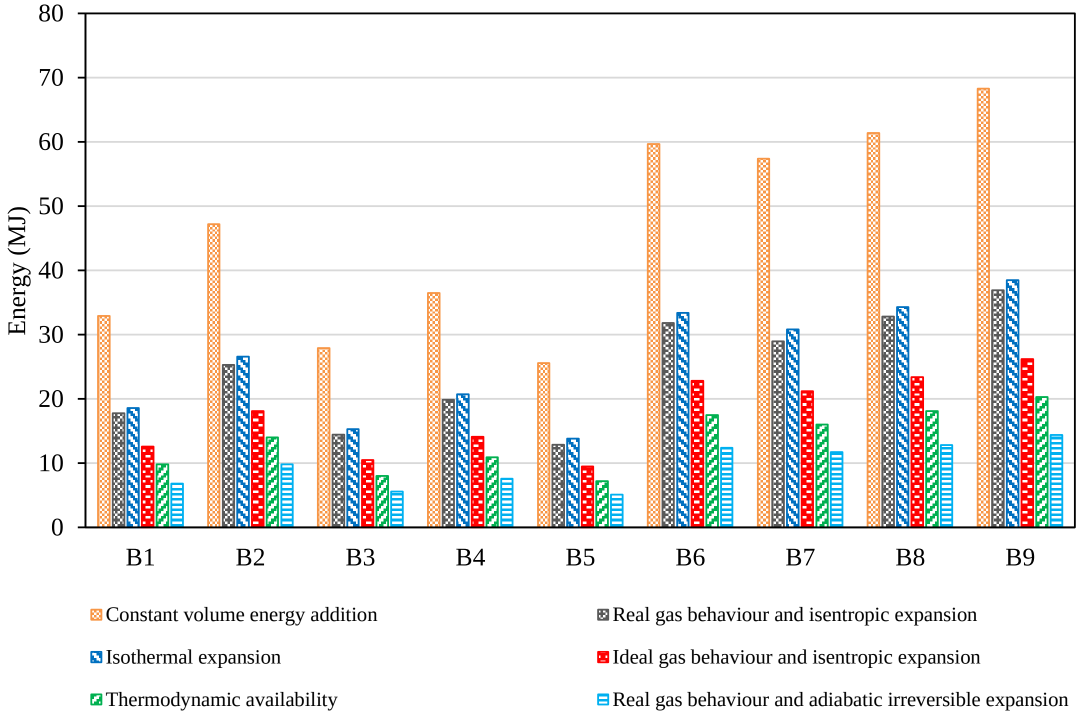


Figure 4-14. Calculated mechanical energy according to the different models for the experiments of Birk et al.

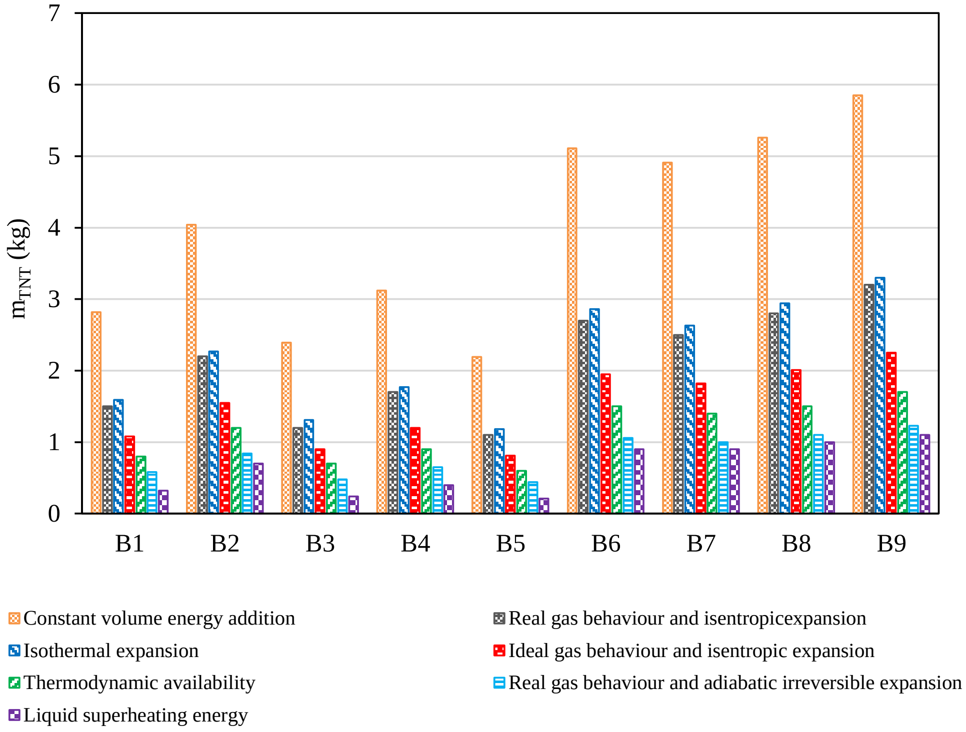


Figure 4-15. Calculated m_{TNT} according to the diverse methods, for Birk's experiments.

The calculated TNT equivalent mass values are shown in Figure 4-15, again including those from the superheating energy method. The methods based on real gas behavior and adiabatic irreversible expansion and on superheating energy still have the smallest values in m_{TNT} calculations; and the method based on constant volume energy addition gives the largest ones.

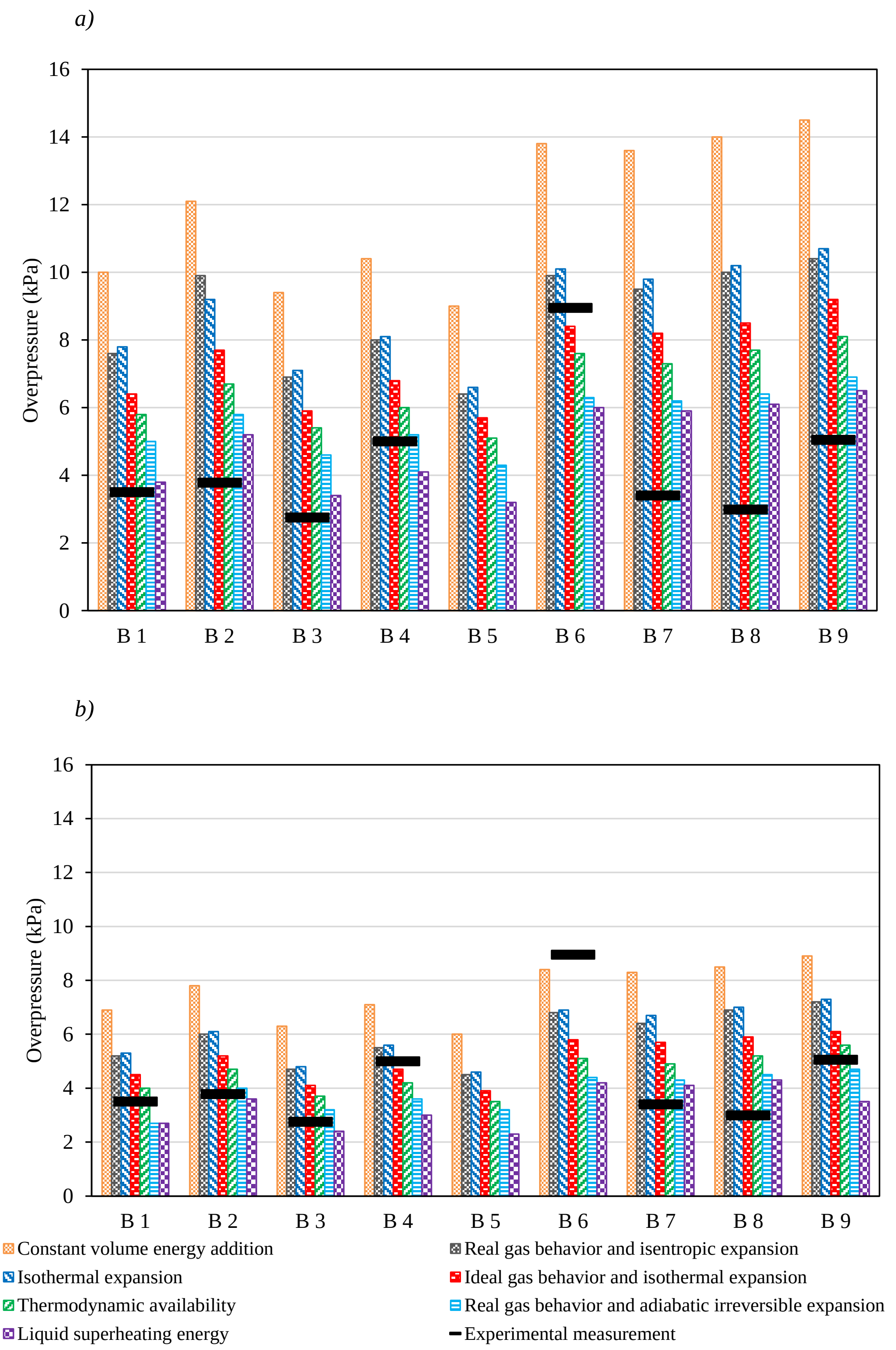


Figure 4-16. Calculated overpressure at a distance of 20 m for Birk's experiments: a) TNT equivalent mass method; b) Sachs method.

Figure 4-16 shows the overpressures at a distance of 20 m predicted by the different methodologies (by applying the TNT equivalent mass curve and Sachs scaled distance curve, respectively, Figure 4-4), together with the experimental value obtained by Birk et al. The results are similar to those previously obtained. Here again, using Sachs scaled distance gives lower values of overpressure than utilizing the TNT equivalent mass method. The methods based on superheating energy and real gas behavior and adiabatic irreversible expansion give the best approximation for the measured overpressures. It should be noticed that there is not any value for experiment B5 at 20 meters. At experiment B6, it was reported that it was a two-step BLEVE; the authors told that the blast would be more severe in this type of explosion.

4.7 Model performance analysis

The models' performances were analyzed by applying the Root-Mean-Square Deviation (RMSD) and Theil theory (Piñeiro et al., 2008). Theil's partial inequality coefficients are used to partition the squared sum of the predictive error. It means that those coefficients partition the variance of observed values which is not explained by the predicted ones. Theil coefficients give a handy toolkit to measure a model's consistency and its bias. RMSD has been calculated with respect to all the aforementioned experimental results (Table 4-5).

The results confirm the values obtained in the previous section. The methods based on real gas behavior and adiabatic irreversible expansion (Planas Cuchi et al., 2004b; Casal and Salla, 2006) still have the lowest RMSD, together with that using thermodynamical availability (Crowl, 1992).

Table 4-5. Overall RMSD considering all thermodynamic assumptions

	Thermodynamic assumption*						
RMSD	**CV**	**RIE**	**IE**	**IIE**	**TA**	**RAIE**	**SE**
Johnson, TNT curve	9.2	4.6	4.5	3.6	2.7	2.3	2.2
Johnson, Sachs curve	4.5	2.1	2.1	1.7	1.3	1.3	1.3
Birk, TNT curve	14.3	8.7	9.6	7.4	6.3	4.9	4.1
Birk, Sachs curve	8.0	4.7	4.9	3.6	3.0	2.4	2.2

*CV = Constant volume energy addition; RIE = Real gas behavior and isentropic expansion; IE = Isothermal expansion; IIE = Ideal gas behavior isentropic expansion; TA = Thermodynamic availability; RAIE = Real gas behavior and adiabatic irreversible expansion; SE = Liquid superheating energy

Even if the RAIE and SE methods are based on real gas behavior and adiabatic irreversible expansion assumption, their RMSE values show some deviations. The reason can be explained by the fact that the SE method considers only the mass of liquid for calculating the overpressure. So, it will be affected by liquid filling levels. Figure 4-17 shows the fact for the experiments with different filling levels.

According to Figure 4-17, the experiments with lower filling levels (i.e., experiments B1, B2, B3, B4, and B5) gave larger ΔP values by using RAIE method, due to the higher contribution of the pre-existing vapor. Therefore, those experiments were studied in detail by comparing with experimental values (Figure 4-18). The predicted values for closer distance (10 m) had larger deviation (overprediction) by using RAIE method. On the other hand, SE method gave closer results for the same points. Two contrary issues , underprediction of SE method for consideration of liquid mass and overprediction of Sachs curve in close distance, affect in the predicted results by SE method and cause smaller deviations at that points in comparing with the results obtained by RAIE methods for the same points.

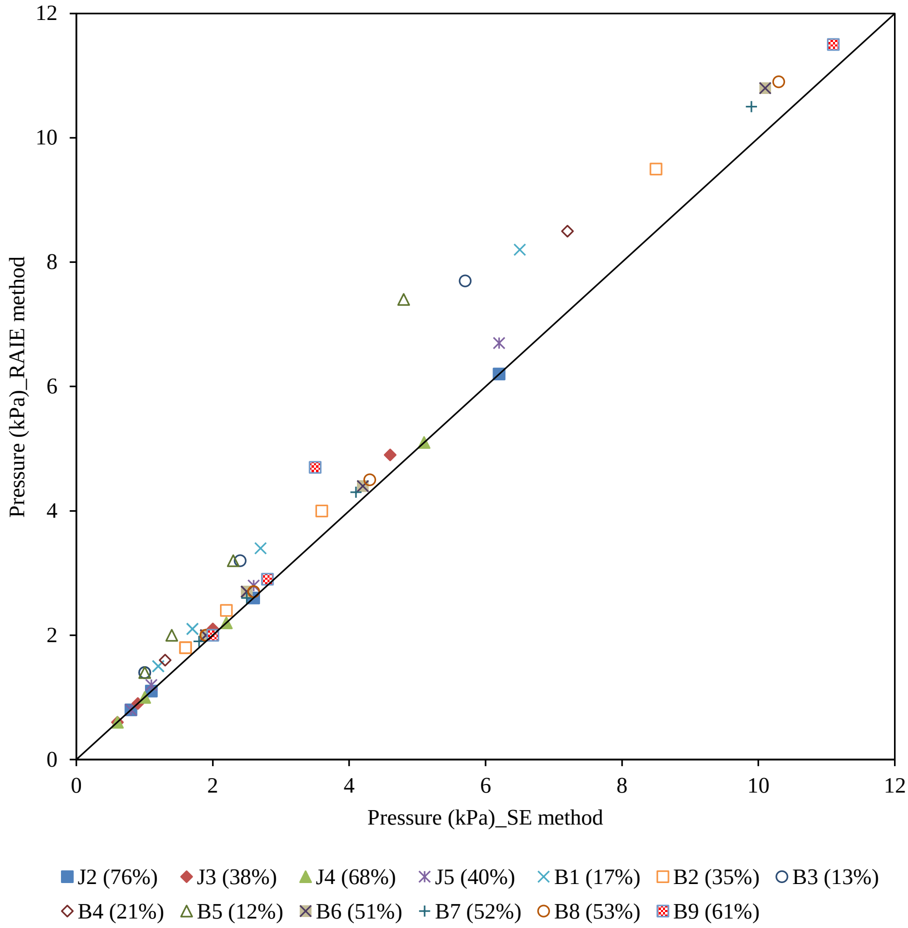


Figure 4-17. Compariosn of SE and RAIE methods for Johnson and Birk experiments by using Sachs curve.

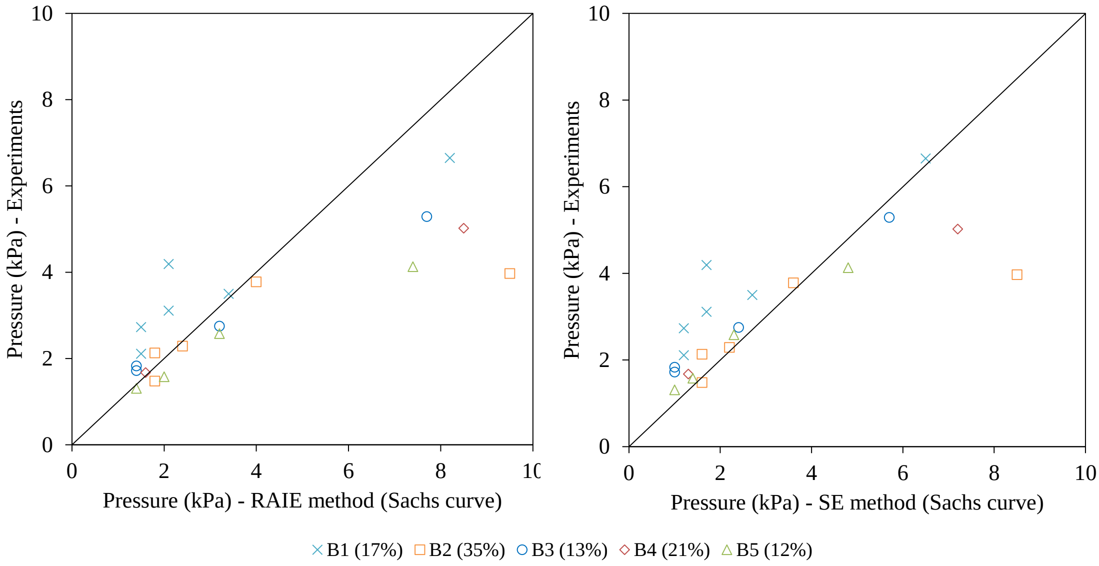


Figure 4-18. Comparison with experimental values for lower filling levels in Birk experiments.

As it was mentioned before, Sachs scaled distance curve gives less conservative values. Based on the results in Table 4-5, the RMSD values are lower when Sachs curve was used than when the TNT scaled distance was applied. That finding can also be seen in Figure 4-19:

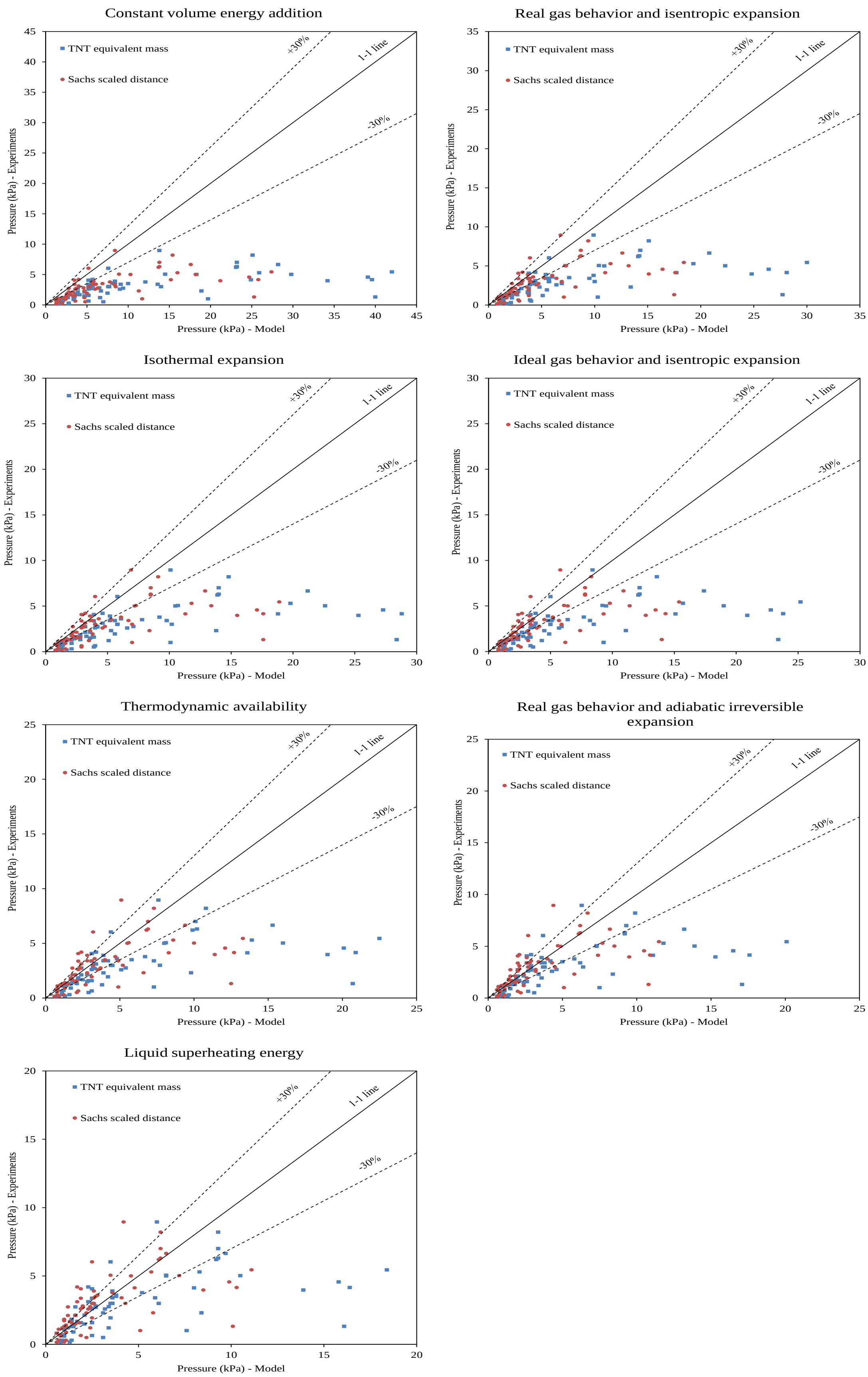


Figure 4-19.Calculated values against experimental ones

In fact, the predicted overpressure could be alleviated about 50% by using Sachs scaled distance curve. This issue is shown in Figure 4-20.

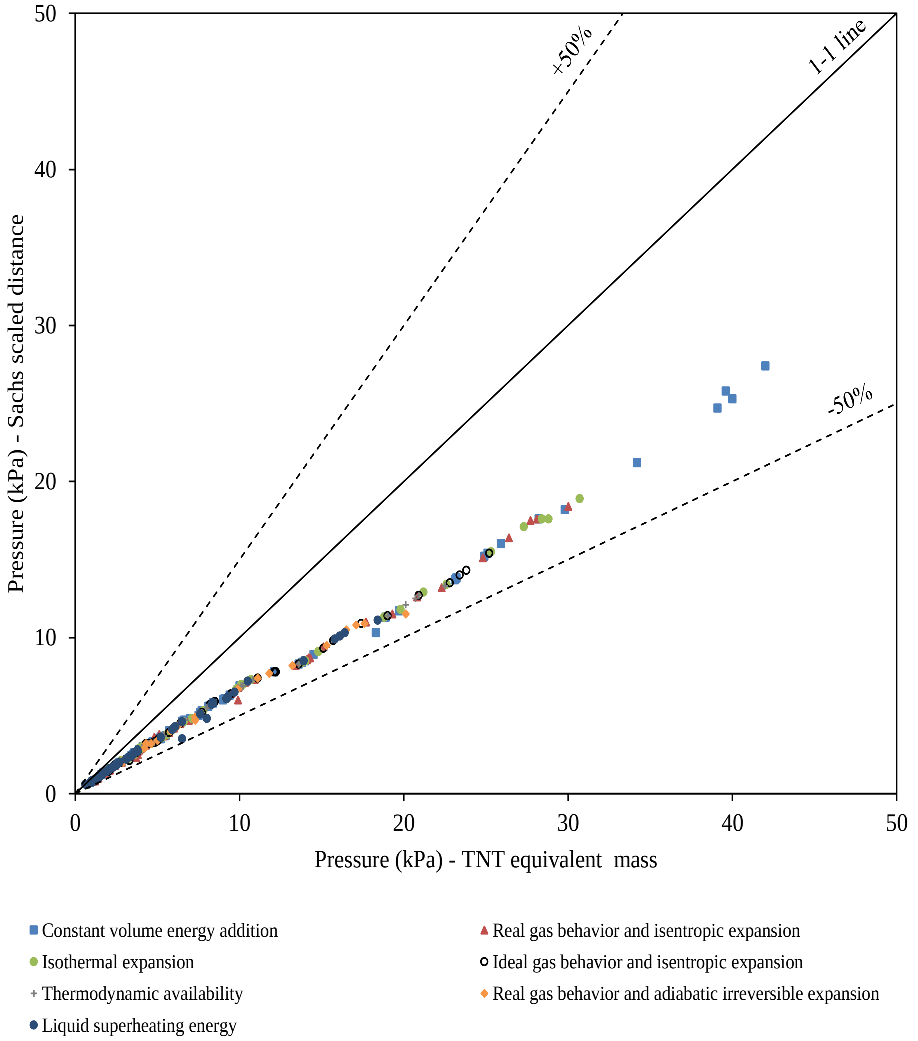


Figure 4-20. Calculated overpresures for Johnson et al. and Birk et al. experiments by using TNT equivalent mass curve and Sachs scaled distance curve.

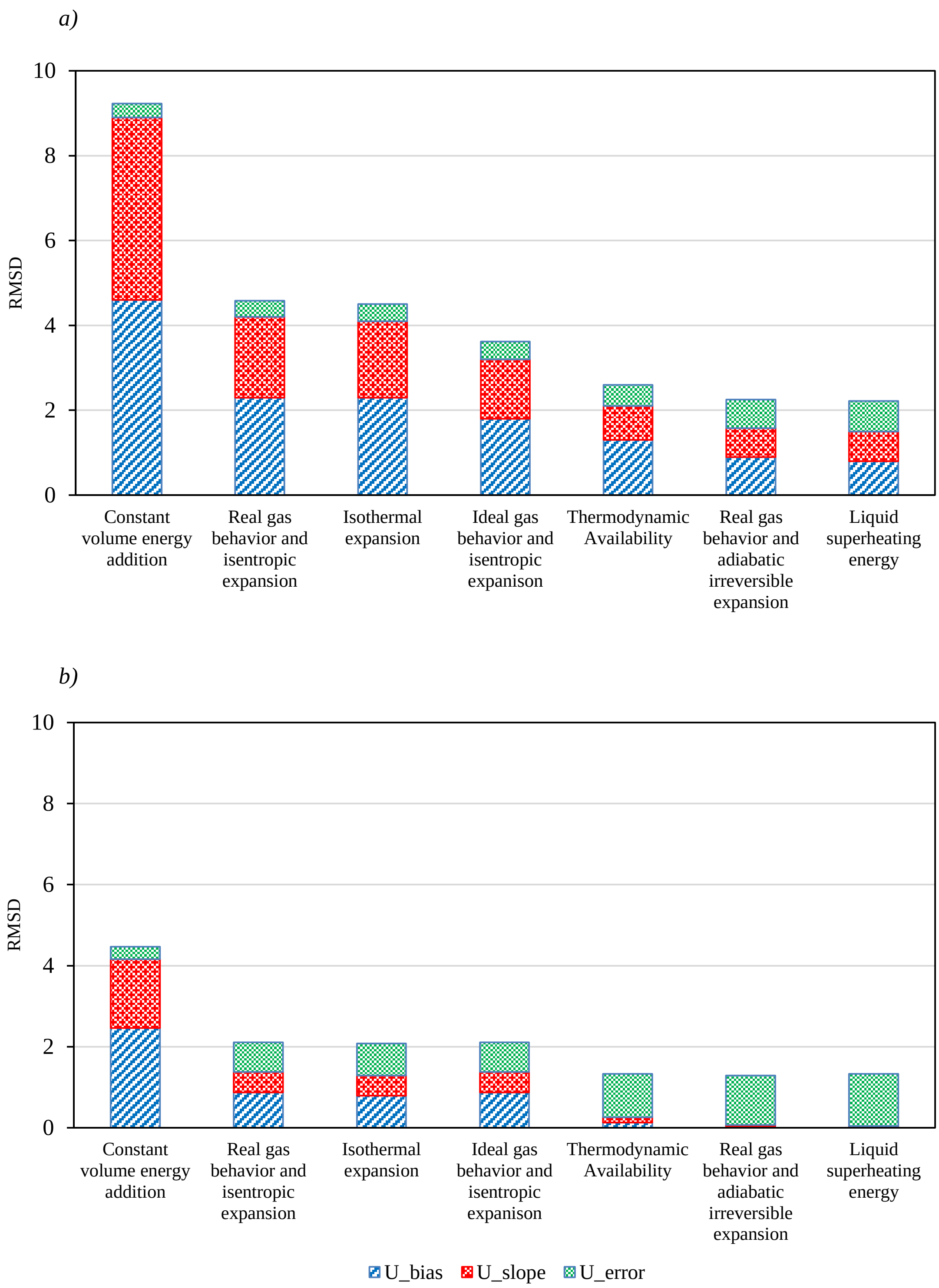


Figure 4-21. Calculated RMSD & U Theil for the prediction of Johnson's experimental values by the diverse models: a) TNT equivalent mass method; b) Sachs method.

In Johnson experiments (Figure 4-21), the models' bias is the main reason of the variance of the observed values not explained by the predicted ones. However, the model consistency is the dominant reason of the squared sum of the error in Birk experiments (Figure 4-22).

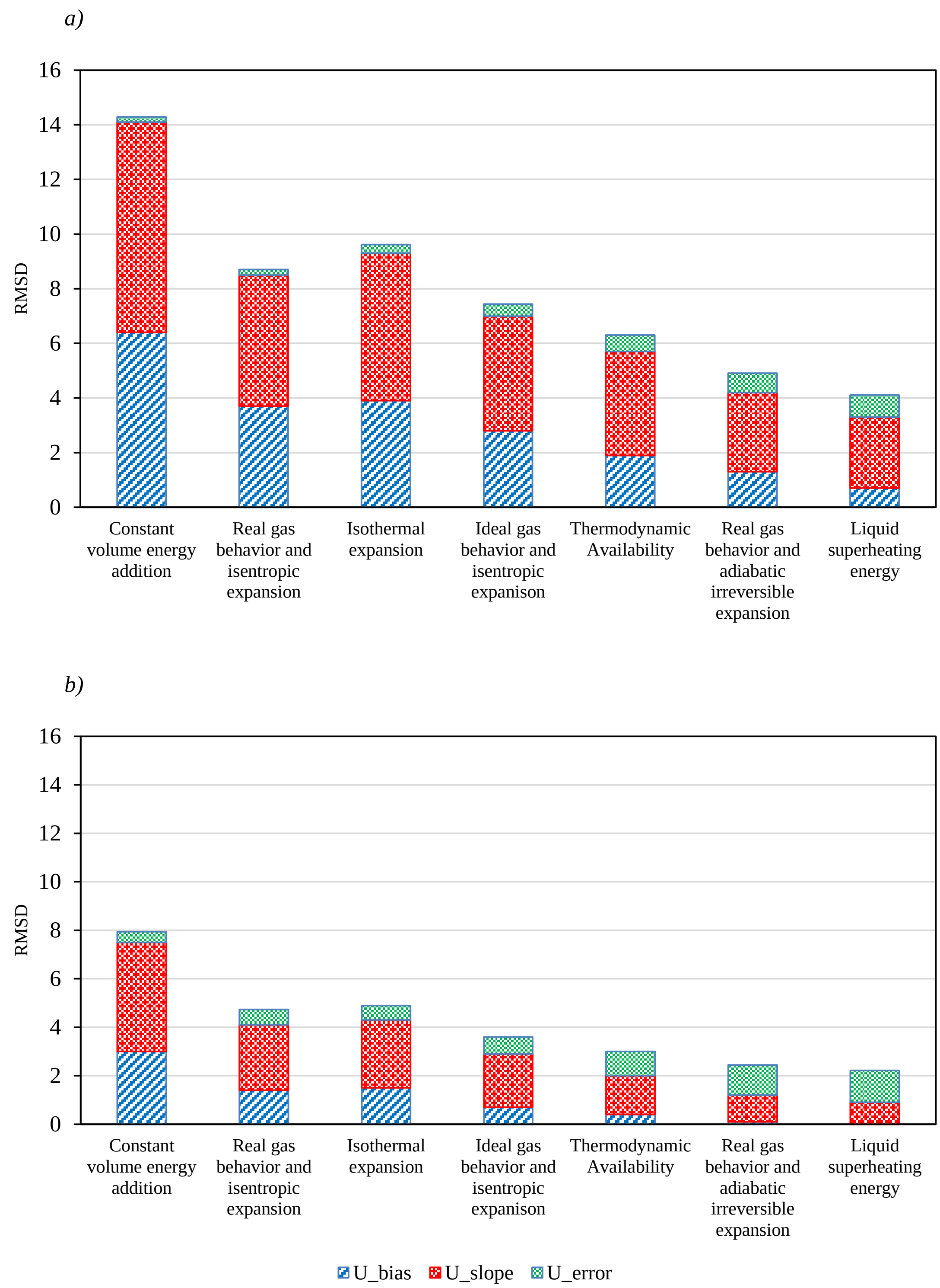


Figure 4-22. Calculated RMSD & U Theil for the prediction of Birk's experimental values by the diverse models: a) TNT equivalent mass method; b) Sachs method.

4.8 Discussion

The estimation of blast from BLEVEs is subjected to diverse uncertainties, some of which are inevitable. For example, an aspect which can be important is the heterogeneity of the blast wave, i.e. its directionality (Birk et al., 2007): for cylindrical tanks, the value of overpressure is not the same on the direction of the tank main axis than on the direction perpendicular to it, especially at short distances. However, nowadays this aspect has not been sufficiently studied and it cannot be included in any estimation of overpressure. Another one is the fraction of the overall energy released in the explosion that is invested in creating the overpressure; it should be taken into account that some of this energy is devoted to breaking the vessel and ejecting the fragments to a certain distance. Thus, some authors assume that it is 50%, some others assume 40% and, finally, those more conservative assume 100%. Furthermore, there is actually some discussion about the respective contributions of the previously existing vapor (just before the explosion) and that of the vapor generated in the liquid flash (Birk et al., 2007; Laboureur et al., 2015)

Another factor which will add incertitude in any analysis is the amount of material involved in the explosion. Will the tank be filled in an 80%? Or, even if it was filled at the beginning of the emergency –for example, a fire heating it– at the moment of the explosion the degree of filling will have decreased significantly, for example to 40%, due to the release through a safety valve?

Therefore, it should be realized that only approximate estimations of overpressure wave can really be performed. However, even if this must be accepted, it is also true that some of the methods proposed in the literature give better predictions than others.

It can be emphasized again that Reid’s theory, establishing the superheat limit temperature as a condition to be fulfilled for an explosion to be a BLEVE, should be restricted to laboratory small scale. The results obtained in this chapter have not shown any discontinuity or significant increase in overpressure when this temperature is reached.

The comparative study here developed of the diverse methods –based on different thermodynamic assumptions– proposed by different authors has shown that, as could be expected, there is an important scattering in the values obtained from them. Looking at these results a rough classification in two categories could be done: a) methods giving a quite conservative value, which in some cases is clearly the upper theoretical value thermodynamically possible, and b) methods giving a lower value, much less conservative but much closer to the real/experimental one.

The methods based on constant volume energy addition, isentropic expansion and isothermal expansion would be in the first category, while those assuming adiabatic irreversible expansion would be in the second one. These latter methods, even though much less conservative, are nevertheless much closer to real values, as certain analyses of full scale BLEVEs have shown (see, for example, Bubbico and Marchini, 2008).

The analysis performed has proven that the methods based on real gas assumption and adiabatic irreversible expansion are the less conservative ones, showing a linear behavior as a function of temperature at different filling levels, thus denying the validity of the superheat limit temperature concept. This linearity can be used to predict the mechanical energy as a function of temperature and filling level.

Finally, it has been observed that the TNT equivalent mass curve gives more conservative values than the Sachs scaled distance curve; in fact, it has been shown that the predicted overpressure could be decreased up to about 50% by using this latter method.

Further experimental work is still needed to improve the knowledge of overpressure from BLEVEs. However, due to the diverse uncertainty factors aforementioned, one may think that it will always exist some uncertainty in its prediction for a given case.

Chapter 5. A NEW PROCEDURE TO ESTIMATE BLEVE BLAST

5.1 Introduction

When a vessel undergoes a BLEVE, part of the released energy is converted into blast. In Chapter 4, different ways to calculate this mechanical energy, based on diverse thermodynamic assumptions, were investigated. The results showed that, in general, all methodologies tend to provide conservative results except those based on real gas behavior and adiabatic irreversible expansion, which give values that are more realistic. These methods, however, are somewhat cumbersome to implement and require many thermodynamic data of the substance involved, which make difficult for them to provide quick results. As for the one based on the superheating energy, although it is easier to apply, it does not take into account the contribution of the previously existing vapor, what in some cases –a vessel with low filling degree– can imply a non-negligible error.

Therefore, the aim of this chapter is to provide a new methodology to calculate the mechanical energy released during a BLEVE phenomenon, easy and fast to implement but, at least, as reliable and precise as the currently existing ones.

5.2 BLEVE mechanical energy and its linear behavior

When in Chapter 4 the influence of the diverse thermodynamic assumptions on the calculation of the mechanical energy was analyzed, something quite interesting was observed. This is the fact that the model based on real gas behavior and adiabatic irreversible expansion –which, as mentioned before, was the one which provided the most realistic results– showed an almost linear variation of the energy released as a function of the temperature inside the vessel just before the explosion; this linearity was observed at any vessel filling level. Instead, the behavior of all other models was clearly non-linear. This happened with all the substances investigated (see Figures 4-6 to 4-8), that were – according to the historical analysis– the ones more frequently involved in BLEVE accidents. In the following sections, a deeper analysis of this linear behavior is performed for the substances listed in Table 5-1. This analysis has allowed developing a new quick and easy method to obtain the total mechanical energy released from a BLEVE.

Table 5-1 Boiling and critical temperatures of the analysed substances.

Substance	**Boiling temperature (K)**	**Critical temperature (K)**
Propane	231.0	369.9
Butane	272.7	425.1
Methane	111.7	190.6
Water	373.1	647.1
Vinyl chloride	259.4	425.0
Ethylene oxide	283.7	468.9
Propylene	225.5	364.2
Ammonia	239.8	405.4
Chlorine	239.1	417.0
Ethylene	169.4	282.4

5.3 A new methodology to predict the BLEVE mechanical energy: polynomial approach

Initially, a set of 2713 scenarios for a 1 m^3 vessel (used as a basis for all calculations), covering both different initial filling levels (from 1% to 99%) and temperatures at the moment of explosion (from storage temperature to the critical temperature), have been defined for all the substances included in Table 5-1. For all the scenarios, the mechanical energy per cubic meter of vessel was determined by assuming real gas behavior and adiabatic irreversible expansion, according to the methodology proposed by Planas et al (2004b). The required thermodynamic data were obtained from NIST Reference Fluid Properties (Version 9.1) (Lemmon et al., 2007). A dataset for each substance was therefore prepared with the values of the mechanical energy recorded, together with the final temperature and related filling level, for each scenario.

However, it should be noticed that some scenarios could not be considered, because the required physical condition was not fulfilled. For example, a container initially filled up to 90% with liquefied propane at 300 K could reach its maximum filling level (100%) at a temperature of 326.3 K, before the temperature increased to the propane critical one (369.89 K). This phenomenon is due to the variation of liquid and gas densities as a function of temperature, according to which, at a certain moment, the decreasing gas volume collapses (Casal, 2008).

Table 5-2 Scenarios used to calculate the mechanical energy for the ten substances used.

Substance	**Initial filling level (%)**	**Temperature at explosion (K)**
Propane	5,10,15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90	300,310,320,330,340,350,360,365
Butane	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	283,293,303,313,323,333,343,353,363,373, 383,393,403
Methane	5,10,15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90	120,130,140,150,160,170,180
Water	10,20,30,40,50,60,70,80,90	383,403,423,443,463,483,503,523,543,563, 583,603,623
Vinyl chloride	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	270,280,290,300,310,320,330,340,350,360, 370,380,390,400,410,420
Ethylene oxide	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	290,300,310,320,330,340,350,360,370,380, 390,400,410,420,430,440,450,460
Propylene	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	235,245,255,265,275,285,295,305,315,325, 335,345,355,360
Ammonia	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,97,98,99	250,260,270,280,290,300,310,320,330,340, 350,360,370,380,390,400
Chlorine	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	250,260,270,280,290,300,310,320,330,340, 350,360,370,380,390,400,410
Ethylene	1,5,10.15,20.25,30,35,40,45,50,55,60, 65,70,75,80,85,90,95,98,99	180,190,200,210,220,230,240,250,260,270, 280

This can be explained in a simple way (Figure 5-1). Consider a vessel containing a mass m_T of a given material; the following relationships apply:

$$m_T = m_L + m_V \tag{5.1}$$

$$V_T = V + L \tag{5.2}$$

With the densities of both phases being:

$$\rho_V = \frac{m_V}{V} \tag{5.3}$$

$$\rho_L = \frac{m_L}{L} \tag{5.4}$$

Therefore, the volume of the vapor/gas phase can be expressed as:

$$V = \frac{V_T \cdot \rho_L - m_T}{\rho_L - \rho_V} \tag{5.5}$$

While the vessel temperature increases, ρ_L and ρ_V decreases. However, as $\rho_L >> \rho_V$, $(V_T \cdot \rho_L - m_T)$ decreases as well and can reach the value zero, this implying that $V = 0$. It is possible therefore to reach a temperature at which the vessel will be completely filled by liquid. The liquid is essentially a non-compressible fluid, a further increase in temperature will lead to the failure of the vessel.

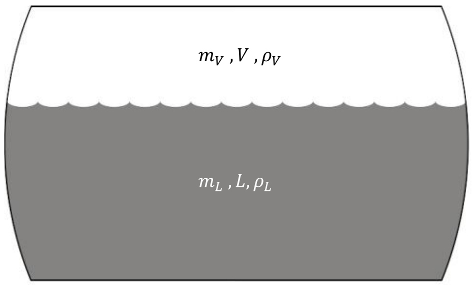


Figure 5-1. Liquid and gas volumes inside the vessel (see Table 5-2).

Therefore, taking this to account, the number of scenarios was finally reduced to 2034.

In order to fit an appropriate surface to data in a plot of energy as a function of temperature and filling degree, we used MATLAB Curve Fitting Toolbox 3.4.1. Indeed, an appropriate surface was found by using the polynomial regression model. A reasonable flexibility for linear data, which is not complicated –the fitting process is simple– is the main advantage for polynomial fits. However, the probability of becoming unstable in the high-degree fits is the main disadvantage of these fits. Moreover, it is necessary to be careful while extrapolating with polynomials, because polynomials of any degree cannot provide a good fit outside the data range (Curve Fitting Toolbox User's Guide-MathWorks, 2015).

While the "best" equations (i.e., the fitted equations keeping a relatively simple expression) were found by using polynomial fits, it was necessary to check how much the proposed equations achieved a good fit. The visual examination or a graphical method was the basic applied approach to see how the surfaces were close to the calculated data (see Figure 5-2 for the case of butane). In this study, a numerical method was also used as another approach to evaluate the goodness-of-fit for the proposed equations.

The four goodness-of-fit statistics used are:

- The sum of squares due to error (SSE)
- R-square
- Adjusted R-square
- Root-mean-square error (RMSE).

Eq. (5.6) provides the sum of squares of residuals (SSE), a value closer to zero meaning that the model has a small random error:

$$SSE = \sum_{i=1}^{n} \omega_i (y_i - \hat{y}_i)^2 \tag{5.6}$$

R-square is another statistical approach that can be used for evaluating the goodness-of-fit. It is the ratio of the sum of squares of the regression (SSR) and the sum of the squares (SST). The value closer to one indicates that the model accounts for a greater proportion of variance. The R-square can be calculated as:

$$SSR = \sum_{i=1}^{n} \omega_i (\hat{y}_i - \bar{y})^2 \tag{5.7}$$

$$SST = \sum_{i=1}^{n} \omega_i (y_i - \bar{y})^2 \tag{5.8}$$

$$SST = SSR + SSE \tag{5.9}$$

$$R - square = \frac{SSR}{SST} = 1 - \frac{SSE}{SST} \tag{5.10}$$

The best indicator to compare two models that are nested is the adjusted R-square, a value closer to 1 indicating a very good fit. If both the number of responses (n) and the number of fitted coefficients (m) estimated from the response values are known, the residual degrees of freedom will be:

$$v = n - m \tag{5.11}$$

Then the adjusted R-square is:

$$adjusted\ R - square = 1 - \frac{SSE(n-1)}{SST(v)} \tag{5.12}$$

The last statistical approach used in this study is the root-mean-square error (RMSE). It shows the differences between the predicted values and the observed ones; a fit closer to zero is more useful for prediction. It is defined as:

$$RMSE = s = \sqrt{MSE} \tag{5.13}$$

Where MSE is the mean square error or the residual mean square:

$$MSE = \frac{SSE}{v} \tag{5.14}$$

In this study, the filling level and the temperature were considered as input variables, and the related mechanical energy was considered as an output variable. Polynomial models were used for surface fitting. The general polynomial term for the fitted models can be summarized as:

$$y = \sum_{i=1}^{n+1} p_i x^{n+1-i} \tag{5.15}$$

where the number of coefficients to be fitted (n+1) is the order of the polynomial and n is the degree of the polynomial, which is the highest power of the predictor variable.

In polynomial surface fits, the polynomial terms can be controlled by defining the degrees for the x and y inputs (e.g. in (5.16) x is the filling level and y is the temperature as inputs, and Z is the energy as an output), the total degree of the polynomial being the maximum degree of x and y. For example, poly13 can be defined as:

$$Z = p00 + p10 * x + p01 * y + p11 * x * y + p02 * y^2 + p12 * x * y^2 + p03 * y^3 \tag{5.16}$$

In this case, the Curve Fitting Toolbox provided different polynomials with various degrees of the input variables (filling level and temperature). Visual examination or a graphical method were used to see how close the surface was to the calculated data. Figure

5-2 shows the fitted surfaces for butane. In this example, the surface for Poly13 covers more calculated points (black dots) than the other surfaces presented by the other polynomials (e.g., Poly11, Poly12, etc.). However, as explained before, numerical methods were also used to have better examinations and decisions.

Multiple fits tested were compared by goodness-of-fit statistics. Table 5-3 summarizes the goodness-of-fit results for different substances. According to these results, the suggested surface model based on Poly13 has a better performance, as it gives smaller Root Mean Square Error (RMSE) and Sum of Square Error (SSE).

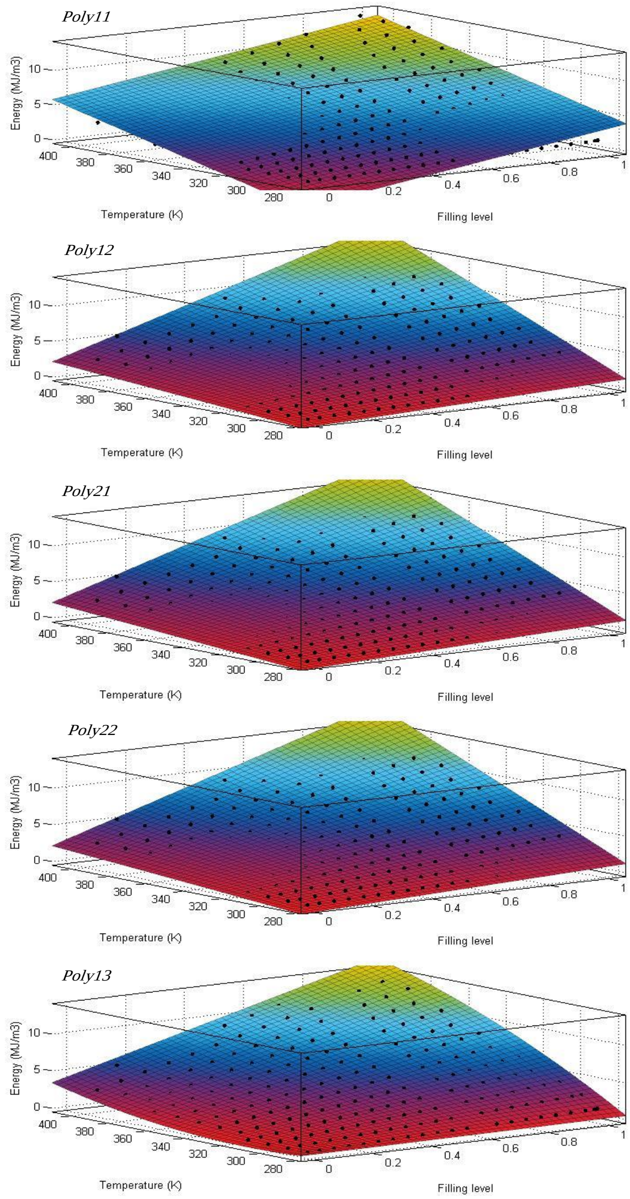


Figure 5-2. Fitted surfaces for butane.

Table 5-3 Goodness-of-fit statistics for different polynomial degrees

Substance	Poly (FL,T)	SSE	R^2	Adjusted R^2	RMSE
Propane	Poly11	6.5	0.9921	0.9919	0.23980
	Poly12	6.1	0.9925	0.9923	0.23450
	Poly13	0.5	0.9994	0.9993	0.06833
	Poly21	6.3	0.9923`	0.9920	0.23800
	Poly31	6.3	0.9923	0.9919	0.23960
	Poly22	6.1	0.9926	0.9922	0.23500
Butane	Poly11	176.6	0.9127	0.9118	0.94440
	Poly12	8.5	0.9958	0.9957	0.20820
	Poly13	0.5	0.9998	0.9998	0.04957
	Poly21	8.5	0.9958	0.9957	0.20840
	Poly31	8.5	0.9958	0.9957	0.20870
	Poly22	8.5	0.9958	0.9957	0.20860
Methane	Poly11	19.1	0.9568	0.9560	0.42090
	Poly12	2.9	0.9935	0.9933	0.16430
	Poly13	0.1	0.9998	0.9997	0.03197
	Poly21	2.9	0.9934	0.9931	0.16650
	Poly31	2.9	0.9934	0.9930	0.16800
	Poly22	2.8	0.9936	0.9933	0.16460
Water	Poly11	2123.5	0.9051	0.9035	4.24210
	Poly12	277.4	0.9876	0.9872	1.54600
	Poly13	33.3	0.9985	0.9984	0.54050
	Poly21	281.3	0.9874	0.9870	1.55700
	Poly31	280.3	0.9875	0.9868	1.56810
	Poly22	272.1	0.9878	0.9873	1.53800
Vinyl chloride	Poly11	195.4	0.9367	0.9362	0.89310
	Poly12	35.5	0.9885	0.9883	0.38220
	Poly13	3.8	0.9988	0.9987	0.12640
	Poly21	35.5	0.9885	0.9883	0.38220
	Poly31	35.4	0.9885	0.9882	0.38350
	Poly22	35.5	0.9885	0.9883	0.38280
Ethylene oxide	Poly11	480.7	0.9253	0.9248	1.30600
	Poly12	81.0	0.9874	0.9872	0.53800
	Poly13	7.8	0.9988	0.9988	0.16720
	Poly21	81.0	0.9874	0.9872	0.53800
	Poly31	80.5	0.9875	0.9872	0.53800
	Poly22	81.0	0.9874	0.9872	0.53890
Propylene	Poly11	946.6	0.8967	0.8959	1.86200
	Poly12	38.0	0.9959	0.9958	0.37420
	Poly13	17.5	0.9981	0.9980	0.25500
	Poly21	38.2	0.9958	0.9958	0.37550
	Poly31	37.1	0.9960	0.9959	0.37110
	Poly22	37.5	0.9959	0.9958	0.37250
Ammonia	Poly11	740.0	0.9275	0.9269	1.72740
	Poly12	179.5	0.9828	0.9825	0.84570
	Poly13	17.2	0.9983	0.9983	0.26520

	Poly21	176.8	0.9827	0.9824	0.84780
	Poly31	173.2	0.9830	0.9826	0.84240
	Poly22	175.8	0.9828	0.9824	0.84710
Chlorine	Poly11	249.1	0.9394	0.9389	0.96600
	Poly12	52.5	0.9872	0.9870	0.44520
	Poly13	3.2	0.9992	0.9992	0.10960
	Poly21	53.4	0.9870	0.9868	0.44870
	Poly31	52.7	0.9872	0.9869	0.44760
	Poly22	52.5	0.9872	0.9870	0.44600
Ethylene	Poly11	53.4	0.9489	0.9483	0.56880
	Poly12	18.3	0.9825	0.9820	0.33540
	Poly13	2.1	0.9980	0.9979	0.11420
	Poly21	18.7	0.9821	0.9817	0.33860
	Poly31	18.2	0.9826	0.9819	0.33610
	Poly22	18.3	0.9825	0.9820	0.33600

Even if there is a linear relationship between the temperature and the predicted mechanical energy, there exists a non-linearity between filling level and temperature. This may cause some difficulties in predicting the appropriate polynomial function at lower degrees of input parameters. Figure 5-3 shows a non-linear behavior for propane by using the methods based on real gas behavior and adiabatic irreversible expansion:

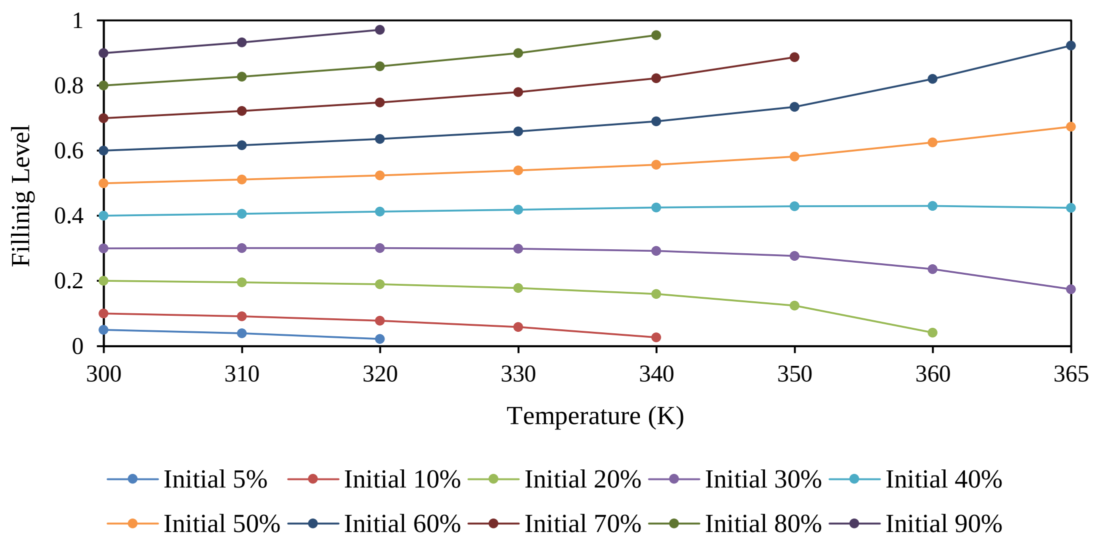


Figure 5-3. Non linear behavior for propane (real gas behavior and adiabatic irreversible expansion).

The appropriate equations for predicting the mechanical energy per cubic meter (e) of superheated liquids as a function of the filling level (FL) and the temperature (T) obtained by this procedure can be seen in Table 5-4. These are the equations for the ten most common substances that have been involved in BLEVE accidents, according to the historical analysis presented in Chapter 1.

A slightly better fitting could probably have been reached by using more complex polynomial expressions; however, the objective was to find a methodology that, while being accurate, was also simple and practical to be applied; these expressions fulfill both conditions.

To go from energy to overpressure, the total vessel volume has to be multiplied by "e" in order to find the total amount of mechanical energy (E) in a given system. Then, the total energy will be converted to the equivalent TNT mass (m_{TNT}). Next, the scaled distance will be calculated considering that β = 0.4 for the ductile failure.

Table 5-4 Mechanical energy per cubic meter as a function of temperature and filling level for different substances

Substance	**Equation; e (MJ/m³); T (K); FL (%)**
Propane	$e = 43.97 - 213.9 \cdot FL - 0.152 \cdot T + 1.349 \cdot FL \cdot T - 0.0004361 \cdot T^2 - 0.002045 \cdot FL \cdot T^2 + 1.55 \cdot 10^{-6} \cdot T^3$
Butane	$e = 21.32 - 87.2 \cdot FL - 0.136 \cdot T + 0.4765 \cdot FL \cdot T + 0.0001885 \cdot T^2 - 0.0005805 \cdot FL \cdot T^2 + 9.693 \cdot 10^{-6}\, T^3$
Methane	$e = 6.13 - 42.71 \cdot FL - 0.06558 \cdot T + 0.5629 \cdot FL \cdot T - 0.0001499 \cdot T^2 - 0.001647 \cdot FL \cdot T^2 + 2.327 \cdot 10^{-6} \cdot T^3$
Water	$e = 56.36 - 275.6 \cdot FL - 0.2341 \cdot T + 1.076 \cdot FL \cdot T + 0.0001696 \cdot T^2 - 0.0009183 \cdot FL \cdot T^2 + 1.626 \cdot 10^{-6}\, T^3$
Vinyl chloride	$e = 20.71 - 92.48 \cdot FL - 0.1206 \cdot T + 0.5346 \cdot FL \cdot T + 9.836 \cdot 10^{-5} \cdot T^2 - 0.0006987 \cdot FL \cdot T^2 + 2.503 \cdot 10^{-7}\, T^3$
Ethylene oxide	$e = 23.61 - 119.4 \cdot FL - 0.1182 \cdot T + 0.6295 \cdot FL \cdot T + 4.505 \cdot 10^{-5} \cdot T2 - 0.0007463 \cdot FL \cdot T^2 + 2.946 \cdot 10^{-7} \cdot T^3$
Propylene	$e = 104.9 - 86.15 \cdot FL - 1.035 \cdot T + 0.5013 \cdot FL \cdot T + 0.00329 \cdot T^2 - 0.0005726 \cdot FL \cdot T^2 - 3.321 \cdot 10^{-6} \cdot T3$
Ammonia	$e = 28.34 - 168.4 \cdot FL - 0.1447 \cdot T + 1.048 \cdot FL \cdot T - 6.71 \cdot 10^{-5} \cdot T^2 - 0.001471 \cdot FL \cdot T^2 + 7.984 \cdot 10^{-7} \cdot T^3$
Chlorine	$e = -2.469 - 81.17 \cdot FL + 0.08234 \cdot T + 0.4975 \cdot FL \cdot T - 0.0005088 \cdot T^2 - 0.0006739 \cdot FL \cdot T^2 + 8.889 \cdot 10^{-7} \cdot T^3$
Ethylene	$e = 9.356 - 69.53 \cdot FL - 0.04289 \cdot T + 0.6194 \cdot FL \cdot T - 0.0003058 \cdot T^2 - 0.001262 \cdot FL \cdot T^2 + 1.454 \cdot 10^{-6} \cdot T^3$

5.3.1 Comparative study

We checked the equations obtained and summarized in Table 5-4 by comparing them with two sets of experimental data from Johnson et al. (1990), Laboureur et al. (2014) and Birk et al. (2007); those experiments have been already commented in Chapter 4. The resulting overpressures at different distances were obtained from the TNT equivalent mass and the well-known plot of the scaled distance vs. peak overpressure for TNT.

The root-mean-square deviation (RMSD) was again used as a statistical toolkit for doing a comparative analysis between the different methods (Piñeiro et al., 2008). As it is shown in Table 5-5, the new method here proposed gave a good accuracy as compared to the other methodologies assuming ideal gas behavior and irreversible expansion.

The new approach gives results similar to those from RAIE methods and sometimes even better. For example, the RMSE value for the Birk experiments is lower for the new approach than the RAIE value (Table 5-5). However, this new approach has been developed from the RAIE method. Actually, Table 5-3 shows that the approach based on polynomial method has some degree of deviation from the data set from which the equations were derived, because the fitting method passes a surface from the minimum distance to a data point. This deviation could be larger in some points based on the fitted surface and its distance to the data points and the degree of polynomial Therefore, the small deviation may make difference in the result when calculating the mechanical energy of a BLEVE and its overpressure (see Figure 5-11).

Table 5-5 Root Mean Square Deviation (RMSD) values for different methods based on their thermodynamic assumptions

RMSD	Thermodynamic assumption*		
	RAIE	**SE**	**New approach (polynomial)**
Johnson-TNT curve	2.3	2.2	2.2
Birk-TNT curve	4.9	4.1	4.2

*RAIE = Real gas behavior and adiabatic irreversible expansion ; SE = Liquid superheating energy

It should be noted that the equations proposed in the new approach give quick and accurate results in an easy and convenient way. In fact, they only require the filling level and the temperature at the moment of explosion as input variables in order to calculate the mechanical energy released by a BLEVE. Contrarily, the other methodologies require many thermodynamic data and calculations to obtain this energy,or do not take into account (S.E. method) the contribution of pre-existing vapor.

The nonlinear relation between temperature and filling level (shown in Figure 5-3) is probably the reason for the observed deviation in the polynomial equations that, as seen in the comparative analysis, remains in the range of the expected accuracy of this type of calculation and, therefore, should be considered acceptable.

5.3.2 Example of application

A cylindrical vessel with a volume of 80 m^3, initially filled to 58% with liquid propane at room temperature (20 ºC), undergoes a BLEVE due to fire engulfment, when the content temperature is 50 ºC. The filling degree is 34% at the burst moment. Estimate overpressure (ΔP) at a distance of 100 m.

Solution:

$$\begin{cases} FL = 0.34 \\ T = 50℃ + 273.15 = 323.15\ K \\ V = 80\ m^3 \end{cases}$$

Then, using the propane equation to find the mechanical energy per cubic meter (e):

$$e\ (MJ/m^3) = 43.97 - 213.9 \cdot\ FL - 0.152 \cdot\ T + 1.349\ \cdot FL\ \cdot T - 0.0004361 \cdot\ T^2 - 0.002045 \cdot\ FL\ \cdot T^2 + 1.55e - 06 \cdot T^3$$

$$\begin{aligned} e\ (MJ/m^3) = 43.97 - 213.9 \cdot\ 0.34 - 0.152 \cdot\ 323.15 + 1.349\ \cdot 0.34\ \cdot 323.15 - 0.0004361 \\ \cdot\ (323.15)^2 - 0.002045 \cdot\ 0.34\ \cdot (323.15)^2 + 1.55e - 06 \cdot (323.15)^3 \\ = 4.5\ (MJ/m^3) \end{aligned}$$

Therefore, the total energy (E) is:

$$E(MJ) = e(MJ/m^3) \cdot V(m^3) = 4.5 \cdot 80 = 360\ (MJ)$$

The TNT equivalent mass is:

$$m_{TNT} = \frac{E(MJ) \cdot 10^3}{4680} = \frac{360 \cdot 10^3}{4680} = 76.9\ kg\ TNT$$

Next, the scale distance for r = 100 m is:

$$\bar{R} = \frac{r}{(\beta \cdot W_{TNT})^{1/3}} = \frac{100}{(0.4 \cdot 76.9)^{1/3}} = 31.9$$

By using the TNT curve, ΔP at 100 m is 3.6 kPa (0.036 bar)

$$\Delta P = 3.6\ kPa = 0.036\ bar$$

It should be taken into account that possibly, during an emergency, it is not possible to know exactly the conditions at the burst moment. In this case, conservative hypothesis can be considered. For instance, a temperature near the equilibrium with the set pressure of the PRV and the initial filling level (if no information about the possible loss of part of the vessel content through the PRV is available).

5.4 Analysis of BLEVE mechanical energy by using the Artificial Neural Network methodology

The Artificial Neural Network (ANN) approach has been used as a handy toolkit for simulation, prediction and modeling in diverse engineering and scientific areas. It can be a useful tool when there is some nonlinearity in the system, requiring a relatively reduced computing time.

Thus, ANN was implemented in order to obtain a function allowing the calculation of the BLEVE mechanical energy. Again, this function should only require and be depending on vessel failure temperature and filling level.

5.4.1 Artificial Neural Network

Neurons are the basic elements of biological neural network in human brain. The structure of a neuron is shown in Figure 5-4. Neuron receives data from neighboring neural cells through dendrites and makes some process in soma (body), transferring a signal to the next neuron through the axon; data transfer is performed by synapses through electrochemical signals.

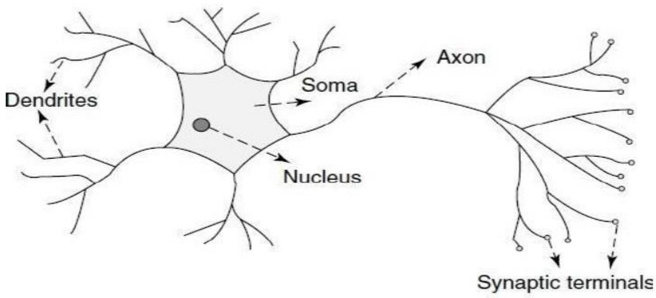


Figure 5-4. Neuron (Yadav et al., 2014).

The Artificial Neural Network is a method that can be applied to analyze and calculate data for different problems and solve them with the same pattern as that of a biological neural network. The first attempts in this field were due to Hebb in the 1940s. After that, some researchers such as Hopfield, Rumellhart, Grossberg and Widrow developed this method in the 1980s.

With ANN, huge problems could be solved through parallel and distributed processing. It solves problems without requiring too complicated formulation; because of this, it could save time significantly in comparison with closed-form solving methods. Moreover, this methodology enables to approximate any non-linear function to a compact set of data with a specified accuracy (Siddique and Adeli, 2013).

Every neuron model consists of a segment that signals import through it and acts like a synapse. At first, each one of the inputs (x_i) is multiplied by its corresponding weight value "$\boldsymbol{w}$". After summation of these values, a bias value "b" can be added to the result. A summary of this process for n inputs is shown in equation (5.17):

$$net = \left(\sum_{i=1}^{n} \omega_i x_i\right) + b \tag{5.17}$$

At the end of this process, the result enters in a transfer function (Eq. (5.18)):

$$y = f(net) \tag{5.18}$$

The usual forms of the transfer function are linear, step, ramp or sigmoid. Figure 5-5 shows the structure of an ANN.

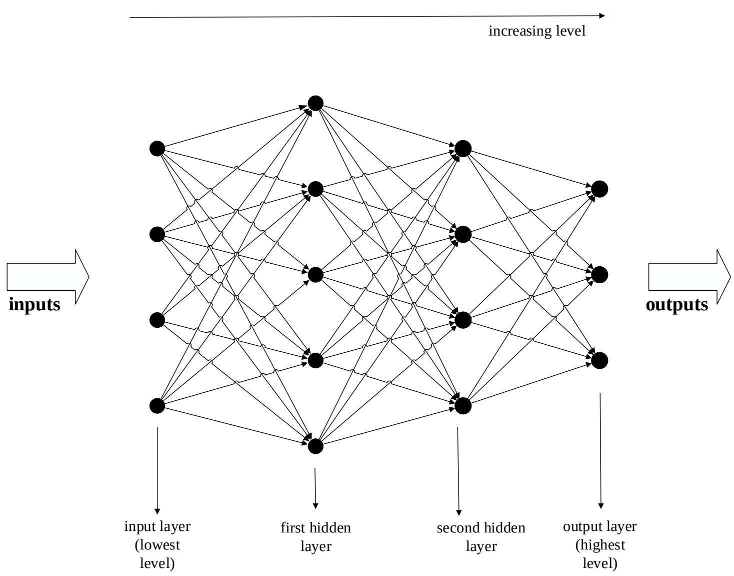


Figure 5-5. Structure of an Artificial Neural Network.

Some neurons connect together, forming a layer of neurons. A network includes one or more of these layers. According to the configuration and the way of connection between neurons, there can be different types of neural networks. Generally, they can be separated into two categories: 1) feedforward neural networks, and 2) feedback neural networks.

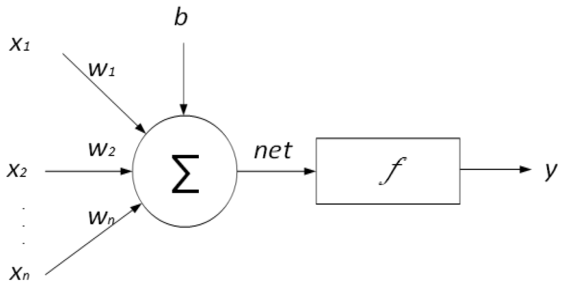


Figure 5-6. Feedforward Neural Network.

In a feedforward neural network, the signals travel in a forward way, they cannot come back and there is no feedback. This type of neural network (e.g. Figure 5-6) can be represented in vector form by equation (5.19):

$$Y = f(W \cdot x + b) \tag{5.19}$$

Here, Y is the output vector, W is the weight matrix, b is a bias vector and f is a transfer function.

The main task of the neural network is to define the weights and biases in a way that adapts the output to the inputs with a minimum error. A training process does the modification of weights and biases. The training method used for solving the network in this work has been the Bayesian Regulation method, which can be applied to feedforward neural networks training. It is based on a statistical approach and assumes that the values of weights and biases are related to a distribution function with an unknown variance. The main task is to estimate the parameters by means of statistical techniques (Foresee and Hagan, 1997; Nguyen, 1998; Siddique et al., 2013).

5.4.2 Dataset preparation

Two datasets for propane and butane were prepared for the ANN by using the aforementioned method based on real gas behavior and adiabatic irreversible expansion (Planas et al., 2004b). The required thermodynamic data were obtained from NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP) version 9.1. Temperature (K), filling level and mechanical energy (MJ/m^3) were registered in the datasets. The database interval was designed for filling level ranging between 1% and 90% in the case of propane, and between 1% and 99% for butane. The initial temperatures were 300 K and 283 K for both propane and butane. Actually, the ANN was trained in those aforementioned intervals. Propane and butane datasets had 121 and 201 data points, respectively. Those datasets were used in the ANN for generating the related functions. Finally, the resulting functions were applied to the two sets of experiments from Birk et al. and Johnson et al. already presented in Chapter 4 to analyze the goodness of the method.

5.4.3 Results of the backpropagation training algorithm

Three different backpropagation (BP) algorithms were studied in order to find the best one for the ANN. Five neurons were considered for the comparative study, and finally the algorithm with the lowest MSE was chosen as BP algorithm.. As it is shown in Table 5-6 and Table 5-7, the Bayesian Regularization algorithm has the lowest MSE for propane and butane, therefore was the one selected in this study. The MSE values for these two substances were $2.29\cdot10^{-4}$ and $4.63\cdot10^{-5}$, respectively.

Table 5-6 Back propagation algorithms for propane

Backpropagation algorithm	Function	Testing Mean square error (MSE)	Epoch	Regression R value	Best linear equation
Levenberg-Marquardt backpropagation	*trainlm*	0.000364	232	0.99996	$Output = 1 \cdot Target + 0.0049$
Bayesian Regularization	*trainbr*	0.000229	385	0.99998	$Output = 1 \cdot Target + 0.00098$
Scaled Conjugate Gradient	*trainscg*	0.0736	39	0.99205	$Output = 0.97 \cdot Target + 0.17$

Table 5-7 Back propagation training algorithms for butane

Bachkpropagation algorithm	Function	Testing Mean square error (MSE)	Epoch	Regression R value	Best linear equation
Levenberg-Marquardt backpropagation	*trainlm*	$5.85 \cdot 10^{-5}$	116	1	$Output = 1 \cdot Target + 0.0019$
Bayesian Regularization	*trainbr*	$4.63 \cdot 10^{-5}$	1000	0.99999	$Output = 1 \cdot Target - 0.0012$
Scaled Conjugate Gradient	*trainscg*	$8.39 \cdot 10^{-6}$	17	0.94398	$Output = 0.93 \cdot Target + 0.33$

Optimizing neurons number

The determination of neurons' number is very important. Considering few neurons causes underfitting and, contrarily overfitting can occur if the number of neurons is higher than a specific value. In this study, an ANN was trained based on Bayesian Regulization BP algorithm for propane and butane. The number of neurons was changed from 1 to 20 and an optimum number of neurons was chosen based on the minimum value of MSE of the training. According to Figure 5-7, the optimum number of neurons for propane and butane were five and four neurons, respectively.

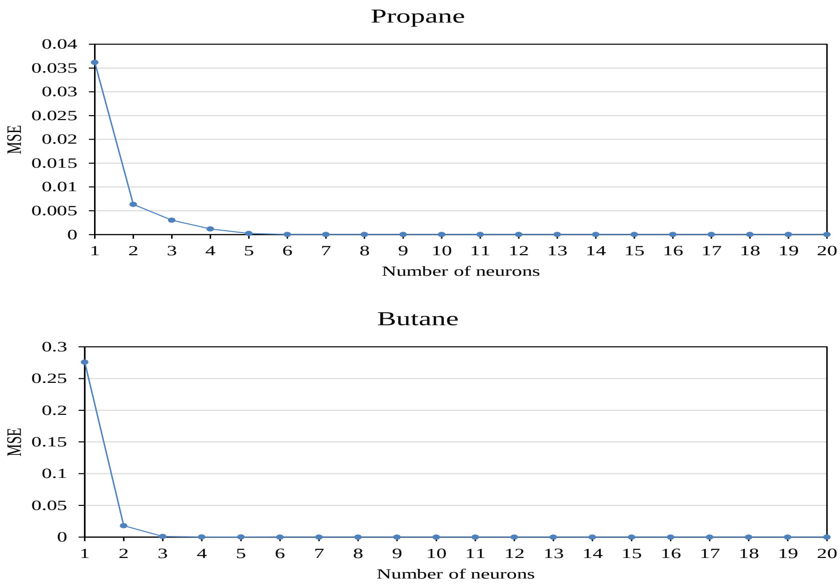
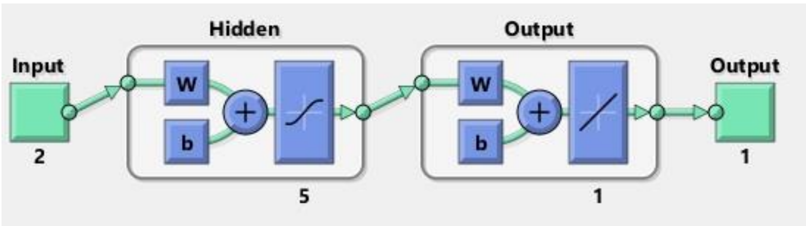


Figure 5-7. Optimized neurons number.

ANN setup and results

For solving the problem, a multilayer feed forward neural network was used. A general picture of this method has been depicted in Figure 5-8. The multilayer feed forward network consists of three layers. The first one is the input layer through which the data are imported to the network, and the last layer is the output one, which gives the target data. Between these two mentioned layers, there is another hidden layer. The number of hidden layers depends on the accuracy that is required for a particular problem. In this analysis, the number of hidden layers was set to one, which provided a good accuracy. Based on the neurons optimization process, the number of neurons at the hidden layer was five in the case of propane and four in the case of butane. The transfer function applied in this layer was a sigmoid because it had an easy and simple differentiation for using in the backpropagation algorithm. For output layer, the number of neurons had to be one in both cases, and the transfer function was *purelin* (linear).

a)



b)

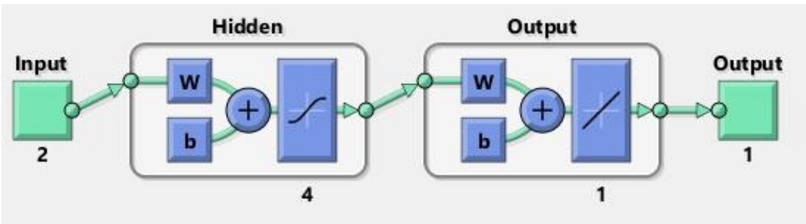


Figure 5-8. Artificial Neural Network structure for propane and butane: a) propane ; b) butane.

The process was performed with the MATLAB Neural Network toolbox version R20015a (8.5.0.197613 – License Number: 107001). The number of input data for the training process was 121 and 201 for propane and butane, respectively. It reached a convergence level after 348 iterations in the case of propane and 191 iterations with butane. The validation process was done with 15% of data to check the network generalization. The resulting network was tested with 15% of data in order to provide an independent measure of the network performance during and after training.

For propane, the designed network regression R-values were close to one, showing that there was a close correlation between output and targets. Figure 5-9 shows how much accurate the ANN model is.

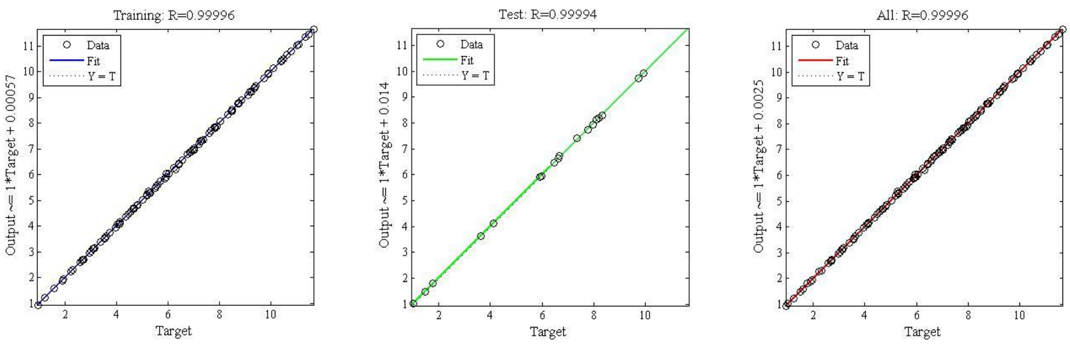


Figure 5-9. Regression plots for propane, left: during training, middle: during the testing, right: all the data including validation.

In addition, the optimized weights for propane produced by the artificial neural network model are summarized in the Table 5-8.

Table 5-8 Propane's weights matrix

Neuron	W1		W2
	Input variables		Output
	Temperature	**Filling level**	**Energy**
1	-1.2335	-0.2862	-0.8641
2	1.7512	0.3928	0.5474
3	-0.8560	0.2377	3.16
4	1.2560	-0.3420	1.1380
5	1.1617	0.2995	1.1103

W1: Weights between input and hidden layers

W2: Weights between hidden and output layers

In the case of butane, the regression results (Figure 5-10) show that the network was trained properly and a linear relation exists between output and target data. R values were close to unity which indicated linearity between target and output data.

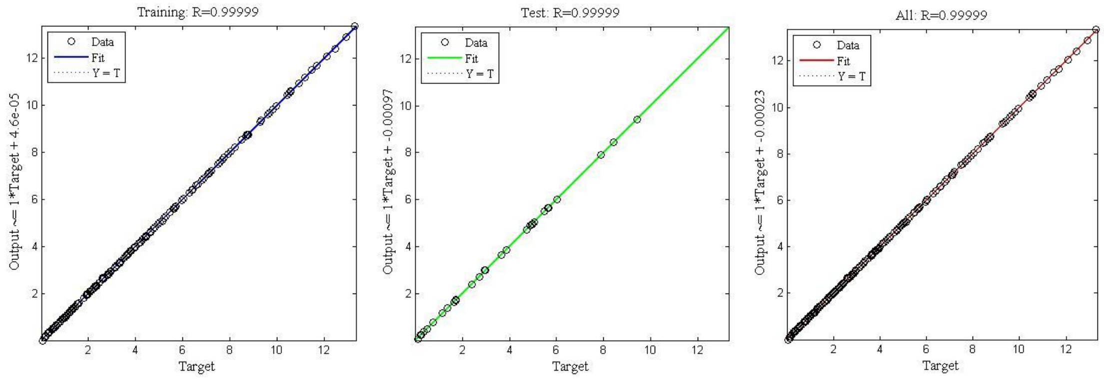


Figure 5-10. Regression plot for butane, left: during training, middle: during the testing, right: all the data including validation..

The optimal weights for butane from the artificial neural network between input and hidden layers (W1) and between hidden and output layers (W2) are shown in the Table 5-9.

Table 5-9 Butane's weights matrix

Neuron	W1		W2
	Input variables		Output
	Temperature	**Filling level**	**Energy**
1	-1.3757	-0.4138	-0.2668
2	0.7913	-0.1637	-1.8164
3	-0.8212	-0.1932	-2.4487
4	-1.5521	0.4522	-0.3672

W1: Weights between input and hidden layers
W2: Weights between hidden and output layers

5.4.4 Comparative study

Root-Mean-Square Deviation (RMSD) (Piñeiro et al., 2008) as a statistical toolkit was also used in the comparison of the results obtained with the ANN method and the aforementioned experimental data from Birk et al. and Johnson et al. The results are shown in the Table 5-10, together with those obtained from polynomial expressions. As can be seen, the functions derived from ANN show a good performance. It can be stated that both methods proposed are accurate and practical to be applied. Again, the same reason explained in section 5.3.1 could be the reason for deviation between the new approach and RAIE method. Figure 5-11 shows these differences between the various approaches and the experimental values.

Table 5-10 RMSD values for different methodologies

	Thermodynamic assumption*			
RMSD	**RAIE**	**SE**	**New approach (Polynomial)**	**New approach (Neural Net Fitting)**
Johnson-TNT Curve	2.3	2.2	2.2	2.2
Birk-TNT curve	4.9	4.1	4.2	4.3

*RAIE = Real gas behavior and adiabatic irreversible expansion; SE = Liquid superheating energy

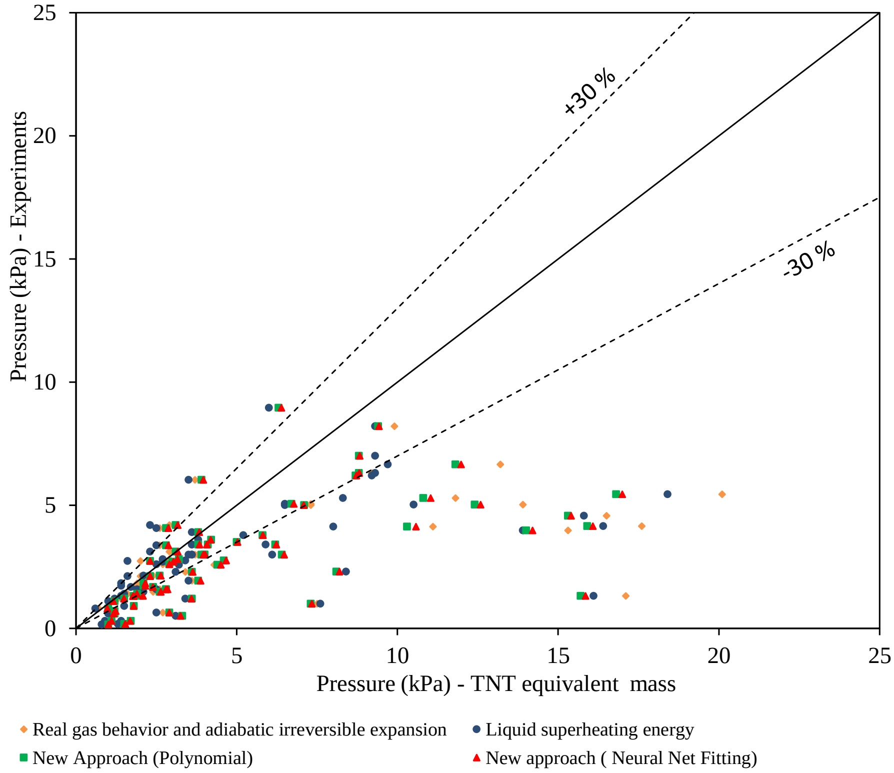


Figure 5-11. Results by different methodologies against their experimental values.

5.4.5 Example of application

The application of Neural Network method is explained for the same example already presented in section 5.3.2:

The Mathlab file for calculating the overpressure in kPa is:

```
clear
clc
T=input('Temperature(K)\n');%Temperature just before the explosion
fl=input('Filling Level\n');%Filling level just before the explosion
d=input('Distance(m)\n');
v=input('Volume(m3)\n');%Volume of vessel
a=[T;fl];
Energy_predicted_per_m3=propanepredictor3(a);% The NNT function is
available in appendix
Energy_predicted=Energy_predicted_per_m3*v;
w_tnt=(((10^3)*0.4)/4680)*Energy_predicted;
c=w_tnt^(1./3);
scaled_distance=d/c;
overpressure_kPa=((1/scaled_distance)+(4/(scaled_distance^2))+(12/(s
caled_distance^3)))*101.32;
name='Overpressure';
X=[name,' is equal to ',num2str(overpressure_kPa),' kPa'];
disp(X)
```

Here is the procedure for calculating the example and the result in kPa when running the previous Mathlab file:

```
Temperature(K)
323.15
Filling Level
0.34
Distance(m)
100
Volume(m3)
80
Overpressure is equal to 3.6435 kPa.
```

5.5 Discussion

There are several thermodynamic methods to predict the mechanical energy of a BLEVE. These methods were compared in previous chapters, and it was concluded that they could be classified in two different categories: a) methods giving a quite conservative value, and b) methods giving a lower value. The methods based on real gas behavior and adiabatic irreversible expansion belong to the second category, being much less conservative but much closer to the real/experimental values than the other ones.

With the adiabatic irreversible expansion method there is almost a linear behavior between the mechanical energy and the temperature and filling level at the moment of explosion. This characteristic was used in this chapter in order to find a quick method (according to time and effect of calculation) to calculate the mechanical energy of a BLEVE. Therefore, the aim of this chapter was to present an easy, fast, and precise method than the existing ones in order to calculate the mechanical energy of a BLEVE.

Thus, the linear relation between the temperature and the released mechanical energy was employed in order to find an appropriate equation. The data sets were created for several substances (selected according to the historical analysis in Chapter 1) by defining a scenario for a 1 m^3 vessel which was heated up; real gas behavior and adiabatic irreversible expansion process was considered. Mechanical energy values were registered for related temperatures and filling levels.

MATLAB Curve Fitting Toolbox was utilized to produce the appropriate polynomials. Therefore, several polynomials with various degrees were derived for the most common fluids found in BLEVE accidents. The derived equations got filling level and temperature as input variables and gave the mechanical energy of BLEVE as an output.

Visual examination and goodness-of-fit statistics were used to see which polynomial provided the best solution. The best fit for proposed equations was the third degree polynomial. Actually, it gave the lower deviation with the data set.

Furthermore, the comparative study on the new approach showed that it had a better level of performance than the other methodologies. In some experiments (e.g. Birk experiments), the results of the new approach may have some deviation from the results of the methods based on real gas behavior and adiabatic and irreversible expansion (Table 5-5). Indeed, the new approach sometimes had closer approximation than the other methods. These differences could be originated from the deviations that happened during the calculation of the polynomials (Table 5-3).

Moreover, Artificial Neural Network (ANN) was used as a handy toolkit for the nonlinear system. The aim was to find an appropriate function between temperature and filling level as input data and mechanical energy as output datum. Two functions were produced for propane and butane by using ANN. For both substances, the designed networks regression R values were close to one, which show that there was a close correlations between outputs and targets. The ANN networks showed good level of performance against the other methods, which combined with its simplicity, allows obtaining quick and accurate results easily.

The presented methodology for calculating mechanical energy is independent from substance's thermodynamic properties information (Enthalpy, Entropy, Internal energy, etc.) and it only requires rupture temperature and filling level to calculate the BLEVE mechanical energy and the resulting effects. ANN is like a black box and what is happening inside the function is not clear. This could be a disadvantage for ANN. However, the aim of using ANN in this study has been to show the application of ANN in the prediction of the energy of explosion. Its capabilities can be developed for further researches in the field of BLEVE such as range of fragmentations and its types.

Finally, the new approach only depends on temperature and filling level of a vessel for estimating the BLEVE released mechanical energy. Comparing the new approach with other thermodynamic methodologies based on several thermodynamic variables, the new approach seems to be quite convenient and handy.

Chapter 6. CONSIDERATIONS ON EMERGENCY MANAGEMENT IN TRANSPORT ACCIDENTS WHICH CAN LEAD TO A BLEVE

6.1 Introduction

Among accidents involving a BLEVE, those occurred in road or rail transportation have an important contribution. From the historical analysis previously performed (Chapter 1), 49.1% of all cases analyzed, i.e. practically half of them, occurred in transportation by road or rail; and in most of these cases, the explosion was followed by a fireball.

When a road or rail tanker transporting a flammable liquid (as, for example, LNG or LPG) undergoes a traffic accident or a derailment, the following accidental sequence can occur: damage of thermal insulation → loss of containment → ignition → flames impingement on the vessel → pressure increase → SRV opening → more flames impingement → BLEVE of the vessel.

This sequence can take a variable time. As mentioned in a previous chapter (see Table 3-6), and especially when the flames impinge on the non-protected vessel wall, the explosion can occur after one minute, after one hour or, even, can never occur.

If there is a certain delay, two things will happen: a) the firefighters will come and will try to control the emergency, and b) as the fire is something relatively "attractive" for many people, probably a certain number of spectators will come to look at the accident. These spectators will adopt a "safety distance" according to their experience and knowledge (in most cases, quite limited) of what an explosion or a large fire is, i.e., of the order of 100 m. However, even though this distance could be enough for a relatively large pool fire, it is completely insufficient if a BLEVE followed by a fireball takes place. And this is the reason why in such accidents often spectators are wounded or even killed. Furthermore, many firefighters have also died, due to the uncertainty concerning the time to failure; even though in industrialized countries firefighters are more and more aware of the convenience of evacuating in the situations which can lead to a BLEVE, still accidents occur in which the explosion occurs when they are trying to extinguish the fire, with the associated severe consequences.

In such situations, the measures taken by those managing the emergency are essential to reduce the consequences of the event.

As an example, two cases can be commented:

1. *Tivissa accident*. A road tanker transporting LNG underwent a traffic accident and turned over on the road near Tivissa, Catalonia (Spain), on June 22, 2002. The tank was made of stainless steel, designed for an operating pressure of 7 bar and had thermal insulation. It also had 5 safety valves connected to a discharge pipe. At that day, the 56 m^3 tanker was filled with LNG up to 85% at -160 ℃ and the pressure of 1 bar. The start to discharge pressure was set at 7 bar. Approximately 2 minutes from the accident, fire appeared and the flames engulfed the tank. The fire probably originated from tanker fuel, the vessel containment (LNG) or both. About 20 minutes later, a BLEVE followed by a fireball occurred. Large fragments were ejected and dispersed up to 257 m around the location of explosion; the two main tank sections were ejected up to 125 m. The driver was killed and two persons located at approximately 200 m were wounded from first and second-degree burns because they had not taken the necessary safety distance. (Planas et al., 2004a).

2. *Zarzalico accident*. A 56.5 m^3 insulated road tanker transporting LNG underwent a traffic accident by colliding against a parked truck on November 20, 2011. The driver was killed in the accident. The tank was loaded with 12000 kg of LNG stored at -160 ℃ and 1 bar. It was also equipped with 3 safety valves. The start to discharge pressure was set at 7 bar. Fire appeared immediately after the accident, the flames affecting the tank. About 20 minutes later, the firefighters reached the location of the accident. They evacuated the people up to a distance of 600 m. The explosion occurred 70 minutes after the beginning of fire. Firefighter had withdrawn to 200 m from the place of the tanker at the moment of explosion. The large windows of the service station located at 125 m from the explosion point fell down. However, the smaller windows were intact. The leaves of trees at 90 m from the explosion were dried as a consequence of the thermal radiation. The ejected fragments were distributed over a range of 200 m from the accident place. Even though there were a large number of spectators, none of them was wounded

when the explosion-fireball occurred, as the firefighters had obliged them to withdraw to a safe distance (Planas et al., 2015).

These two cases are a good example of the importance of the safety measures taken by the emergency managers concerning both the firefighters and the people in the zone. Unfortunately, in many cases these measures –which can be very simple– are ignored, with lethal consequences. In this chapter, the results obtained from the historical analysis and from the application of BLEVE and fireball mathematical models are used to define the main measures which should be taken in these accidents, with an especial emphasis in the transportation of LNG and LPG.

6.2 Amount of hazardous materials involved

For safe transportation of hazardous materials by rail and road, several regulations and treaties exist in different parts of the world (e.g., ADR (2015), RID (2015), etc.). The UN Recommendations on the Transport of Dangerous Goods developed by the United Nations Economic and Social Council's Committee of Experts on the Transport of Dangerous Goods (2011) is the basis for many national and international regulations. However, the regulations could be different in diverse parts of the world.

In road and rail tankers carrying flammable liquefied gasses is mandatory to be equipped with pressure relief valves and also with thermal protection in North America, but not in Europe (Birk, 2014; Paltrinieri et al., 2009). Based on US Department of Transportation (DOT), the diverse classes of tankers, especially tank cars, must follow a specific marking system which shows the information about the tank. For example, the class of DOT 111A60ALW1 for a tank car has the following meaning (Figure 6-1):

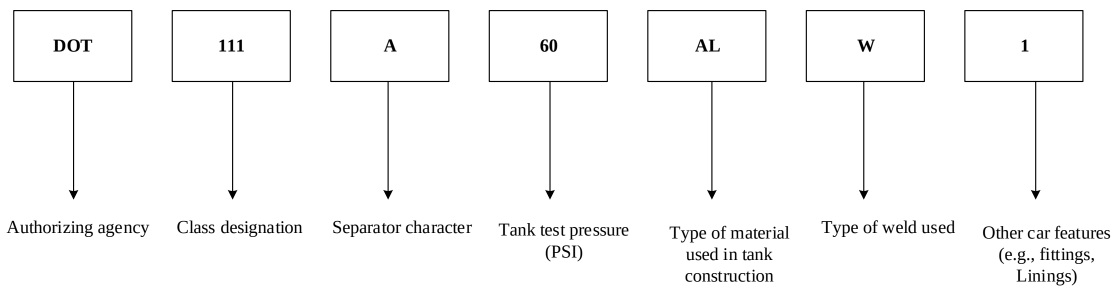


Figure 6-1.US marking system for tank cars.

According to the US Department of Transportation (DOT), several classes of tank cars and cargo tanks are available for the transportation of pressurized gases. There are about five classes within the regulations: DOT-105,-109,-112,-114 and -120 for LPG rail transportations; and DOT-113 for LNG rail transportations. Moreover, MC-330 and -331 are used as LPG cargo tanks and MC-338 is in the case of LNG transportations based on the regulations.

In this chapter, the common classes of tank cars and cargo tanks used for transportation of LPG and LNG have been taken from the US Department of Transportation. The main regulations for calculating the required information are based on the US DOT (Department of Transportation) for Tank Cars and Cargo Tanks: Code of Federal Regulations (2016), Title 49 - sections 173.314, 179.101, 179.301, 179.15, and 179.401-1 for LPG/LNG tank cars and 173.315 and 173.318 for LPG/LNG cargo tanks. Moreover, the experiments from Johnson et al. (1990) and Birk et al (2007) and the report from Molag and Kruithof (2006) are also considered for defining the various scenarios.

Here the analysis will be centered on the appropriate tankers for the transportation of LPG and LNG (the materials most frequently involved in BLEVE accidents) by road and rail.

The classes of tankers and their specific parameters considered in this chapter are summarized in Table 6-1:

Table 6-1.Scenarios for different tankers in rail and road

	Tank (rail) cars		Cargo (road) tanks	
Substance	**Volume (m^3)**	**Filling degree (%) at loading temperature and P_{rup} (kPa)***	**Volume (m^3)**	**Filling degree (%) at loading temperature and P_{rup} (kPa)***
Propane	127.1; 121.1; 110; 94.1; 63	90% → 1137 kPa 86% → 1500 kPa 81% → 2000 kPa	64; 45.4; 34.1; 24.6; 13.2; 10.6; 2.8	86% → 1500 kPa 81% → 2000 kPa
Butane	127.1; 121.1; 110; 94.1; 63	90% → 1137 kPa 86% → 1500 kPa 81% → 2000 kPa	64; 45.4; 34.1; 24.6; 13.2; 10.6; 2.8	85% → 700 kPa 76% → 1500 kPa
Methane	111	91% → 206.8 kPa 87% → 482.6 kPa 85% →689.5 kPa	56	94% → 103.4 kPa 93% → 137.9 kPa 91% → 206.8 kPa 90% → 275.8 kPa 89% → 344.7 kPa 87% → 482.6 kPa 85% → 689.5 kPa

*The loading temperature is considered as 288.75 K for Propane and Butane and 113.15 for Methane.

Different capacities of tank cars and cargo tanks are used in the transportation of LPG. The tank car capacities range between 63 m^3 and 127.2 m^3, and the cargo tank capacities range from 2.8 m^3 to 64 m^3 (Leffler; 2014). In the case of LNG, the capacities of 111 m^3 and 56 m^3 were considered for tank cars and cargo tanks, respectively.

Evidently, the vessels are not completely filled. The maximum filling degree is in fact determined by the existing regulations (which are not the same for all countries) and by the properties of the transported material.

In the European Union this is regulated by the *European **A**greement concerning the International Carriage of **D**angerous Goods by **R**oad (ADR)*; the maximum allowed filling degree in the worst conditions (i.e., at the conditions at which the safety relief valve will open) is 95%. However, these values correspond to the highest pressure and temperature and, therefore, in these conditions the density of LNG will have a significantly lower value than the one at loading conditions. Thus, the filling degree when loading the tank will have to be lower and will depend on these conditions; furthermore, it will depend on the density of the LNG, which will be a function of its composition (methane is considered here). If the loading temperature is -160 ºC (about 1 barg), the density of LNG is 420.18 kg m^{-3}. If the set point for the PRV is about 7 barg (a common value, for which the density will be 374.3 kg m^{-3}), then the maximum filling degree when loading will be:

$$Filling\ degree = 95\% \cdot \frac{374.3}{420.18} = 85\%$$

Thus, that assumption (95% filling degree at the safety relief valve condition) will be assumed for the diverse calculations here.

6.3 Physical effects from a BLEVE: reach and threshold values

As it was mentioned in previous chapters, the overpressure wave and ejected fragments are the mechanical effects of a BLEVE. Moreover, if the substance is flammable, thermal effects will follow the explosion ones.

6.3.1 Overpressure

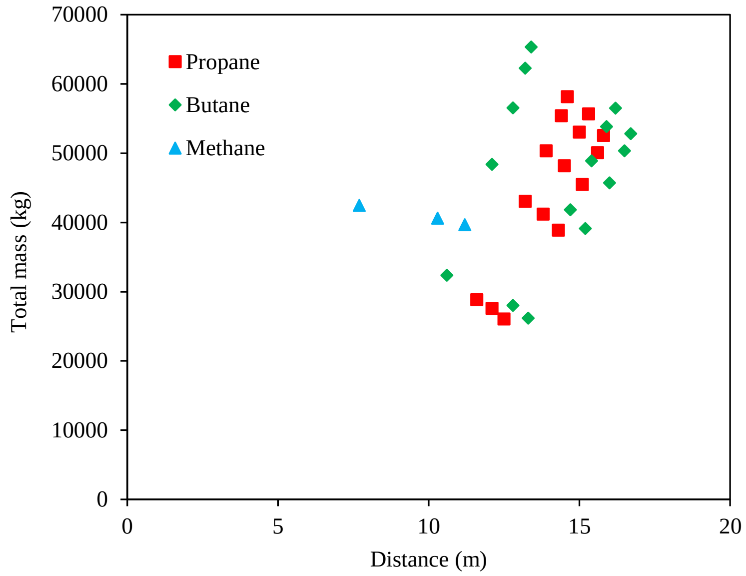
To find the corresponding consequences on people, the Probit expressions (Y) can be used.

Thus, for direct overpressure effects the lethality due to pulmonary hemorrhage can be estimated using the following equation (Casal, 2008):

$$Y = -77.1 + 6.91 \cdot ln\Delta P \tag{6.1}$$

where ΔP is the overpressure in $N \cdot m^{-2}$. As practically usually, transportation accidents will occur in a free (non congested) zones, reflected overpressure should not be considered.

a)



b)

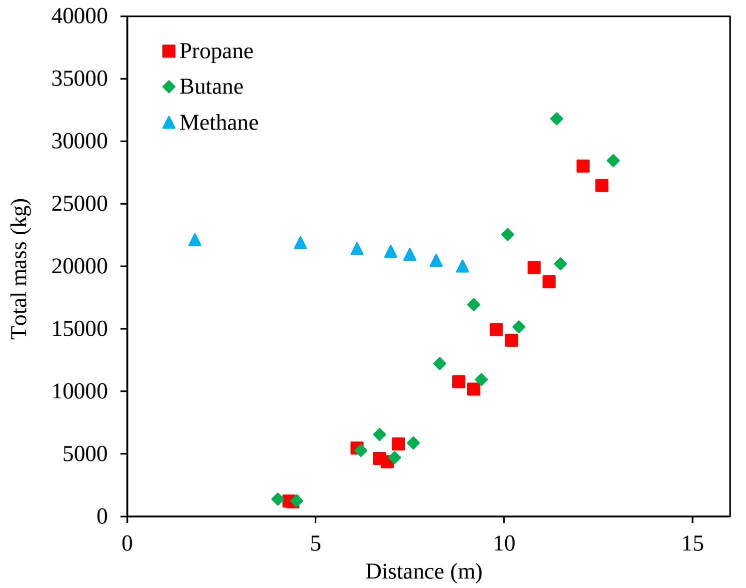


Figure 6-2. Threshold distances of overpressure for 1% lethality (direct effect). a) Rail tankers; b) Road tankers.

For the 1% of lethality, a threshold value of 103.17 kPa is obtained. The corresponding distances for propane, butane and methane (assimilated to natural gas) have been calculated for different vessel start-to discharge pressures and volumes (Figure 6-2). In the case of LNG road tankers, it should be reminded that the allowed loading filling level of methane decreases by increasing the start-to-discharge pressure in the road transportation according to the defined scenarios in Table 6-1. As it can be seen in this figure, the reach for lethality due to overpressure direct effects is quite reduced (up to approximately 14 m), as could have been expected: the value required for lethality is rather high and the peak overpressure decreases relatively quickly with the distance.

6.3.2 Ejected fragments

As for the ejected fragments, the most common vessel breaking patterns are those shown in Figure 6-3 (Gubinelli and Cozzani, 2009). Among them, the one dividing the vessel in one bottom and the rest is the most frequent one (approximately 60% of cases).

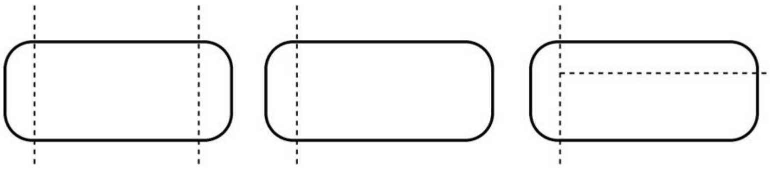


Figure 6-3. Most frequent fragmentation patterns of cylindrical vessels.

The prediction of the range of ejected fragments is rather difficult, and an accurate prediction is in fact impossible. However, a few authors have proposed expressions to calculate in an approximate way the maximum distance which can be reached by the fragment originated from cylindrical vessels (those used in transportation). Baum (1988) proposed the following expressions:

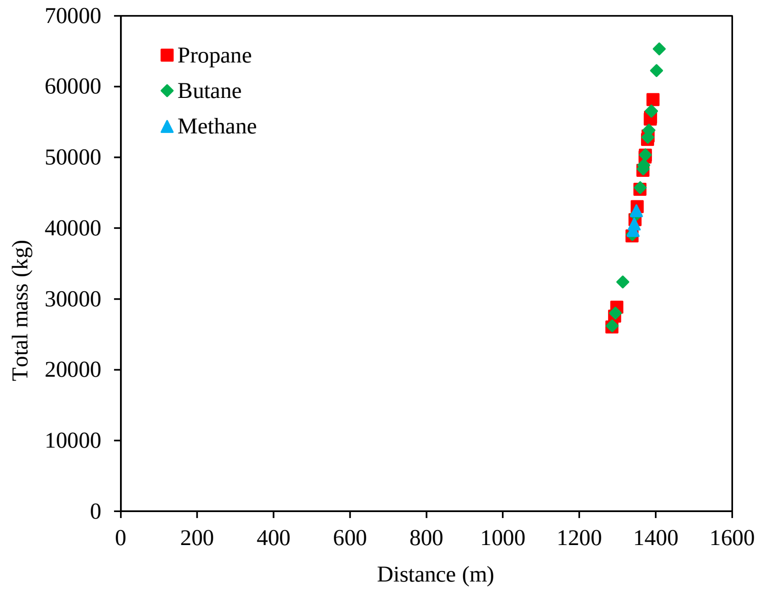
For tanks < 5 m^3 in capacity: $$l = 90 \cdot {m_T}^{0.33} \tag{6.2}$$

For tanks > 5 m^3 in capacity: $$l = 465 \cdot {m_T}^{0.1} \tag{6.3}$$

Where M is the mass of substance contained in the vessel (kg) and l is the range (m).

The resulting distances for different values of vessel volume and filling degree have been calculated (Figure 6-4). Very large distances can be covered by the fragments (much larger than those found with overpressure). This is due to the special way usually found in cylindrical tanks fragmentation, which gives rise to relatively aerodynamical fragments which travel in a way similar to that of a rocket or a missile; thus, ranges larger than one kilometer can be reached. Instead, for the case of spherical vessels, shorter distances are reached (the maximum distance registered for a large fragment of these tanks is 600 m).

a)



b)

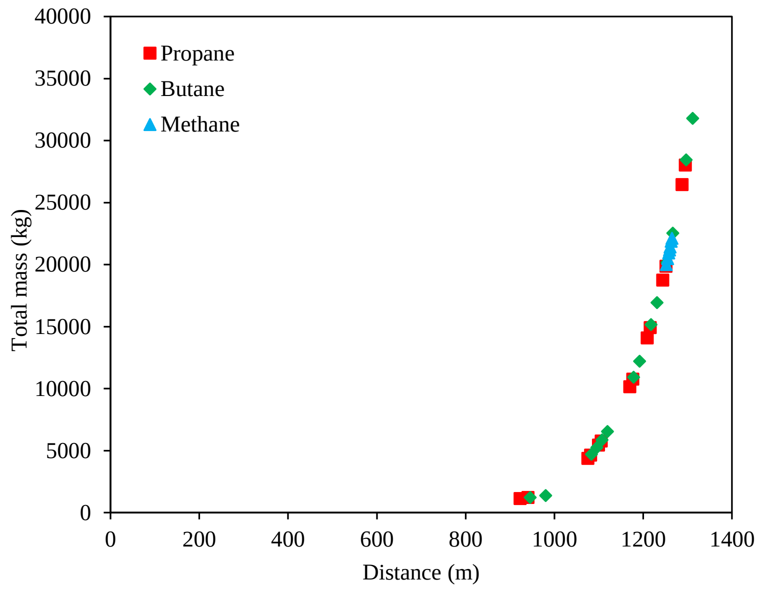


Figure 6-4. Distances reached by the ejected fragments.a) Rail tankers; b) Road tankers.

Another aspect which should be considered is the direction followed by the fragments. Whereas for a spherical vessel this cannot be predicted due to the irregular shape of fragments, for cylindrical vessels (those found in road and rail transportation) often the fragments are ejected following the vessel longitudinal axis (Figure 6-5). Although this is completely true in some cases (see, for ex., Tivissa accident case), often there is a certain scattering; Holden and Reeves (1985) suggested that in 62.5% of cases the fragments were ejected in the main axis direction, with a scattering covering an angle of 45º.

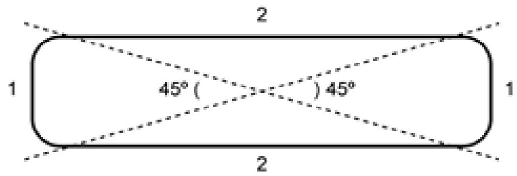


Figure 6-5. Most frequent direction of cylindrical vessel fragments.

6.3.3 Thermal radiation from a fireball

BLEVE will be probably followed by a fireball if the contained substance is flammable. In this situation, predicting the effects of fire and its thermal radiation is crucial from the point of view of emergency management and preventive measures. The solid flame model (Casal, 2008) can be used as a well-known model to calculate thermal radiation from a fireball located at a certain height and distance (Figure 6-6) (see Appendix 2).

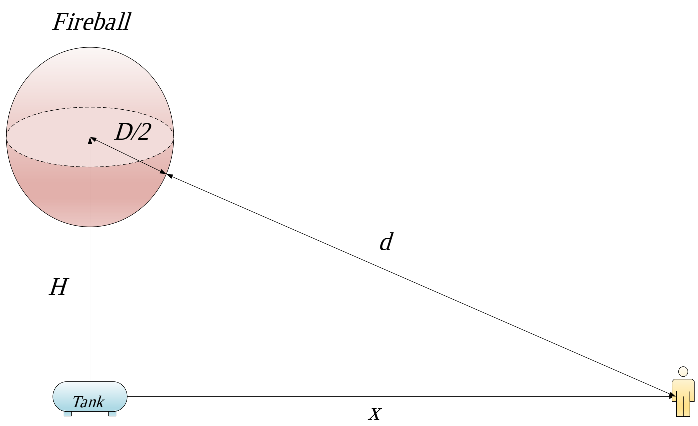


Figure 6-6. Fireball geometry in relation to a given target.

Even though the size and position of the fireball –and of its wake- change with time, usually models assuming non-variable values are used, as the error between both approaches has been proved to be negligible. Thus, the threshold values for thermal radiation were calculated for 1% lethality (with and without protection; protection is considered when, as in the case of firefighters, special resistant dresses are used), 1% second degree burns (with and without protection) and 1% first degree burns (with and without protection).

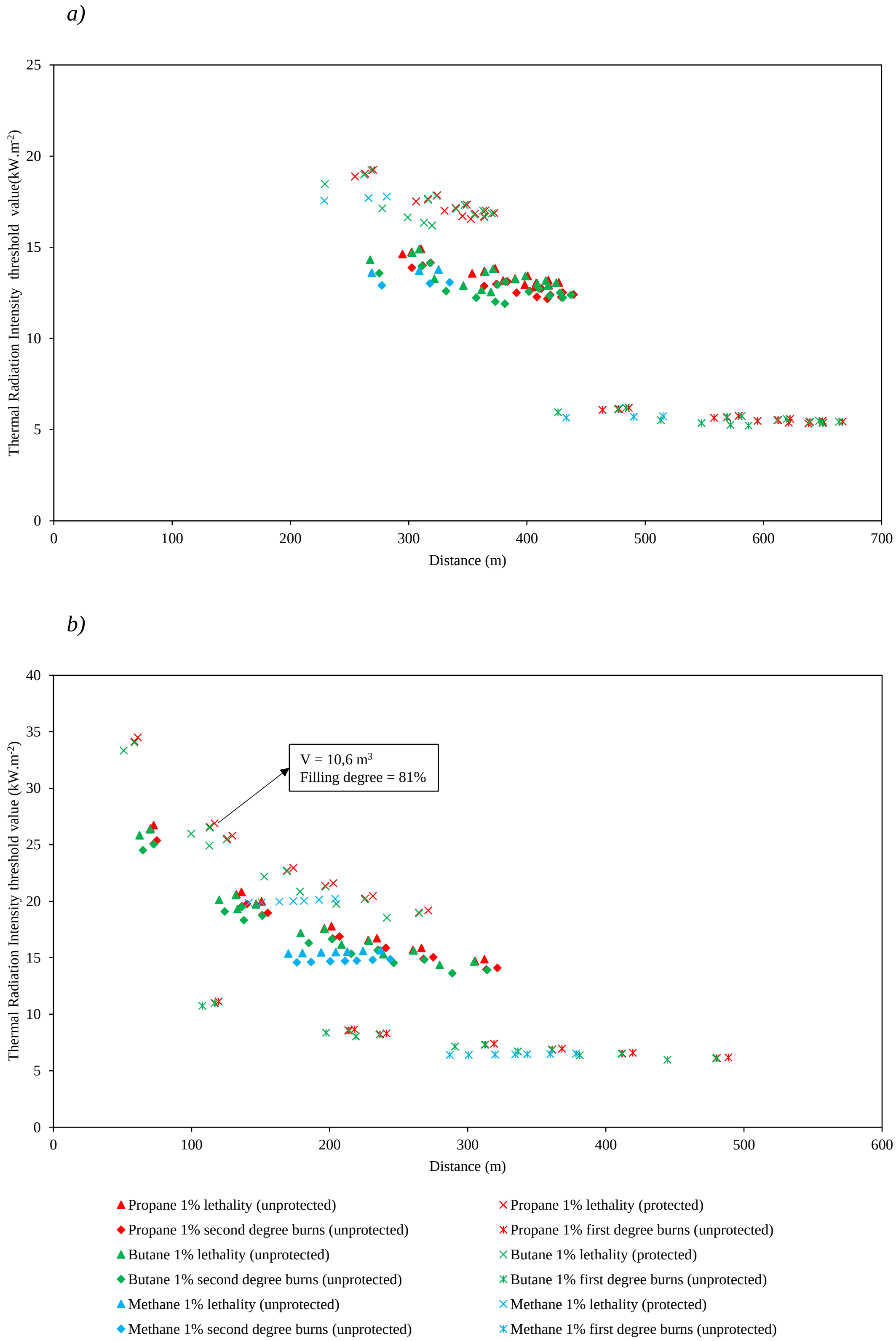


Figure 6-7.Variation of the thermal radiation intensity as a function of distance (each point corresponds to one of the scenarios specified in Table 6-1; as an example, one of the cases has been indicated). a) Rail tankers; b) Road tankers.

The variation of the thermal intensity radiation corresponding to each threshold value as a function of the distance (Figure 6-6) has been plotted in Figure 6-7 for the different scenarios specified in Table 6-1. Due to geometrical reasons, the variation of the intensity with the distance is more important at short distances. In all cases, large distances are required to avoid consequences on people, much higher than those corresponding to overpressure wave.

6.4 Discussion

The values obtained from the data exposed in the previous section have allowed the calculation of the distances corresponding to the lethality threshold (1% lethality) for both blast and thermal radiation. It is obvious that blast damage reach is much shorter in all cases than thermal effects, therefore only thermal effects and fragments distances will be taken into account here to consider the order of magnitude that evacuation distances should cover. The values obtained for the maximum distances corresponding to thermal radiation lethality have been summarized in Table 6-2.

Table 6-2. Maximum distances for the thermal radiation consequences

Consequences	Maximum distance for the consequence (m)					
	Propane		Butane		Methane	
	Rail	Road	Rail	Road	Rail	Road
1% lethality (protected)	370	270	370	265	280	205
1% lethality (unprotected)	430	310	425	305	325	240
1% second degree burns (unprotected)	440	320	440	315	335	245
1% first degree burns (unprotected)	670	490	665	480	515	380

Approximate distances of 500 m (LPG) and 400 m (LNG) have been obtained for the typical tanks used in road transport, while approximate distances of 700 m (LPG) and 550 m (LNG) have been obtained in the case of rail transportation, due to the larger size of the tanks and the higher amounts of dangerous material usually transported. These values, together with those obtained for the ejection of fragments (Table 6-3), give therefore an idea of the order of magnitude of the evacuation distances that should be considered in these type of accidents.

Table 6-3. Maximum distance for the fragments reach

Consequence	Maximum distance for the fragments reach (m)					
	Propane		Butane		Methane	
	Rail	Road	Rail	Road	Rail	Road
Ejected fragments	1390	1295	1410	1310	1350	1265

Once the police or the firefighters reach the location of the accidents, probably there will be a certain number of people in the area covered by the aforementioned effects. The time required by firefighters can vary significantly, but some values have been suggested; see, as an example, those in Table 6-4. Depending on this time and on the accident circumstances, the explosion could happen before firefighters' arrival (the time to failure can be estimated for a vessel subjected to a fire, but in the case of a road or rail accident the correlations proposed are not at all liable), or a short time after, or even more than one hour later.

Table 6-4.Approximate fire brigade response time for effective prevention of a BLEVE, including the time to get a supporting water supply over 2.5 km (Molag and Kruithof, 2006)

Accident location	Fire brigade response time (minutes)	
	Tank vehicle	Tank wagon
City center, urban area, industrial area	45	105
Rural area	75	105
Highway with multiple accident and blocked access for fire brigade	75	-

Therefore, it is evident that, in a situation that can lead to a BLEVE-fireball certain emergency measures must be taken as soon as possible.

6.5 Recommendations

In road or rail transportation of dangerous materials, especially flammable liquids or liquefied flammable gasses, if there is a situation (fire affecting a tank) which can potentially lead to a BLEVE followed by a fireball the following points should be taken into account and applied in order to avoid or reduce the consequences on people:

- The BLEVE –probably followed by a fireball– can occur at any moment from the beginning of the accident.
- People should be evacuated to a distance of at least 700 m and preferably –if possible– to 1200 or 1400 m.
- Unless there is the need of rescuing someone from the trucks or wagons that suffered the accident, the firefighters should withdraw to the same distances too.

Chapter 7. CONCLUSIONS

The work done in this thesis has allowed the following summarized conclusions:

1. A series of definitions for a BLEVE exist in the literature, many of them not completely correct (some of them assuming that it is a fireball). The following definition has been proposed. "*A BLEVE is the explosion of a vessel containing a liquid (or liquid plus vapor) at a temperature significantly above its boiling point at atmospheric pressure*".

2. The historical survey performed on 330 accidents has confirmed the importance of domino effect in enlarging the scale and consequences of major accidents, especially with flammable substances such as LPG, gasoline and other hydrocarbons. It has also confirmed the influence of human factor, still very important, primarily in developing countries. The analysis has clearly shown the positive results of the regulating measures applied in the developed countries, as correspond to the developing ones.

3. 127 BLEVE accidents were also analyzed. Half of them occurred in transportation, essentially by rail and road, and almost 20% in transfer (loading/unloading) operations.

4. The specific analysis of those sequences leading to a BLEVE has shown that fire is the most important escalation vector, triggering almost 70% of cases. The existence of fireproofing and safety relief valves can reduce the chance of BLEVE or mitigate its effects, but they can not guarantee preventing it.

5. The analysis of the time to failure when fire affects a vessel has given values ranging from 69 s up to several hours. This time depends on the specific circumstances of each case (damage of fireproofing, jet fire impingement) and its accurate prediction is practically impossible.

6. The comparative of the diverse methods available in the literature to calculate the mechanical effects of these explosions has shown that those based on real gas behavior and adiabatic irreversible expansion and the ones based on the liquid superheating energy give the values closest to the experimental ones, even though some authors prefer to use other which are more conservative.

7. The analysis of these methods has shown as well that none of them takes into consideration the "superheat limit temperature". This is a concept which should be considered of theoretical interest for the phenomenological interpretation of BLEVE, but without any practical application when calculating it effects in real situations.

8. A linear relationship has been detected between the vessel temperature and filling level and the mechanical energy of a BLEVE. Based on this fact, a new method has been developed to calculate the energy released in the explosion, which is simple and easy to apply.

9. The analysis of both a large number of accidents and of the mechanical effects (overpressure, ejection of fragments) of BLEVEs has proved that in a situation in which fire is affecting a closed vessel which contains a liquid or liquid plus vapor, the explosion can occur at any moment from the beginning of the emergency. Therefore, evacuation should be immediately applied. An evacuation distance of at least 700 m is proposed, although 1,200 m or 1,400 m would be much better concerning the possible fragments damage.

Nomenclature

ΔB Batch availability, J·mol^{-1}

c_{p_V} Specific heat of the vapour, J·mol^{-1}·K^{-1}

$c_{p_{L,Tb}}$ Specific heat of the liquid at atmospheric-pressure boiling point, J·kg^{-1}·K^{-1}

c_v Specific heat capacity of vapor for constant volume, kJ·kg^{-1}·K^{-1}

e Explosion energy considering the expansion of the pre-existing vapour plus the vapour generated in the flashing of the liquid per cubic meter, MJ·m^{-3}

E Explosion energy considering only the expansion of the pre-existing vapour, J

E^* Explosion energy considering the expansion of the pre-existing vapour plus the vapour generated in the flashing of the liquid, J

E_w Part of the explosion energy used to generate the pressure wave, J

f Mass fraction of liquid vaporized in the depressurization, --

h_{L0} Enthalpy of the liquid in the vessel at atmospheric-pressure boiling point, J·kg^{-1}

h_L Enthalpy of the liquid in the vessel at conditions just before the explosion, J·kg^{-1}

$\Delta h_{v,Tb}$ Latent heat of vaporization at atmospheric-pressure boiling point, J·kg^{-1}

ΔH_c Heat of combustion of the fuel, J·kg^{-1}

ΔH_{TNT} TNT heat of explosion, J·kg^{-1}

L Volume of liquid in the vessel just before the explosion, m^3

m_{L0} Mass of liquid at the final state of the isentropic process, kg

m_L Mass of liquid in the vessel at conditions just before explosion, kg

m_T Total mass of the vessel content, kg

m_{TNT} Equivalent mass of TNT, kg

m_V Mass of vapour in the vessel at conditions just before explosion, kg

m_{V0} Mass of vapour at the final state of the isentropic process, kg

P Pressure in the vessel just before explosion, Pa

P_c Critical pressure, Pa

P_0 Atmospheric pressure, Pa

P_{rup} Failure pressure, Pa

P_s Overpressure at a given distance, Pa

r_0 Distance between the centre of the explosion or the centre of the fireball and the point at which the overpressure or the radiation has to be estimated, m

R Ideal gas constant, 8.3145 $J \cdot mol^{-1} \cdot K^{-1}$

$\bar{R}$ Scaled distance, $m \cdot kg^{-3}$

R_s Sachs Scaled distance, --

S_L Specific entropy of the liquid at conditions just before explosion, $J \cdot kg^{-1} \cdot K^{-1}$

S_{L0} Specific entropy of the liquid at the final state of the adiabatic process, $J \cdot kg^{-1} \cdot K^{-1}$

S_V Specific entropy of the vapour at conditions just before explosion, $J \cdot kg^{-1} \cdot K^{-1}$

S_{V0} Specific entropy of the vapour at the final state of the adiabatic process, $J \cdot kg^{-1} \cdot K^{-1}$

SE Superheating energy of liquid, $kJ \cdot kg^{-1}$ or $MJ \cdot m^{-3}$

T Temperature of the vapour in the vessel just before the explosion, K

T_b Atmospheric-pressure boiling point, K

T_c Critical temperature, K

T_0 Ambient temperature, K

T_{p_0} Temperature at atmospheric pressure, K

T_{sl} Superheat limit temperature, K

T_{sl-E} Superheat limit temperature from energy balance, K

u_L Specific internal energy of the liquid at conditions just before explosion, $J \cdot kg^{-1}$

u_{L0} Specific internal energy of the liquid at the final state of the adiabatic process, $J \cdot kg^{-1}$

u_V Specific internal energy of the vapour at conditions just before explosion, $J \cdot kg^{-1}$

u_{V0} Specific internal energy of the vapour at the final state of the adiabatic process, $J \cdot kg^{-1}$

U Overall internal energy of the vessel at conditions just before the explosion, J

ΔU Overall variation of the internal energy of the vessel content, J

v_{V0} Specific volume of vapour at the final state of the adiabatic process, $m^3 \cdot kg^{-1}$

v_{L0} Specific volume of liquid at the final state of the adiabatic process, $m^3 \cdot kg^{-1}$

V Volume of vapour in the vessel just before the explosion, m^3

V_f Volume of vapour generated in the flashing of the liquid, m^3

V_T Total vessel volume, m^3

V^* Total volume of vapour contributing to the explosion at conditions just before the explosion, m^3

ΔV Volume variation of the total content of the vessel when going from the explosion state to atmospheric pressure conditions, m^3

W Expansion work, $J \cdot mol^{-1}$

x Vapour fraction (with respect to the total mass) at the final state of the adiabatic irreversible process

x_V Fraction of the vapour mass at explosion state that does not condense when going to the final state of the isentropic process

x_L Fraction of the liquid mass at explosion state that flashes to vapour when going to the final state of the isentropic process

y_i i^{th} value of the variable to be predicted

$\hat{y}_i$ the predicted value of y_i

$\bar{y}_i$ the mean value of the response variable

Greek Letters

β Fraction of the explosion energy converted into blast wave, --

γ Ratio of constant pressure to constant volume specific heats of the gas in the vessel, --

ρ_V Density of the saturated vapour at conditions just before explosion, $kg \cdot m^{-3}$

ρ_L Density of the saturated liquid at conditions just before explosion, $kg \cdot m^{-3}$

References

Abbasi, T., Abbasi, S. A. (2007a). Accidental risk of superheated liquids and a framework for predicting the superheat limit. *Journal of Loss Prevention in the Process Industries, 20*(2), 165-181. doi: dx.doi.org/10.1016/j.jlp.2005.11.002

Abbasi, T., Abbasi, S. A. (2007b). The boiling liquid expanding vapour explosion (BLEVE): Mechanism, consequence assessment, management. *Journal of Hazardous Materials, 141*(3), 489-519. doi: dx.doi.org/10.1016/j.jhazmat.2006.09.056

Abbasi, T., Pasman, H. J., Abbasi, S. A. (2010). A scheme for the classification of explosions in the chemical process industry. *Journal of Hazardous Materials, 174*(1–3), 270-280. doi: dx.doi.org/10.1016/j.jhazmat.2009.09.047

Abdolhamidzadeh, B., Abbasi, T., Rashtchian, D., Abbasi, S. A. (2010). A new method for assessing domino effect in chemical process industry. *Journal of Hazardous Materials, 182*(1–3), 416-426. doi: dx.doi.org/10.1016/j.jhazmat.2010.06.049

Abdolhamidzadeh, B., Abbasi, T., Rashtchian, D., Abbasi, S. A. (2011). Domino effect in process-industry accidents – An inventory of past events and identification of some patterns. *Journal of Loss Prevention in the Process Industries, 24*(5), 575-593. doi: dx.doi.org/10.1016/j.jlp.2010.06.013

Abdolhamidzadeh, B., Rashtchian, D., Morshedi, M. (2009). *Statistical survey of domino past accidents.* Paper presented at the 8th World Congress of Chemical Engineering, Montreal.

ARIA. (2012). Analysis, Research and Information on Accidents. Retrieved 10/04/2013, from www.aria.developpement-durable.gouv.fr

Badri, N., Rad, A., Kareshki, H., Abdolhamidzadeh, B., Parvizsedghy, R., Rashtchian, D. (2013). A risk-based decision making approach to determine fireproofing requirements against jet fires. *Journal of Loss Prevention in the Process Industries, 26*(4), 771-781. doi: dx.doi.org/10.1016/j.jlp.2013.02.003

Bagster, D. F., Pitblado, R. M. (1991). Estimation of domino incident frequencies - an approach. *Process Safety and Environmental Protection: Transactions of the Institution of Chemical Engineers, Part B, 69*(4), 195-199.

Bernatik, A., Senovsky, P., Pitt, M. (2011). LNG as a potential alternative fuel – Safety and security of storage facilities. *Journal of Loss Prevention in the Process Industries, 24*(1), 19-24. doi: dx.doi.org/10.1016/j.jlp.2010.08.003

Berwanger, P. C., Kreder, R. A., Lee, W.-S. (2000). Analysis identifies deficiencies in existing pressure relief systems. *Process Safety Progress, 19*(3), 166-172. doi: 10.1002/prs.680190308

Birk, A. M. (1996). Hazards from propane BLEVEs: An update and proposal for emergency responders. *Journal of Loss Prevention in the Process Industries, 9*(2), 173-181. doi: dx.doi.org/10.1016/0950-4230(95)00046-1

Birk, A. M., Cunningham, M. H. (1996). Liquid temperature stratification and its effect on BLEVEs and their hazards. *Journal of Hazardous Materials, 48*(1–3), 219-237. doi: dx.doi.org/10.1016/0304-3894(95)00157-3

Birk, A. M., Davison, C., Cunningham , M. (2007). Blast overpressures from medium scale BLEVE tests. *Journal of Loss Prevention in the Process Industries, 20*(3), 194-206. doi: dx.doi.org/10.1016/j.jlp.2007.03.001

Birk , A. M., Ye , Z., Maillette , J., Cunningham , M. (1993). *Hot and cold bleves: Observation and discussion of two different kinds of bleves*. Paper presented at the AiChE Heat Transfer Conference,AiChE Symposium Series.

Birk, A. M., VanderSteen, J. D. J. (2006). On the transition from non-BLEVE to BLEVE failure for a 1.8 m3 propane tank. *Journal of pressure vessel technology, 128*(4), 648-655.

Birk, A. M. (2014). Cost‐Effective Application of Thermal Protection on LPG Road Transport Tanks for Risk Reduction Due to Hot BLEVE Incidents. Risk analysis, 34(6), 1139-1148.

Bradley, I. (2012). SEVERE JET FIRES AND VAPOR EXPLOSIONS: Treatment options and the limitations of the existing guidance are discussed. *Hydrocarbon processing, 91*(5).

Brode, H. L. (1959). Blast Wave from a Spherical Charge. *Physics of Fluids (1958-1988), 2*(2), 217-229. doi: doi:dx.doi.org/10.1063/1.1705911.

Bubbico, R., Marchini, M. (2008). Assessment of an explosive LPG release accident: A case study. *Journal of Hazardous Materials, 155*(3), 558-565. doi: dx.doi.org/10.1016/j.jhazmat.2007.11.097.

Casal, J. (2008). *Evaluation of the Effects and Consequences of Major Accidents in Industrial Plants* (1st ed): Elsevier Science, Amsterdam.

Casal, J. (2013). *BLEVE: Blast and Projectiles*. Paper presented at the "Source term characterization of the consequences of storage tank aggregations". Von Karman Institute. Belgium.

Casal, J., Salla, J. M. (2006). Using liquid superheating energy for a quick estimation of overpressure in BLEVEs and similar explosions. *Journal of Hazardous Materials, 137*(3), 1321-1327. doi: dx.doi.org/10.1016/j.jhazmat.2006.05.001.

CCPS. (1994). Guidelines for evaluating the characteristics of vapour cloud, explosions, flash fires and BLEVEs. New York: CCPS-AIChE.

CCPS. (2010). *Guidelines for Vapor Cloud Explosion, Pressure Vessel Burst, BLEVE, and Flash Fire Hazards, 2nd Edition (August 2010)*: Wiley Subscription Services, Inc., A Wiley Company, New York.

Convention concerning International Carriage by Rail (COTIF). (2015). from www.otif.org/fileadmin/user_upload/otif_verlinkte_files/07_veroeff/99_geschuetzt/RID_2015_e/RID%202015%20E.pdf

Cozzani, V., Gubinelli, G., Salzano, E. (2006). Escalation thresholds in the assessment of domino accidental events. *Journal of Hazardous Materials, 129*(1–3), 1-21. doi: dx.doi.org/10.1016/j.jhazmat.2005.08.012.

Crowl, D. A. (1991). Using thermodynamic availability to determine the energy of explosion. *Plant/Operations Progress, 10*(3), 136-142. doi: 10.1002/prsb.720100306.

Crowl, D. A. (1992). Using thermodynamic availability to determine the energy of explosion for compressed gases. *Plant/Operations Progress, 11*(2), 47-49. doi: 10.1002/prsb.720110206.

Crowl, D. A. (2010). Understanding explosions (Vol. 16), John Wiley and Sons, New York.

CSB. (2012). U.S. Chemical Safety Board. Retrieved 10/04/2013, from www.csb.gov

Curve Fitting Toolbox User's Guide-MathWorks. (2015). Retrieved 17.08.2015, from www.mathworks.com/help/pdf_doc/curvefit/curvefit.pdf.

Darbra, R. M., Palacios, A., Casal, J. (2010). Domino effect in chemical accidents: Main features and accident sequences. *Journal of Hazardous Materials, 183*(1–3), 565-573. doi: dx.doi.org/10.1016/j.jhazmat.2010.07.061.

Delvosalle, C. (1998). A methodology for the identification and evaluation of domino effects. *Rep. CRC/MT/003, Belgian Ministry of Employment and Labour, Bruxelles (B).*

Demichela, M., Piccinini, N., Poggio, A. (2004). Analysis of an LPG Accidental Release. *Process Safety and Environmental Protection, 82*(2), 128-131. doi: dx.doi.org/10.1205/095758204322972762.

Directive, C. (2012). 18/EU of the European parliament and of the Council of 4th July 2012 on the control of major-accident hazards involving dangerous substances, amending and subsequently repealing Council Directive 96/82: EC.

Electronic Code of Federal Regulations. (2016). from www.ecfr.gov/cgi-bin/text-idx?SID=3473559888abbc126f0a361b82ffb676&mc=true&tpl=/ecfrbrowse/Title49/49CIsubchapC.tpl

European Agreement concerning the International Carriage of Dangerous Goods by Road.(2015).from www.unece.org/trans/danger/publi/adr/adr2015/15contentse.html

FACTS. (2010). Failure and ACidents Technical information System (FACTS). Retrieved 10/04/2013, from www.factsonline.nl.

Foresee, F. D., Hagan, M. T. (1997). Gauss-Newton approximation to Bayesian learning. Paper presented at the International Conference on Neural Networks, 1997.

Gómez-Mares, M., Zárate, L., Casal, J. (2008). Jet fires and the domino effect. *Fire Safety Journal, 43*(8), 583-588. doi: dx.doi.org/10.1016/j.firesaf.2008.01.002.

Gubinelli, G., Cozzani, V. (2009). Assessment of missile hazards: Evaluation of the fragment number and drag factors. Journal of hazardous materials, *161*(1), 439-449.

Hemmatian, B., Planas, E., Casal, J. (2016). On BLEVE definition, the significance of superheat limit temperature (T_{sl}) and LNG BLEVE's. *Journal of Loss Prevention in the Process Industries, 40,* 81.

Holden, P. L., Reeves, A. B. (1985). Fragment hazards from failures of pressurized liquefied gas vessels. In *IchemE symposium series* (Vol. 93, pp. 205-220).

Johnson, A., Cowley, L. (1992). *Oil and gas fires characteristics and impact*. Health Safety Executive London.

Johnson , D. M., Pritchard , J. M., Wickens , M. J. (1990). Large catastrophic release of flammable liquids. UK.

Kourniotis, S. P., Kiranoudis, C. T., Markatos, N. C. (2000). Statistical analysis of domino chemical accidents. *Journal of Hazardous Materials*, *71*(1–3), 239-252. doi: dx.doi.org/10.1016/S0304-3894(99)00081-3.

Kreder, R., Berwanger, P. (1995). Making safety data safe. *Chemical Engineering, 102*(4), 131-131.

Laboureur, D., Heymes, F., Lapebie, E., Buchlin, J., Rambaud, P. (2014). BLEVE overpressure: multiscale comparison of blast wave modeling. *Process Safety Progress*, *33*(3), 274-284.

Laboureur, D., Birk, A. M., Buchlin, J. M., Rambaud, P., Aprin, L., Heymes, F., Osmont, A. (2015). A closer look at BLEVE overpressure. *Process Safety and Environmental Protection*, *95*, 159-171.

Lacoursière, J.-P., Dastous, P.-A., Lacoursière, S. (2015). Lac-Mégantic accident: What we learned. Process Safety Progress, 34(1), 2-15. doi: 10.1002/prs.11737.

Landucci, G., Cozzani, V., Birk, A. M. (2013). Heat Radiation Effects in *Domino Effects in the Process Industries: Modelling, Prevention and Managing,* 70. . Elsevier Science, Amsterdam.

Landucci, G., Gubinelli, G., Antonioni, G., Cozzani, V. (2009). The assessment of the damage probability of storage tanks in domino events triggered by fire. *Accident Analysis & Prevention,* *41*(6), 1206-1215. doi: dx.doi.org/10.1016/j.aap.2008.05.006

Lees, F. P. (1996). Loss prevention in the process industries: hazard identification, assessment and control *Loss prevention in the process industries: hazard identification, assessment and control*: Butterworth-Heinemann. New York.

Leffler, W. L. (2014). Natural Gas Liquids: A Nontechnical Guide. PennWell Books.

Lemmon, E., McLinden, M., Huber, M. (2007). REFPROP: Reference fluid thermodynamic and transport properties. *NIST standard reference database, 23*(8.0).

Leslie, I. R. M., Birk, A. M. (1991). State of the art review of pressure liquefied gas container failure modes and associated projectile hazards. *Journal of Hazardous Materials, 28*(3), 329-365. doi: dx.doi.org/10.1016/0304-3894(91)87083-E.

Mannan, S. (2014). *Lees' Process Safety Essentials*. Oxford: Butterworth-Heinemann.

Manu, C. C., Birk, A. M., Kim, I. Y. (2009). Stress rupture predictions of pressure vessels exposed to fully engulfing and local impingement accidental fire heat loads. *Engineering Failure Analysis, 16*(4), 1141-1152. doi: dx.doi.org/10.1016/j.engfailanal.2008.07.018.

MARS. (2012). Accident Reporting System (MARS). Retrieved 10/04/2013, from emars.jrc.ec.europa.eu

Meyer, T., Reniers, G. (2013). *Engineering risk management*: Walter de Gruyter. Berlin/Boston.

MHIDAS. (2007). Major Hazard Incident Data Service (MHIDAS).

Molag, M.,Kruithof,A. (2006). BLEVE prevention of a LPG tank vehicle or a LPG wagon,TNO Report R2005/364,Apeldoorn (NL).

Moodie, K., Cowley, L. T., Denny, R. B., Small, L. M., Williams, I. (1988). Fire engulfment tests on a 5 tonne LPG tank. *Journal of Hazardous Materials, 20*(0), 55-71. doi: dx.doi.org/10.1016/0304-3894(88)87006-7

Moorhouse, J., Pritchard, M. J. (1982). Thermal radiation hazards from large pool fires and fireballs-a literature review. *IChemE Sym Ser: Assessment of Major Hazards*, 397-428.

Muñoz, M., Arnaldos, J., Casal, J., Planas, E. (2004). Analysis of the geometric and radiative characteristics of hydrocarbon pool fires. *Combustion and Flame, 139*(3), 263-277. doi: dx.doi.org/10.1016/j.combustflame.2004.09.001.

Napier, D. H., Roopchand, D. R. (1986). An approach to hazard analysis of LNG spills. *Journal of Occupational Accidents, 7*(4), 251-272. doi: dx.doi.org/10.1016/0376-6349(86)90017-9

NFPA. (2012). National Fire Protection Association (NFPA). Retrieved 10/04/2013, from www.nfpa.org.

Nguyen, T. T. (1998). Earth-return path impedances of underground cables. II. Evaluations using neural networks. Generation, Transmission and Distribution, IEE Proceedings-, 145(6), 627-633. doi: dx.doi.org/10.1049/ip-gtd:19982354.

Niemitz, K. (2010). *Process safety culture or what are the performance determining steps.* Paper presented at the Workshop on safety performance indicators, Ispra.

Nizner, G. A., Eyre, J. A. (1983). Radiation From Liquefied Gas Fires On Water. *Combustion Science and Technology, 35*(1-4), 33-57. doi: dx.doi.org/10.1080/00102208308923702.

NTSB. (2013). U. S. National Transport Safety Board. Retrieved 10/04/2013, from www.ntsb.gov.

Ogle, R. A., Ramirez, J. C., Smyth, S. A. (2012). Calculating the explosion energy of a boiling liquid expanding vapor explosion using exergy analysis. *Process Safety Progress, 31*(1), 51-54. doi: dx.doi.org/10.1002/prs.10465.

Palacios, A., Muñoz, M., Darbra, R. M., Casal, J. (2012). Thermal radiation from vertical jet fires. *Fire Safety Journal, 51*(0), 93-101. doi: dx.doi.org/10.1016/j.firesaf.2012.03.006.

Paltrinieri, N., Landucci, G., Molag, M., Bonvicini, S., Spadoni, G., Cozzani, V. (2009). Risk reduction in road and rail LPG transportation by passive fire protection. Journal of hazardous materials, 167(1), 332-344.

Piñeiro, G., Perelman, S., Guerschman, J. P., Paruelo, J. M. (2008). How to evaluate models: Observed vs. predicted or predicted vs. observed? *Ecological Modelling, 216*(3–4), 316-322. doi: dx.doi.org/10.1016/j.ecolmodel.2008.05.006.

Pitblado, R. M., Woodward, J. L. (2011). Highlights of LNG risk technology. *Journal of Loss Prevention in the Process Industries, 24*(6), 827-836. doi: dx.doi.org/10.1016/j.jlp.2011.06.009.

Planas Cuchi, E., Casal, J., Lancia, A., Bordignon, L. (1996). Protection of equipment engulfed in a pool fire. *Journal of Loss Prevention in the Process Industries, 9*(3), 231-240. doi: dx.doi.org/10.1016/0950-4230(96)00014-9.

Planas Cuchi , E., Gasulla , N., Ventosa , A., Casal , J. (2004a). Explosion of a road tanker containing liquified natural gas. *Journal of Loss Prevention in the Process Industries, 17*(4), 315-321. doi: dx.doi.org/10.1016/j.jlp.2004.05.005.

Planas Cuchi , E., Salla , J. M., Casal , J. (2004b). Calculating overpressure from BLEVE explosions. *Journal of Loss Prevention in the Process Industries, 17*(6), 431-436. doi: dx.doi.org/10.1016/j.jlp.2004.08.002.

Planas, E., Pastor, E., Casal, J., Bonilla, J. M. (2015). Analysis of the boiling liquid expanding vapor explosion (BLEVE) of a liquefied natural gas road tanker: The Zarzalico accident. *Journal of Loss Prevention in the Process Industries, 34*, 127-138. doi: dx.doi.org/10.1016/j.jlp.2015.01.026.

Prugh, R. W. (1991). Quantitative Evaluation of "Bleve" Hazards. *Journal of Fire Protection Engineering, 3*(1), 9-24. doi: dx.doi.org/10.1177/104239159100300102.

Reid, R. C. (1979). Possible mechanism for pressurized liquid tank explosions or BLEVEs. *Science*, 1263-1265.

Reid, R. C. (1983). Rapid phase transitions from liquid to vapor. Advances in Chemical Engineering, 12, 105-208.

Reniers, G. (2010). An external domino effects investment approach to improve cross-plant safety within chemical clusters. *Journal of Hazardous Materials*, *177*(1–3), 167-174. doi: dx.doi.org/10.1016/j.jhazmat.2009.12.013.

Reniers, G., Cozzani, V. (2013). *Domino Effects in the Process Industries: Modelling, Prevention and Managing.* Newnes. Elsevier Science, Amsterdam.

Roberts, T. A., Buckland, I., Shirvill, L. C., Lowesmith, B. J., Salater, P. (2004). Design and Protection of Pressure Systems to Withstand Severe Fires. *Process Safety and Environmental Protection, 82*(2), 89-96. doi: dx.doi.org/10.1205/095758204322972735.

Ronza, A., Félez, S., Darbra, R. M., Carol, S., Vílchez, J. A., Casal, J. (2003). Predicting the frequency of accidents in port areas by developing event trees from historical analysis. *Journal of Loss Prevention in the Process Industries, 16*(6), 551-560. doi: dx.doi.org/10.1016/j.jlp.2003.08.010.

Salla, J. M., Demichela, M., Casal, J. (2006). BLEVE: A new approach to the superheat limit temperature. *Journal of Loss Prevention in the Process Industries, 19*(6), 690-700. doi: dx.doi.org/10.1016/j.jlp.2006.04.004.

Schneider, M. E., Kent, L. A. (1989). Measurements of gas velocities and temperatures in a large open pool fire. *Fire Technology, 25*(1), 51-80. doi: dx.doi.org/10.1007/BF01039723.

Siddique, N., Adeli, H. (2013). Computational intelligence: synergies of fuzzy logic, neural networks and evolutionary computing: John Wiley & Sons.

Sigales, B. T. (1990). A. Modelado de estallidos de recipientes. Modelado fenomenológico de estallidos de recipientes conteniendo líquidos a presión, debidas a calentamiento exterior por llamas. Ingeniería Química, 465-473.

Smith, J., Van Ness, H., Abbott, M. (1996). *Introduction to Chemical Engineering Thermodynamics*: McGraw Hill.

Standard, A. P. I. (2007). 521. *Pressure-relieving and Depressuring Systems*.

Tauseef, S. M., Abbasi, T., Abbasi, S. A. (2010). Risks of Fire and Explosion Associated With the Increasing Use of Liquefied Petroleum Gas. *Journal of Failure Analysis and Prevention*, *10*(4), 322-333. doi: dx.doi.org/10.1007/s11668-010-9360-9.

Townsend, W., Anderson, C., Zook, J., Cowgill, G. (1974). Comparison of thermally coated and uninsulated rail tank cars filled with LPG subjected to a fire environment.

UN Recommendations on the Transport of Dangerous Goods - Model Regulations Nature, Purpose and Significance of the Recommendations (2011). www.unece.org/?id=3598

van den Berg, A. C., van der Voort, M. M., Weerheijm, J., Versloot, N. H. A. (2004). Expansion-controlled evaporation: a safe approach to BLEVE blast. *Journal of Loss Prevention in the Process Industries*, *17*(6), 397-405. doi: dx.doi.org/10.1016/j.jlp.2004.07.002.

Venart , J. E. S. (2005). Letter to the editor. *Process Safety Progress, 24*(4), 226-226. doi: dx.doi.org/10.1002/prs.10104.

Venart, J. E. S., Rutledge, G. A., Sumathipala, K., Sollows, K. (1993). To BLEVE or Not To BLEVE: Anatomy of a Boiling Liquid Expanding Vapor Explosion. *Process Safety Progress*, *12*, 67-70.

Vílchez, J. A., Sevilla, S., Montiel, H., Casal, J. (1995). Historical analysis of accidents in chemical plants and in the transportation of hazardous materials. *Journal of Loss Prevention in the Process Industries, 8*(2), 87-96. doi: dx.doi.org/10.1016/0950-4230(95)00006-M.

Walls, W. L. (1978). What is a BLEVE? *Fire, 31*, 46-47.

Walls, W. L. (1979). The BLEVE-part 1. *Fire Command., 17*, 35-37.

Yadav, J. S., Yadav, M., Jain, A. (2014). Artificial neural network. International Journal Of Scientific Research And Education, 1(06).

Appendix 1. MATLAB Artificial Neural Network functions for propane and butane

The ANN function for propane is:

```
function [Y,Xf,Af] = propanepredictor3(X,~,~)
%MYNEURALNETWORKFUNCTION neural network simulation function.
%
% Generated by Neural Network Toolbox function genFunction, 20-Jul-
2015 10:17:45.
%
% [Y] = myNeuralNetworkFunction(X,~,~) takes these arguments:
%
%   X = 1xTS cell, 1 inputs over TS timsteps
%   Each X{1,ts} = 2xQ matrix, input #1 at timestep ts.
%
% and returns:
%   Y = 1xTS cell of 1 outputs over TS timesteps.
%   Each Y{1,ts} = 1xQ matrix, output #1 at timestep ts.
%
% where Q is number of samples (or series) and TS is the number of
timesteps.

%#ok<*RPMT0>

  % ===== NEURAL NETWORK CONSTANTS =====

  % Input 1
  x1_step1_xoffset = [300;0.007];
  x1_step1_gain = [0.0307692307692308;2.03458799593082];
  x1_step1_ymin = -1;

  % Layer 1
  b1 = [-1.4006238480645015;-1.3795979575436832;-
0.14059650543583493;0.2631971132089671;0.038261783010536697];
  IW1_1 = [-1.2335376598426022 -0.28615137715319239;1.7511886300735793
0.39277273694863146;-0.85599255081018899
0.23769364234551904;1.2559822674312529 -
0.34203990018871339;1.1617411647737819 0.2994760246919812];
```

```
  % Layer 2
  b2 = -0.1202331016783611;
  LW2_1 = [-0.86414413858158401 0.54741455066742639 3.1600126032151543
1.1380493679600932 1.1103236663066267];

  % Output 1
  y1_step1_ymin = -1;
  y1_step1_gain = 0.186586503576241;
  y1_step1_xoffset = 0.95;

  % ===== SIMULATION ========

  % Format Input Arguments
  isCellX = iscell(X);
  if ~isCellX, X = {X}; end;

  % Dimensions
  TS = size(X,2); % timesteps
  if ~isempty(X)
    Q = size(X{1},2); % samples/series
  else
    Q = 0;
  end

  % Allocate Outputs
  Y = cell(1,TS);

  % Time loop
  for ts=1:TS

    % Input 1
    Xp1 =
mapminmax_apply(X{1,ts},x1_step1_gain,x1_step1_xoffset,x1_step1_ymin);

    % Layer 1
    a1 = tansig_apply(repmat(b1,1,Q) + IW1_1*Xp1);

    % Layer 2
    a2 = repmat(b2,1,Q) + LW2_1*a1;

    % Output 1
    Y{1,ts} =
mapminmax_reverse(a2,y1_step1_gain,y1_step1_xoffset,y1_step1_ymin);
```

```
  end

  % Final Delay States
  Xf = cell(1,0);
  Af = cell(2,0);

  % Format Output Arguments
  if ~isCellX, Y = cell2mat(Y); end
end

% ===== MODULE FUNCTIONS ========

% Map Minimum and Maximum Input Processing Function
function y =
mapminmax_apply(x,settings_gain,settings_xoffset,settings_ymin)
  y = bsxfun(@minus,x,settings_xoffset);
  y = bsxfun(@times,y,settings_gain);
  y = bsxfun(@plus,y,settings_ymin);
end

% Sigmoid Symmetric Transfer Function
function a = tansig_apply(n)
  a = 2 ./ (1 + exp(-2*n)) - 1;
end

% Map Minimum and Maximum Output Reverse-Processing Function
function x =
mapminmax_reverse(y,settings_gain,settings_xoffset,settings_ymin)
  x = bsxfun(@minus,y,settings_ymin);
  x = bsxfun(@rdivide,x,settings_gain);
  x = bsxfun(@plus,x,settings_xoffset);
end
```

The ANN function for butane is:

```
function [Y,Xf,Af] = butanepredictor2(X,~,~)
%MYNEURALNETWORKFUNCTION neural network simulation function.
%
% Generated by Neural Network Toolbox function genFunction, 20-Jul-
2015 10:53:18.
%
% [Y] = myNeuralNetworkFunction(X,~,~) takes these arguments:
%
```

```
%   X = 1xTS cell, 1 inputs over TS timsteps
%   Each X{1,ts} = 2xQ matrix, input #1 at timestep ts.
%
% and returns:
%   Y = 1xTS cell of 1 outputs over TS timesteps.
%   Each Y{1,ts} = 1xQ matrix, output #1 at timestep ts.
%
% where Q is number of samples (or series) and TS is the number of
timesteps.

%#ok<*RPMT0>

  % ===== NEURAL NETWORK CONSTANTS =====

  % Input 1
  x1_step1_xoffset = [283;0.000615966428987831];
  x1_step1_gain = [0.0166666666666667;2.00295823639263];
  x1_step1_ymin = -1;

  % Layer 1
  b1 = [-0.53771579361104227;-
0.59598487453006654;0.66879204443674933;-2.2071537928682843];
  IW1_1 = [-1.3756657836491561 -
0.41380823571371089;0.79130818364785172 -0.1637366261518885;-
0.82117374051141334 -0.19319323140676317;-1.5520501008245915
0.45218140851592037];

  % Layer 2
  b2 = -0.31980020721414332;
  LW2_1 = [-0.26677419106558381 -1.8163939923560939 -
2.4486523332602506 -0.36715175364696184];

  % Output 1
  y1_step1_ymin = -1;
  y1_step1_gain = 0.151254042096522;
  y1_step1_xoffset = 0.0571057339899198;

  % ===== SIMULATION ========

  % Format Input Arguments
  isCellX = iscell(X);
  if ~isCellX, X = {X}; end;
```

```
  % Dimensions
  TS = size(X,2); % timesteps
  if ~isempty(X)
    Q = size(X{1},2); % samples/series
  else
    Q = 0;
  end

  % Allocate Outputs
  Y = cell(1,TS);

  % Time loop
  for ts=1:TS

    % Input 1
    Xp1 =
mapminmax_apply(X{1,ts},x1_step1_gain,x1_step1_xoffset,x1_step1_ymin);

    % Layer 1
    a1 = tansig_apply(repmat(b1,1,Q) + IW1_1*Xp1);

    % Layer 2
    a2 = repmat(b2,1,Q) + LW2_1*a1;

    % Output 1
    Y{1,ts} =
mapminmax_reverse(a2,y1_step1_gain,y1_step1_xoffset,y1_step1_ymin);
  end

  % Final Delay States
  Xf = cell(1,0);
  Af = cell(2,0);

  % Format Output Arguments
  if ~isCellX, Y = cell2mat(Y); end
end

% ===== MODULE FUNCTIONS ========

% Map Minimum and Maximum Input Processing Function
function y =
mapminmax_apply(x,settings_gain,settings_xoffset,settings_ymin)
  y = bsxfun(@minus,x,settings_xoffset);
```

```
  y = bsxfun(@times,y,settings_gain);
  y = bsxfun(@plus,y,settings_ymin);
end

% Sigmoid Symmetric Transfer Function
function a = tansig_apply(n)
  a = 2 ./ (1 + exp(-2*n)) - 1;
end

% Map Minimum and Maximum Output Reverse-Processing Function
function x =
mapminmax_reverse(y,settings_gain,settings_xoffset,settings_ymin)
  x = bsxfun(@minus,y,settings_ymin);
  x = bsxfun(@rdivide,x,settings_gain);
  x = bsxfun(@plus,x,settings_xoffset);
end
```

Appendix 2. Solid flame model

The procedure for calculating thermal radiation ($I, kW\ m^{-2}$) reaching a given target is as follows:

$$I = \tau \cdot F \cdot E_p \tag{A.1}$$

Where,

τ is the atmospheric transmissivity (-)

F is the view factor (-)

E_p is the average emissive power of the flames (kWm^{-2}).

The atmospheric transmissivity can be calculated as:

$$\tau = 1.53 \cdot (P_w \cdot d)^{-0.06} \quad \text{for} \quad P_w \cdot d < 10^4 \text{ N.m}^{-1} \tag{A.2}$$

$$\tau = 2.02 \cdot (P_w \cdot d)^{-0.09} \quad \text{for} \quad 10^4 \leq P_w \cdot d \leq 10^5 \text{ N.m}^{-1} \tag{A.3}$$

$$\tau = 2.85 \cdot (P_w \cdot d)^{-0.12} \quad \text{for} \quad P_w \cdot d > 10^5 \text{ N.m}^{-1} \tag{A.4}$$

Where,

P_w is the partial pressure of water in the atmosphere (N·m^{-2})

d is the distance between the surface of the flame and the target (m)

P_w is estimated as:

$$P_w = P_{wa} \cdot \frac{RH}{100} \tag{A.5}$$

P_{wa} can be estimated by considering the atmospheric condition of $T_a = 289.15\ K$ and $RH = 50\%$:

$$ln\ P_{wa} = 23.18986 - \frac{3816.42}{(T_a - 46.13)} \quad \text{(A.6)}$$

Where P_{wa} is in N·m^{-2}.

An average value of the emissive power is calculated as:

$$E_p = \frac{\eta_{rad} \cdot M \cdot \Delta H_c}{\pi \cdot D^2 \cdot t} \quad \text{(A.7)}$$

Where,

t is the duration of the fireball (s)

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

η_{rad} is the radiant heat fraction (-)

The radiant heat fraction can be calculated as:

$$\eta_{rad} = 0.00325 \cdot P^{0.32} \quad \text{(A.8)}$$

Where P is the pressure in the vessel just before the explosion in N·m^{-2}. The value of radiant heat fraction usually ranges from 0.2 and 0.4; however, its maximum value is limited to 0.4. The view factor, diameter of fireball, the time corresponding to the duration of the fireball, the height to the center of fireball and the distance between the fireball surface and a given target are calculated as follows, respectively:

$$F = \frac{D^2}{4 \cdot \left(\frac{D}{2} + d\right)^2} \quad \text{(A.9)}$$

$$D = 5.8 \cdot M^{1/3} \quad \text{(A.10)}$$

$$t = 0.9 \cdot M^{0.25} \quad \text{(A.11)}$$

$$H = 0.75 \cdot D \quad \text{(A.12)}$$

$$d = \sqrt{x^2 + H^2} - \frac{D}{2} \quad \text{(A.13)}$$

The effects of thermal flux on human beings can be estimated with the Probit equations (Casal, 2008):

First degree burns (FDB):

$$Y = -39.83 + 3.0186 \cdot ln\left(t \cdot I^{4/3}\right) \tag{A.14}$$

Second-degree burns (SDB)

$$Y = -43.14 + 3.0186 \cdot ln\left(t \cdot I^{4/3}\right) \tag{A.15}$$

Lethality (unprotected) (L)

$$Y = -36.38 + 2.56 \cdot ln\left(t \cdot I^{4/3}\right) \tag{A.16}$$

Lethality (protected) (LP):

$$Y = -37.23 + 2.56 \cdot ln\left(t \cdot I^{4/3}\right) \tag{A.17}$$

Where,

I is the radiation intensity in $W \cdot m^{-2}$

t is the exposure time in seconds