UNIVERSITY OF CHEMICAL TECHNOLOGY AND METALLURGY

Department of Chemical Engineering

BACHELOR THESIS

TITLE: “Analysis of risk and LPG accidents”

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1.- Risk analysis

The quicker evolution of industry, especially chemical industry and, therefore, the increasing of the inventories of chemicals to various facilities and transports have caused an increase in the probability of major accidents with significant impact on people, environment and equipment. Some of them, like for example ones that happened in Sao Paulo, Mexico City and Bhopal, all in 1984, involved the death of more than 4000 people.

If we look back and we analyse when more of the accidents happened, we can see a big increasing after the decade of 70's. If we look more carefully, we will see that it increase after Oil crisis in 1973, but we are not going to be so deep.

In the next graphic, we can see the amount of accidents at any decade, according with "Failure and Accidents Technical information System" (FACTS) database, which contains more than 25700 industrial accidents. **[1]**

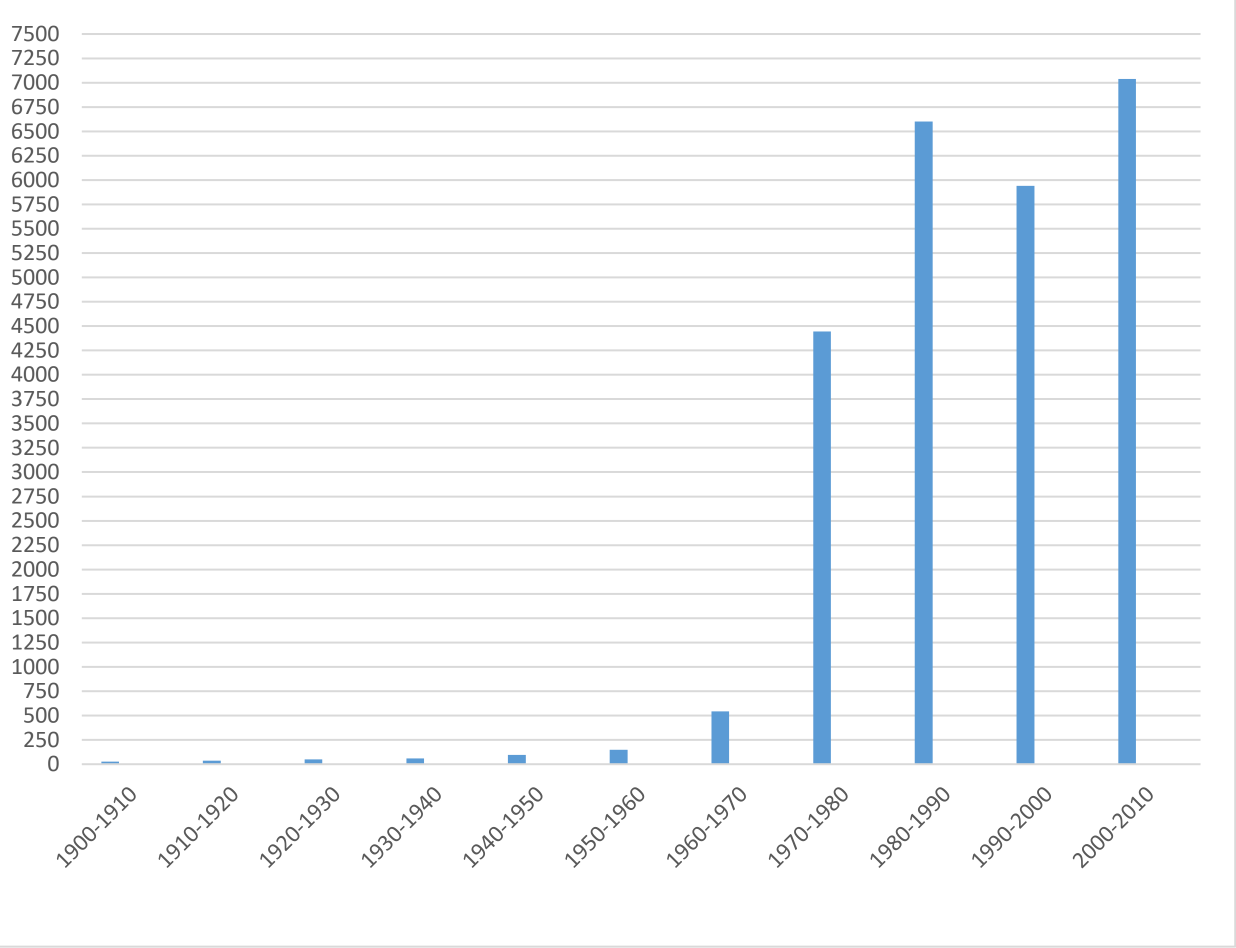


Figure 1.1 Distribution of the accidents in the time

It is appreciated a progressive increase with the time, it becomes increasingly important; approximately 95% of cases correspond to the last 40 years. This has been attributed both to better access to information on accidents and the development of industrial activity in many countries and the consequent increase of the transporting of hazardous products.

To show how to classify the accidents, we will use another database, at this case 6.168 MHIDAS database records from the beginning of the century until July of 1992.

Regarding the type of accident, the statistical treatment can be seen in Table 1.1. The database used classifies accidents into four different types: leak, fire, explosion and gas clouds.

This table it's shown the distribution of the accident in which one of the four types was involved: since in one case can be classified in more than one type, the sum of the percentages is greater than 100. There were leak over than 50% of cases, fire was the most frequent (44%) of other accidents, followed by the explosion (36%) and gas cloud (12%).

	Number of accidents	% of know types
Leak	3022	51.0
Fire	2603	44.0
Explosion	2133	36.0
Gas Cloud	719	12.1

Regarding the activity or facility in which the accident took place, the information is summarized in the next diagram

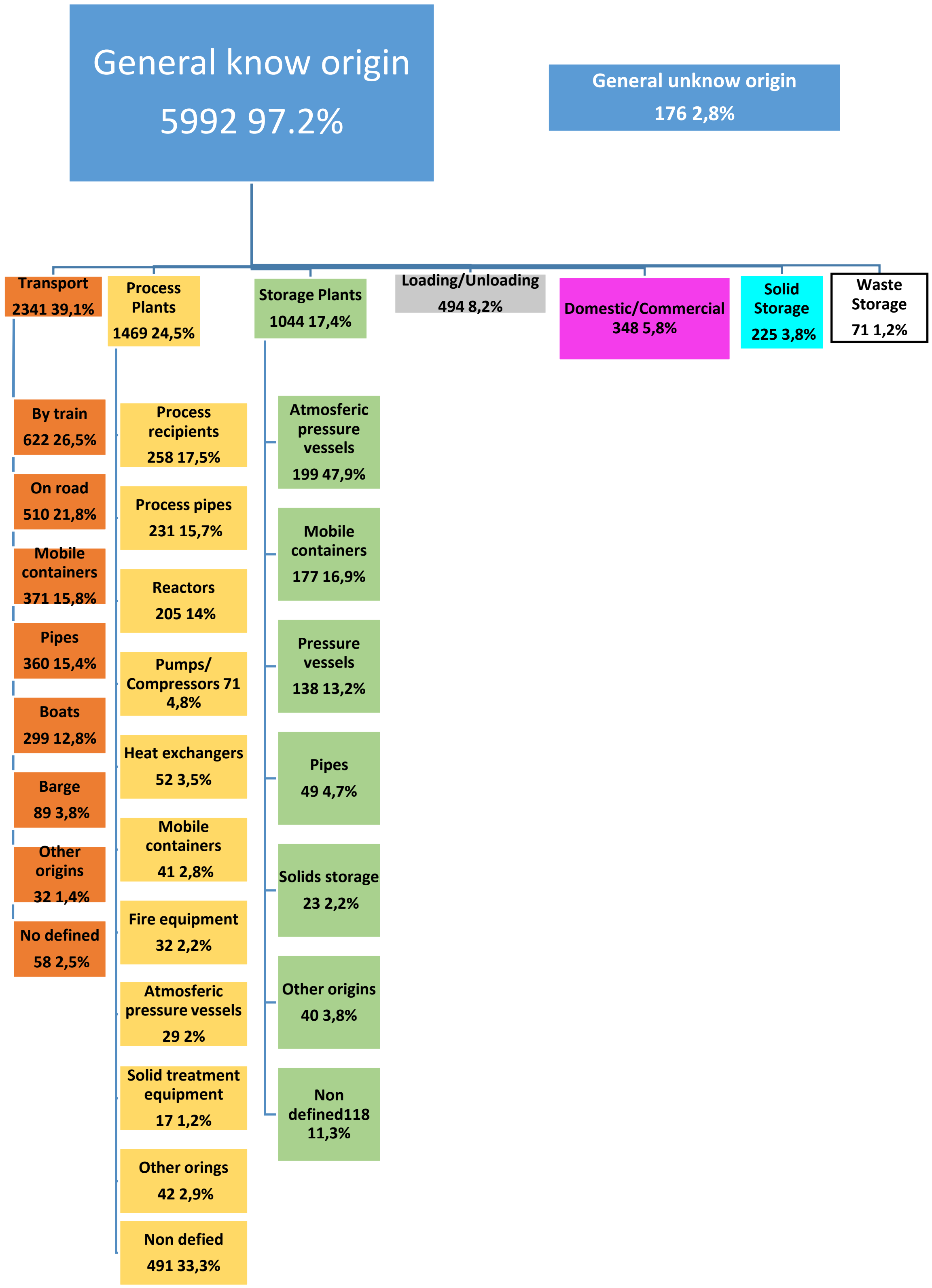


Figure 1.2 Origin of the accidents

The origin was known in 5992 cases (97% of database records used). It can be seen that the most important contribution corresponds to accidents occurred in transport, with 39% of cases, followed by the process plants, with 24.5% storage plants (17.4%) and loading and unloading operations appears with an 8%. These are the four most important contributions, so we will be interesting on it.

If we analyse carefully each contribution, we can see that accidents trasporting by train are higher than road ones. Into the processes that occurs in a plant, the more riskfully are receptacles process, pipes and reactors . Talking about storage about half of them happens at atmospheric pressure tanks, and then mobile containers and pressure vessels, but far away.

Finally, figure .3 shows the number of victims of accidents in each arbitrary category (0 deaths, 1 - 10 deaths, etc.): the highest value, relates to the accident occurred at Bhopal in 1984, agas leak forming a toxic cloud, with over 3.000 deads.

The values in parentheses indicate the percentage of accidents in which this information is known. Only 55% of database's records indicated the number of deaths caused by the accident, the rest don't gave any indication.

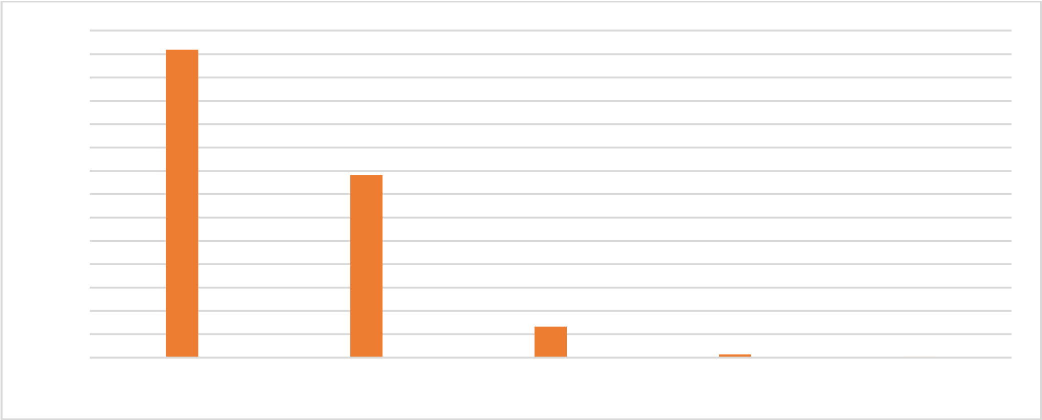


Figure 1.3 Dead / number of accidents

The information showed in Figure 3 signs the need for improved security, the say it with other words, the need to reduce the risk of accidents with people dead. This has led to several urgent changes in the legislation, the most important of all the notifications of SEVESO Directive (82/501 / EEC) on the prevention of major accidents in certain industrial activities applicable in different countries of then European Economic Comisión.

There is no doubt about the greater legislative effort during transport as an increasingly important for the EU countries to face the major risks, and represents a very important one to know more about the methodology and the philosophy of how treate the problem of technological risks. The Seveso Directive contains no a specific price for tolerable risk, it establishes a legal framework to facilitate the administration of risk control caused by industrial installations; considers the use of a range of grouped assessment techniques what is called risk analysis, and reaches even in some cases the application of probabilistic assessment (estimating of the probable frequency of the accident). Overall, it is a very good tool and, if used well, it may represent an important step forward in the work required to control the risk

1.2. Risk: definition and types

Some definitions has been proposed to risk, for example "situation that can lead to a negative unintended consequence of an event", or "becoming probability of a particular potential danger", or even, "unwanted consequences of an activity given in relation to the probability of occurrence".

A rigorous treatment of risk requires a more precise definition to allow its quantification. A definition that meets these requirements and is used by many professionals is the one based on the product of the expected frequency for a given event by the magnitude of the probable consequence

RISK = Frequency x magnitude consequences

We will not make confusion between risk and danger. Danger can be defined as that which can produce an accident or a damage. The risk, otherwise, would be associated to the probability that a danger becomes an accident with some determined consequences.

As there is different variety of risk, they usually be classified at the following categories:

- Risk category A: they are inevitable and accepted, without compensation (for example, to die struck by a lightning)
- Risk category B: avoidable at first, but considered to be inevitable if one wants to fully integrate into the modern society (for example, to die owe to an accident travelling by plane or by car).
- Risk category C: normally avoidable, voluntary and with compensation (for example: to practise a dangerous sport).

From a more specific point of industrial activities, risks can be grouped into other three categories:

- Conventional risks: related with the activity and the existing equipment in any sector (electrocution, falls).
- Specific risks: associated with the use or handling of products that, by their nature, can cause damage (toxic products, radioactive).
- Major risks: related with accidents and exceptional situations. Their consequences can present a particularly seriousness because the rapid expulsion of dangerous products or energy is able to affect significant areas (gas leak, explosions).

From these three types of risk, the first two correspond to the classic treatment of health and safety at work and by their behaviour are generally relatively easy to prevent. Moreover, the special characteristics of the major risks likely become the most fearsome contingency. Acting with sometimes extreme severity these accidents may have an important feature: to overtake the limits of installation and influence the foreign population and the environment.

1.3. Risk measurement parameters

Several parameters have been proposed to quantify and briefly summarize the risk of a given activity. One of the most used is called Fatal Accident Rate, FAR, defined as the number of fatal accidents after $10^8 (hours \cdot person)$ for a particular activity.

This quantity equals approximately the number of hours worked by a group of 1,000 people after a lifetime of work, and includes only accidents with immediate consequences and deaths from disease. In the following table we can see the FAR values for diferent countries.

COUNTRY	FAR
WEST GERMANY	5.0
FRANCE	8.5
GREAT BRITAIN	4.0
USA	5.0

ACTIVITY	FAR
MANUFACTURING INDUSTRY	0.15
CAR INDUSTRY	1.30
WOOD INDUSTRY	3.00
CHEMICAL INDUSTRY	4.00
MECHANIC INDUSTRY	7.00
AGRICULTURE	10.00
MINING	12.00
FISHING INDUSTRY	35.00
BUILDING	64.00

1.4 RISK IDENTIFICATION / ANALYSIS.

Technological disasters management represents the sum of activities taken for technological risk reduction, technological disasters prevention and of the measures developed for emergency response management, in order to protect the population, environment and economy against entropic disasters.

Technological disasters management can be divided into two main parts: Chemical Risks Management and Emergency Situations Management.

Risk management is defined as the sum of all activities and measures developed for risk reduction. Risk management aims at balancing the conflicts emerging at opportunities exploitation, in one way, and losses, accidents and disasters reduction, on the other way.

1.4.1. Structure of the technological risk analysis

Technological risk analysis and assessment can be divided into several major phases. Figure .4 shows the risk assessment procedure and the used methods.

In the field of risk assessment there are differences of opinion regarding the use of qualitative or quantitative risk analysis methods. The qualitative-quantitative factor is the basic property of hazards analyses methods. Most of the analysis methods are developed in order to identify hazards and to determine the risk of that hazard will turn into an accident.

For determining the accident risk of the identified hazard, a methodology for the characterization of probability and magnitude parameters must be used. There were developed both qualitative and quantitative methods, which are successfully used, each methods having its specific advantages and disadvantages.

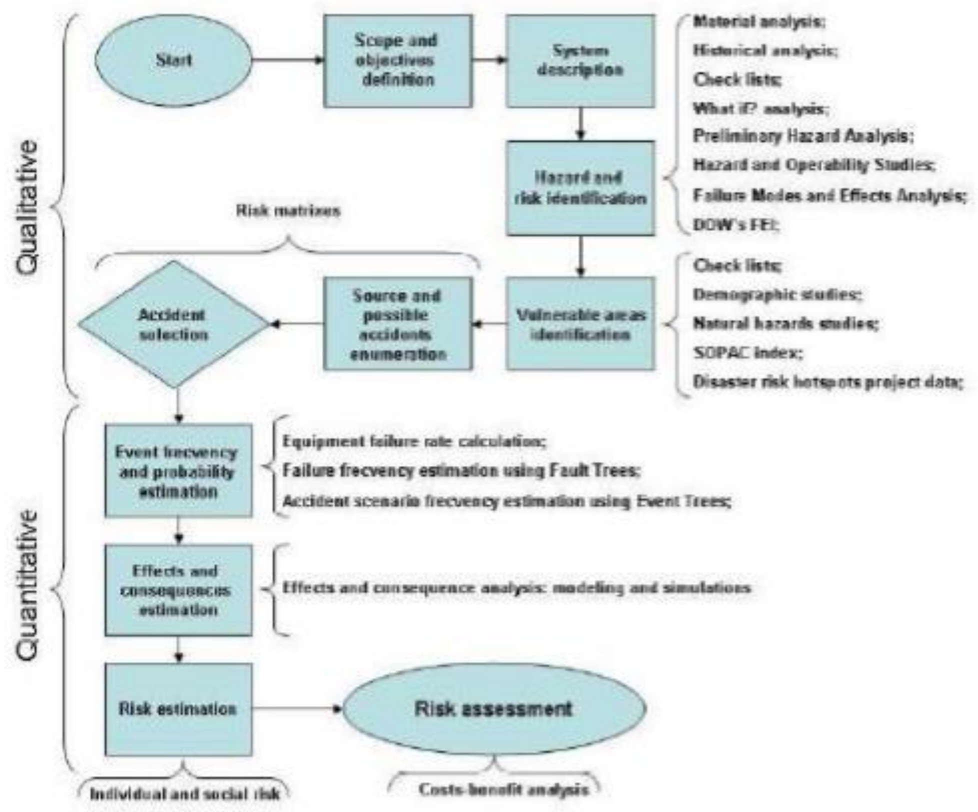


Figure 1.4 Technological risk assessment.

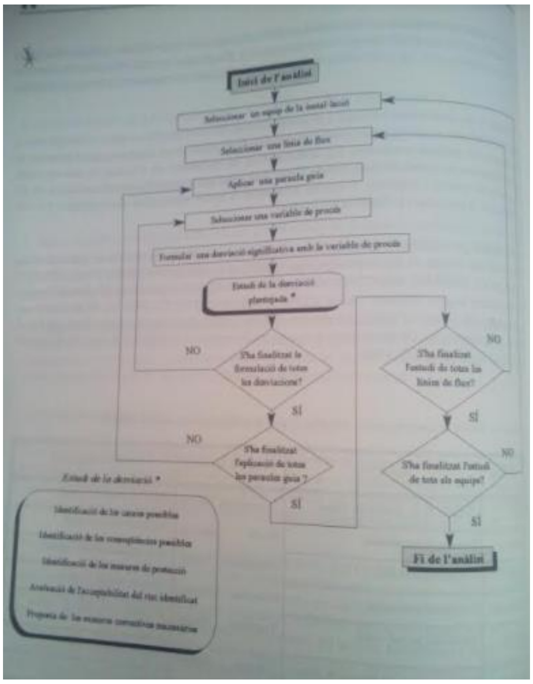
- Qualitative analysis implies the use of qualitative criteria, using different categories for parameters separation, with qualitative definition which establish the scale for each category. Also, qualitative decisions are made, based on the field experience, in order to assign elements into categories. This approach is subjective, but it allows a higher generalization degree, being less restrictive.
- Quantitative analysis includes the use of numerical or quantitative data and provides quantitative results. This approach is more objective and more precise. It must be mentioned that the quantitative results can be highly affected by the precision and validity of the input parameters. Therefore, the quantitative results within the risk analyses should not be taken into consideration as exact numbers, but as estimates, with a variable scale depending on data quality.

*The methods and techniques of technological hazards identification and risk analysis reported within the thesis are listed below

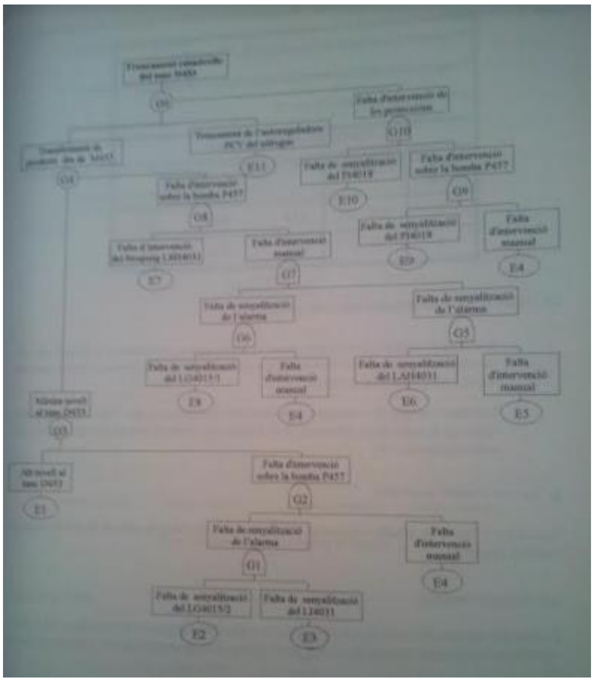
- Qualitative methods of hazards identification and risk assessment:
  - Analysis of hazardous substances properties;
  - Check list method;
  - "What if?" analysis method;
  - "Preliminary Hazard Analysis" (PHA) method;
  - "Failure Mode and Effects Analysis" (FMEA) method;
  - "Hazard and Operability" HAZOP Study method;
  - Risk assessment method using the DOW index;
  - Probability determination through Historical Analysis;

- Quantitative risk assessment methods:
  - Top events frequency assessment. Failure trees;
  - Accidental scenarios frequency assessment. Event trees;
  - Effects and consequences analysis through mathematical modelling and technological accident simulation.

We are not going to entering depth in any of the different methods, but let's put as an example the structures of two of them.



HAZOP Study method



Failure tree method

2. SEVESO DIRECTIVES

2.1 What was Seveso disaster? [2]

The Seveso disaster was an industrial accident that occurred around 12:37 pm on July 10, 1976, in a small chemical manufacturing plant approximately 20 kilometres north of Milan in the Lombardy region of Italy. It resulted in the highest known exposure to 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in residential populations which gave rise to numerous scientific studies and standardized industrial safety regulations. The EU industrial safety regulations are known as the Seveso II Directive.

The accident occurred in the chemical plant's building B. The chemical 2,4,5-trichlorophenol was being produced there from 1,2,4,5-tetrachlorobenzene by the nucleophilic aromatic substitution reaction with sodium hydroxide. The 2,4,5-trichlorophenol was intended as an intermediate for hexachlorophene

This reaction must be carried out at a temperature above what was achievable using the normal process utilities available at the plant, so it was decided to use the exhaust steam from the onsite electricity generation turbine, and pass that around an external heating coil installed on the chemical reactor vessel. The exhaust steam pressure was normally 12 bar and temperature 190 °C, which resulted in a reaction mixture temperature of 158 °C, very close to its boiling point of 160 °C. Safety testing showed the onset of an exothermic side reaction if the reaction mixture temperature reached 230 °C. Crucially, no steam temperature reading was made available to plant operators responsible for the reactor.

The chemical-release accident occurred when a batch process was interrupted prior to the completion of the final step – removal of ethylene glycol from the reaction mixture by distillation, due to conformance with an Italian law requiring shutdown of plant operations over the weekend. Other parts of the site had already started to close down as the processing of other batches finished, which reduced power consumption across the plant, causing a dramatic drop in the load on the turbine and a consequent increase in the temperature of the exhaust steam to around 300 °C. This much hotter steam then proceeded to heat the portion of the metal wall of the accident reactor above the level of the liquid within it to the same temperature. Not having a steam temperature reading among their instruments, operators of the reactor were unaware of the presence of this additional heating, and they stopped the batch as they normally would – by isolating the steam and turning off the stirrer in the reactor vessel. The abnormally-hot upper region of the reactor jacket then heated the adjacent reaction mixture. With the stirrer not running, the heating was highly localised – confined to just the portion of the upper layers of reaction mixture adjacent to the reactor wall, and increased the local temperature to the critical temperature for the exothermic side reaction seen in testing. Indeed, the critical temperature proved to be only 180 °C, 50 °C lower than believed. At that lower critical temperature, a slow runaway decomposition began, releasing more heat and leading to the onset of a rapid runaway reaction when the temperature reached 230 °C seven hours later

The reactor relief valve eventually opened, causing the aerial release of 6 tonnes of chemicals, which settled over 18 km^2 of the surrounding area. Among the substances released was 1 kg of TCDD. At the nominal reaction temperature, TCDD is normally seen only in trace amounts of less than 1 ppm (parts per million). However, in the higher-temperature conditions associated with the runaway reaction, TCDD production apparently reached 100 ppm or more

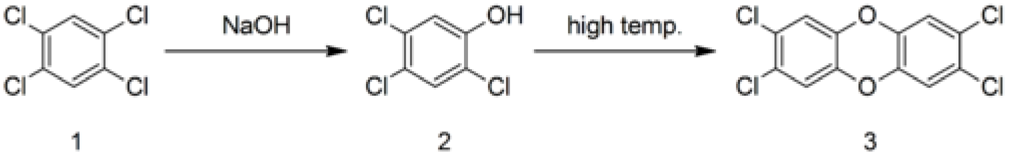


Figure 2.1 Reaction scheme.

After this accident, new directives were made, giving place to SEVESO DIRECTIVES

2.2 SEVESO DIRECTIVES [3]

There are 3 SEVESO directives, SEVESO I (adopted in 1982) SEVESO II (adopted in 1996) and SEVESO III (adopted in 2012)

2.2.1Principes

The Seveso Directive aims at the prevention of major accidents involving dangerous substances. However, as accidents may nevertheless occur, it also aims at limiting the consequences of such accidents not only for human health but also for the environment.

The Directive covers establishments where dangerous substances may be present (e.g. during processing or storage) in quantities above a certain threshold. Excluded from the Directive are certain industrial activities which are subject to other legislation providing a similar level of protection (e.g. nuclear establishments or the transport of dangerous substances).

Depending on the amount of dangerous substances present, establishments are categorised in lower and upper tier establishments, the latter are subject to more stringent requirements.

2.2.2Main obligations for operators

Operators are obliged to take all necessary measures to prevent major accidents and to limit their consequences for human health and the environment. The requirements include:

- Notification of all concerned establishments (Article 7);
- Deploying a major accident prevention policy (Article 8);
- Producing a safety report for upper-tier establishments (Article 10);
- Producing internal emergency plans for upper tier establishments (Article 12);
- Providing information in case of accidents (Article 16).

2.2.3.Main obligations for Member State authorities

Member States need to ensure that a number of requirements are fulfilled, those include:

- Producing external emergency plans for upper tier establishments (Article 12);
- Deploying land-use planning for the siting of establishments (Article 13);
- Making relevant information publically available (Article 14);
- Ensuring that any necessary action is taken after an accident including emergency measures, actions to ensure that the operator takes any necessary remedial measures and informing the persons likely to the affected (Article 17);
- Reporting accidents to the Commission (Article 18);
- Prohibiting the unlawful use or operation of establishments (Article 19);
- Conducting inspections (Article 20).
- Member States may maintain or adopt stricter measures than those contained in the Seveso Directive.

2.2.4Citizens' rights

- The public concerned needs to be consulted and involved in the decision making for specific individual projects (Article 15);
- Subject to the conditions outlined, Member State authorities need to make available any information held pursuant to the Seveso Directive (Articles 14 and 22);
- Access to justice needs to be granted on the cases listed in Article 2.

2.3 Main changes from SEVESO II to SEVESO III

- Updating and aligning the list of substances covered by the Directive to the EU legislation on the classification of dangerous;
- Strengthening citizens' rights on access to information, justice and on participation in decision-making;
- Improving the way information is collected, managed, made available and shared;
- Introducing stricter standards for inspections ensuring a more effective implementation and enforcement;
- Clarifying and updating of provisions, including streamlining and simplification to reduce administrative burden.

If we analyse it article by article:

- Article 1. Objetive
  - No change
- Article 2. Area of application
  - It specifies that the Directive excludes underground gas storage and the hazards created by radiation onizing substances originating in substances.

    - It makes clear the exclusion of Oil Platforms.
- Article 3 Definitions:
    - New definitions for establishments: Lower level establishment, Higher level establishment, new establishment, establishment, Existing establishment and Further establishment
    - Clarifies the definition of Industrial
    - New definitions appear: Mix, Presence of hazardous substances.
    - Definition of 'public' and 'interested public'
    - The definition of Inspection
    - It is about aligning the definitions with other Directives, make clear the inclusion of underground facilities and specify the different types of establishments.
- Article 4 Assessment of major accident hazards by one dangerous substance
    - New article that collects the mechanisms to be able to modify the list of substances or categories of annex I aimed at including certain exemptions and safeguard clauses.
- Article 5 Obligations of a general nature of the industrial
    - No change
- Article 6 Competent authorities.
    - Initially, it was thinking to obligate states with more than one Competent authority, to designate one, but Final only requires a correct coordination.
    - Improve writing when there is more than one competent authority
    - Forces the Competent authorities to accept the equivalent information provided by Industrialists by virtue of another European legislation.

*There are more, but they are summarized in the next article:

http://www.proteccioncivil.es/documents/20486/57af124e-fa3e-4b6b-a377-8833fbedfaef (Spanish document) **[4]**

3.LPG

3.1 What is LPG? [5] [6] [8]

LPG (Liquid Petroleum Gas) is a mixture of the volatile hydrocarbons like propene, propane, butene, isobutane, butane (all of them in liquid state), being in more proportion propane (C_3H_8) and Butane (C_4H_{10}). LPG is a gas at atmospheric pressure and normal ambient temperatures, but it can be liquefied when moderate pressure is applied or when the temperature is sufficiently reduced.

LPG was discovered in 1912 by Dr. Walter O. Snelling. As usual, there is a story before this discover.

That story is that the owner of a car asked to Snelling why half of the gasoline that he had purchased disappears when he arrived at home. Snelling decided to take a glass jug of the gasoline from the car and went to his laboratory. During this way back, he discovered that vapours were forming in the jug causing the cork to keep popping out. And also half of the gasoline had disappear. This vapours was LPG.

3.2 Properties of LPG. [7]

3.2.1 Composition:

LPG can be propane, butane or mixture of both hidrocarbures. Composition usually changes depending of the region. It those that average temperatures are high, LPG has a higher percentage of butane. In the other hand, in places where average temperatures are lower, it has a high percentage of propane. This different is due to the boiling point of both gases (-42.1ºC for propane, -0.5ºC for butane).

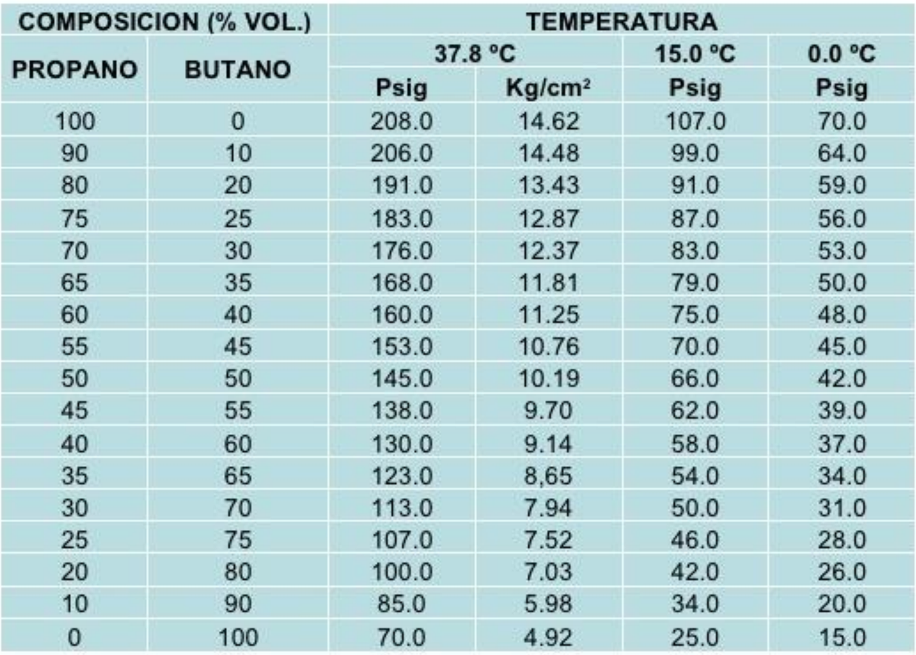
3.2.2 Vapour pressure.

Vapour pressure is the pressure at one vapour phase is at equilibrium with its liquid phase at a given temperature. It valour it’s independent of liquid and vapour amount (but it’s necessary to be both phases).

Lighter substances has a higher vapour pressure than heavier ones.

When a mixture of substances is taken, vapour pressure has relation with temperature, but additionally, it depends of the liquid phase composition too. This relation is shown at *Figure .1*

As it’s shown in *Figure .2* we can see that there is a relative high different at vapour pressure at different mixture proportions. Another important aspect shown it’s that can be seen its how vapour pressure increase with temperature. That is directly related with some of security rules that it’s forbidden to completely fill a recipient with LPG.



COMPOSICION (% VOL.)		TEMPERATURA			
PROPANO	BUTANO	37.8 ºC		15.0 ºC	0.0 ºC
		Psig	Kg/cm²	Psig	Psig
100	0	208.0	14.62	107.0	70.0
90	10	206.0	14.48	99.0	64.0
80	20	191.0	13.43	91.0	59.0
75	25	183.0	12.87	87.0	56.0
70	30	176.0	12.37	83.0	53.0
65	35	168.0	11.81	79.0	50.0
60	40	160.0	11.25	75.0	48.0
55	45	153.0	10.76	70.0	45.0
50	50	145.0	10.19	66.0	42.0
45	55	138.0	9.70	62.0	39.0
40	60	130.0	9.14	58.0	37.0
35	65	123.0	8,65	54.0	34.0
30	70	113.0	7.94	50.0	31.0
25	75	107.0	7.52	46.0	28.0
20	80	100.0	7.03	42.0	26.0
10	90	85.0	5.98	34.0	20.0
0	100	70.0	4.92	25.0	15.0

FIGURE 3.1 VAPOUR **PRESSURE OF DIFFERENT MIXTURES OF LPG**

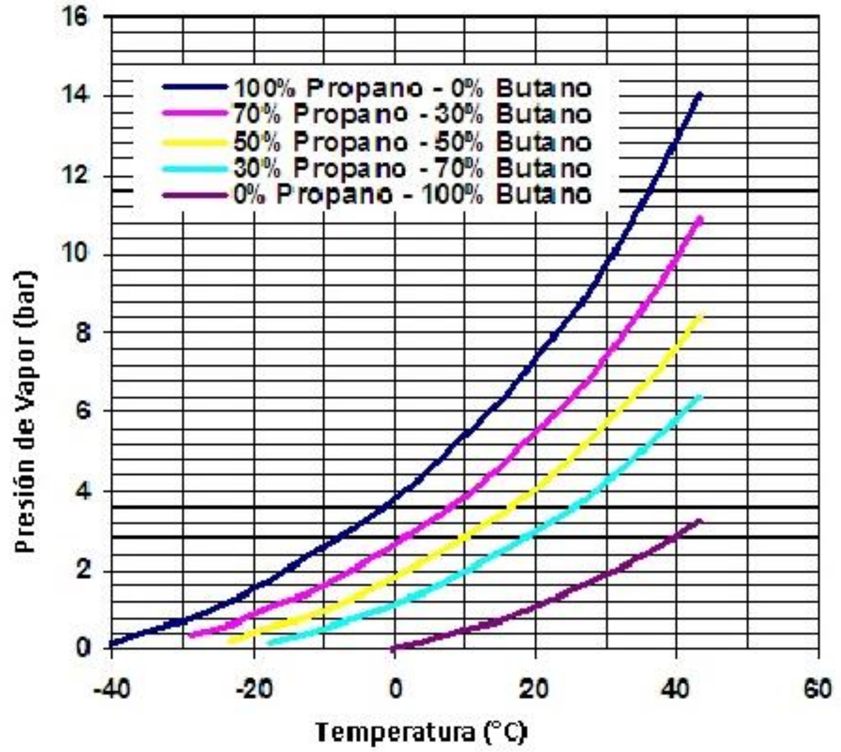


FIGURE 3.2 VAPOUR **PRESSURE OF LPG (T/VAPOUR PRESSURE) AT DIFFERENT % MIXTURE**

3.2.3 Boiling point.

Boling point is the temperature at matter change from liquid state to gaseous one. It can be define too like the temperature at liquid's vapour pressure its equal to the pressure of the environment around the liquid.

LPG has a boiling point of -26 ºC, so it will be boil at practically anyplace, don't be needed an external heat source, with air will be enough. If we were under that temperature, it would be conserve as liquid and in an open recipient.

3.2.4 Specific weight of liquid.

Specific weight of a liquid it's the comparison between a given mass of a volume of a liquid at a certain temperature, with the same volume of water at that temperature. At 15ºC, the specific weight of LPG is 0.539,

3.2.5 Specific weight of vapour.

Specific weight of a vapour it's the comparison between a given mass of a volume of a vapour at a certain temperature, with the mass of the same volume of air at that temperature. At 15ºC, the specific weight of LPG is 1.716.

3.2.6 Flammability.

That property shows how easy a material can be combusted.

For a combustion it's need: Combustible, O_2 of air and an ignition source.

When all this elements are in properly amount, a combustion it's made. Gas concentration must be between limits of

The limits for a LPG-air mixture are (in % of LPG) 2.1% for Lower Flammable Limit[1] and 9.5% for Upper Flammable Limit[2].

Flammability limits can change due to:

Oxygen effect: If a high percentage of O_2 it's use, limits increase, especially UPL.

Use of inert gas: If we use an inert gas in addition, we decrease the limits, removing danger of explosion or fire.

Pressure effect: Low pressure decrease Limits of Flammability, high one increase them.

Temperature effect: Limit of flammability is proportional to T. If its raise up, limits increase too, increasing the risk.

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[1] Under this amount, there isn't spread of flame. Mixture it's too poor.

[2] Over this amount, there isn't spread of flame. Mixture it's too rich.

3.2.7 Calorific power.

Calorific power it’s the amount of energy (or heat) that it’s liberate by a determinate amount of a substance (fuel) during the complete combustion of it.

3.2.7.1 Upper calorific power.

It’s define supposing that all elements of combustion (air and fuel) are at 0ºC and products (combustion gases) are at 0ºC too (water steam it’s completely as liquid water)

3.2.7.2 Lower calorific power.

Lower calorific power consider that water steam don’t condense, so there isn’t any additional input of heat due to the condensation of water.

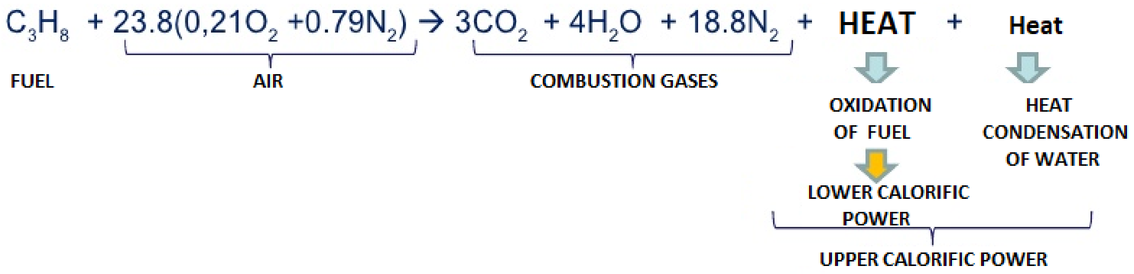


FIGURE 3.3 SCHEMA OF CALORIFIC POWERS

3.2.8 Another generic characteristics.

Its use as liquid, liquefy around 60-120 psi. When it change from liquid to vapour state, its volume increase 260 times.

LPG don’t corrode steel, copper or its alloys and don’t dissolve synthetic rubbers, making that materials able to be use, but it dissolve oils and natural rubber.

LPG is not toxic, except if there is a high concentration in a close place. But its irritating

LPG is the second most respectfully fuel with nature, it combustion don’t polluted the atmosphere when it burned, also it can be diluted into water.

It’s odourless, so mercaptans are added to give it odour.

		PROPANE	**LPG**	**BUTANE**
Composition (%Vol)				
Propanes	%	**100.00**	**60.00**	**0.00**
Butanes	%	**0.00**	**40.00**	**100.00**
Physic/Chemistry Properties				
Vapour pressure (at 37.8 ºC)	psig	**208**	**160**	**70**
Vapour pressure (at 0.0 ºC)	psig	**70**	**48**	**15**
Boiling point (at 1 atm)	ºC	**-42.1**	**-25.5**	**-0.5**
Liquid:				
Specific weight (at 15ºC) (Water=1)		**0.5083**	**0.5389**	**0.5847**
Density (at 15ºC)	Kg/gal	**1.922**	**2.038**	**2.211**
Vapour				
Relative Density (air=1)		**1.5225**	**1.7162**	**2.0068**
Flammability				
Lower Explosive Limit (LFL) %Vol Air	%	**2.00**	**1.80**	**1.50**
Upper Explosive Limit (UFL) %Vol Air	%	**9.50**	**9.30**	**9.00**
Combustion				
Vol air / Gas for combustion (ideal)		**23.86**	**26.72**	**31.02**
Calorific Power	BTU/Kg	**47.375**	**47.063**	**46.596**
Calorific Power (Vapour at 15ºC)	BUT/m^3	**88.353**	**98.940**	**114.544**
Calorific Power (Liquid at 60ºF)	BTU/gal	**90.823**	**95.657**	**102,909**

Figure 3.4 Summary of main properties of Propane, LPG and Butane.

3.3 Uses of LPG. [9]

It can be use in agricultural uses as:

Green House Heating, flame weeding, crop drying, poultry rearing, waste incineration or distillation process

Commercial uses of LPG can be like heating, refrigeration or air-conditioning

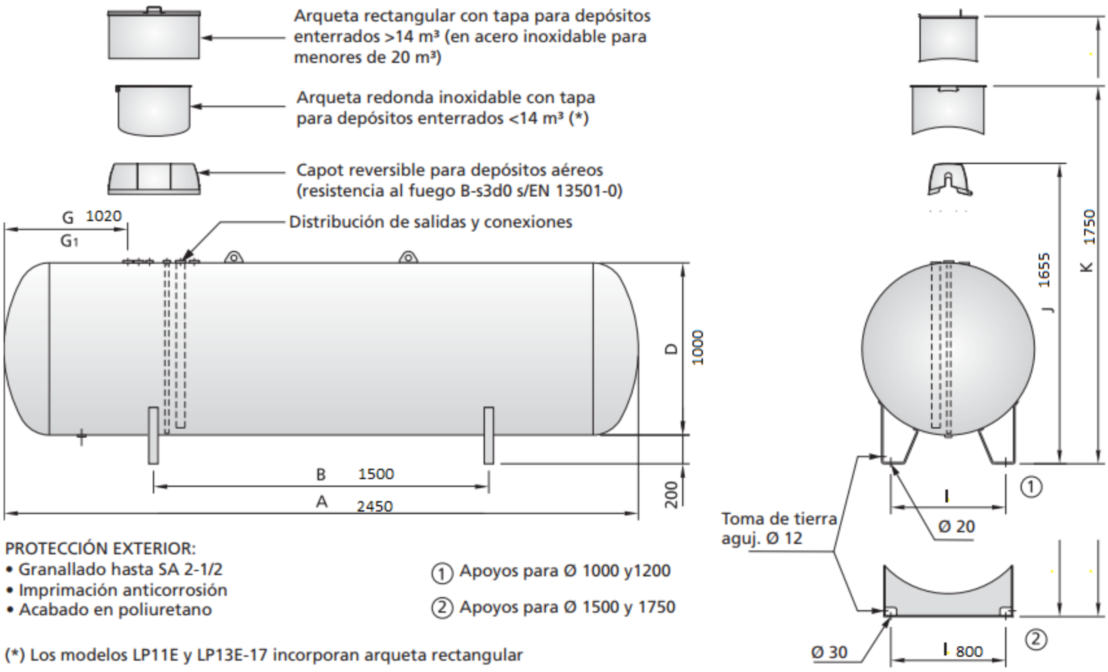
Some of Industrial uses of LPG are ceramic industry, food processing industry, metal processing industry, textile industry, printing industry or chemicals production industry

It can be at mining process too.

And finally, domestic uses, as cooking, heating, lighting, cooling, braining or clothes drrying

3.4 Storage of LPG. [10]

There are so many ways to storage it, but the common one is static deposits. In the next lines, we will analyse the measurements for a deposit of around 1 ton (that it's going to be used when we make the estimate of risk of explosion. The material that is made of is standard carbon steel for pressure equipment



Capacidad nominal (litros)	Modelo Ref.	Peso en vacío aprox. (Kg.)	Propano almacenado (Kg.)	Superficie total (m²)	Descarga mínima de válvula de seguridad (m³/min. aire)		Dimensiones (mm)							
					Aéreo	Enterrado	D	A	B	G	G1	I	J	K
990	LP1000*	280	415	5,2	41,2	28,8	1.000	1.470	700	520	-	670	1.370	1.460
1.450	LP1450*	390	609	6,7	50,7	35,5	1.200	1.562	700	565	-	800	1.655	1.750
1.825	LP1825*	470	766	7,9	58,0	40,6	1.200	1.872	900	720	-	800	1.655	1.750
2.250	LP2250*	550	945	9,3	66,3	46,4	1.200	2.255	1.300	915	-	800	1.655	1.750
2.450	LP2450*	590	1.029	10,1	71,0	49,7	1.200	2.450	1.500	1.020	-	800	1.655	1.750

Figure .5 Sketches and measurements of a tank for 1 ton LPG.

3.5 Obtaining of LPG. [11]

There are two principal ways to obtain LPG.

3.5.1 LPG Stripped from Natural Gas

This method has 3 different stages:

1. **Separating the Gas from the oil**
   The gas/oil mixture is piped out of the well and into a gas trap, which separates the stream into crude oil and "wet" gas, which contains LPG and natural gas. The heavier crude oil sinks to the bottom of the trap and is then pumped into an oil storage tank for refining.
   The "wet" gas, off the top of the gas trap, is processed to separate the gasoline (petrol) from the natural gas and LPG.

2. **Processing the methane**
   Impurities such as water, carbon dioxide, nitrogen and hydrogen sulphide must be removed before either the natural gas (methane) or LPG can be used.
   The refined and purified natural gas, which is mostly methane, is fed into the pipelines that supply our cities and towns.
3. **Processing the LPG**

   The LPG must be separated from an intricate mixture of hydrocarbons. The plants that do the processing are frequently called “stripper plants”, as the LPG is stripped from the natural gas flow. Impurities must also be removed from the propane and butane or they will prevent the LPG from liquefying properly. The refrigeration technique is common for recovery of LPG from a natural gas stream. With this technique, they refrigerate the gas stream to obtain the LPG. Refrigeration is employed in three different processes: expander plants, low temperature separation and combined processes. Other separation techniques may also be employed, including lean oil absorption.

3.5.2 LPG Processed from Oil Refining

This method has 2 different stages:

1. **Refining the Crude Oil.**
   Crude oil undergoes a variety of refining processes including fluid catalytic cracking, delayed cokers, and crude distillation. One of the refined products is LPG. After desalting, the heated crude oil is pumped into the distillation tower. Fractions of the flow are extracted from the side of the distillation tower at various heights between the bottom and the top. Each extraction point is temperature controlled to extract a specific fraction including gasoline, naphtha, kerosene, diesel, light gas oil and heavy gas oil. These are then sent to unique streams for storage or possible further processing.
2. **Refining the LPG.**
   LPG, with the lowest boiling point, is extracted from the top of the distillation tower. This LPG component can be used as a mixture or further separated into its three primary parts: propane, butane and isobutane. This further fractionation can be achieved with Depropaniser, Debutaniser and Deisobutaniser fractionators.

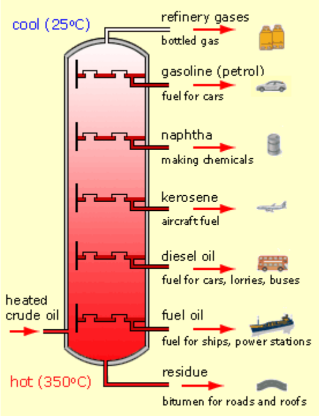


Figure .6 Destilation tower for Crude Oli

4.Simulating of accidents with LPG using ALOHA.

In this section there have been simulated real accidents related with LPG - either stored or transported - trying to get as close as possible the data of the scenario in which they occurred. The simulation of these accidents by ALOHA Software will allow to assess the consequences of an explosion related with LPG and which can be the dangers.

1. **Accident with a train in Viareggio (Italy). 29th June 2009. [13] [14]**
   ***FOR THAT EXPERIMENT, we suppose LPG as propane.**
   The accident happened nearby an Italian railway station, in June 2009.
   Thestation serves the city of Viareggio, in the region of Tuscany
   Train services to and from the station are operated by different railway undertakings authorized by RFI (now by ANSF - Agenzia Nazionale per la Sicurezza Ferroviaria).
   Due to its position, the station is one of the most important in the north-centre-west coast of Italy and in particular in the Province of Lucca, and it is an important junction connecting Pisa, Livorno and Rome with La Spezia, Genoa, Parmaand Milan, providing interchange for passengers to and from all of these cities.On the 29th of June 2009 (day of the accident), the 50325 train was transporting LPG from the oil refinery of Trecate, near Milan, to a LPG storage depot located in Gricignano, near Naples. The train was crossing the Viareggio's railway station shortly before midnight.
   According to the news of days before, 32 people died and 26 were injured.

SITE DATA:

Location: VIAREGGIO, ITALY

Building Air Exchanges Per Hour: 0.18 (unsheltered single storied)

Time: June 29, 2009 2338 hours ST (using computer's clock)

CHEMICAL DATA:

Chemical Name: **PROPANE**

CAS Number: 74-98-6 Molecular Weight: 44.10 g/mol

AEGL-1 (60 min): 5500 ppm AEGL-2 (60 min): 17000 ppm AEGL-3 (60 min): 33000 ppm

IDLH: 2100 ppm LEL: 21000 ppm UEL: 95000 ppm

Ambient Boiling Point: -42.0° C

Vapor Pressure at Ambient Temperature: greater than 1 atm

Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: .54 meters/second from SE at 3 meters

Ground Roughness: urban or forest Cloud Cover: 5 tenths

Air Temperature: 22° C Stability Class: F

No Inversion Height Relative Humidity: 92%

SOURCE STRENGTH:

Leak from hole in horizontal cylindrical tank

Flammable chemical is burning as it escapes from tank

Tank Diameter: 3.04 meters Tank Length: 15.95 meters

Tank Volume: 115,770 liters

Tank contains liquid Internal Temperature: 22° C

Chemical Mass in Tank: 45000 kilograms

Tank is 78% full

Opening Length: 0.4 meters Opening Width: 0.05 meters

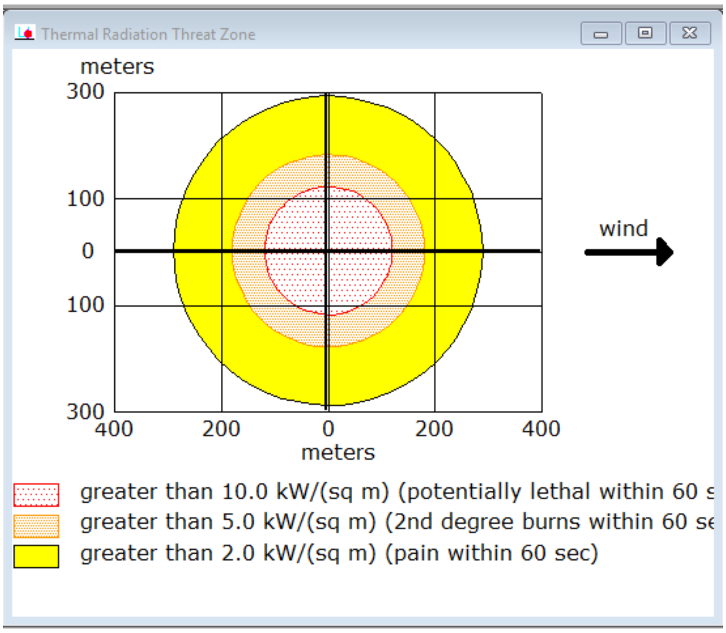
Opening is 0 meters from tank bottom

Max Flame Length: 92 meters Burn Duration: 2 minutes

Max Burn Rate: 20,500 kilograms/min

Total Amount Burned: 45,000 kilograms

Note: The chemical escaped from the tank and burned as a jet fire.



▨ greater than 10.0 kW/(sq m) (potentially lethal within 60 s

▨ greater than 5.0 kW/(sq m) (2nd degree burns within 60 se

🟨 greater than 2.0 kW/(sq m) (pain within 60 sec)

Figure 4.1 Flammable threat zone

Figure 4.2 Stimate of region affected by Thermal radiation of threat zone

Figure 4.3 Real picture of the accident

2. **- Manufacture of refined petroleum products at Feyzin. 4th January 1966.** [15] ***FOR THE EXPERIMENTS, we determinate only butane firstly and then only propane because we can’t measure both at same time**

The Feyzin refinery, located south of Lyon, was commissioned in July 1964 and designed to process 1.7 million tons of petroleum per year. In early 1966, the refinery was fitted with a pressurised liquid petroleum gas (LPG) storage facility having a total capacity of 13,100 m^3.

The LPG storage area is located in the refinery's zone B, south of the production units. In addition to the LPG storage facility, which includes 10 tanks, 8 spheres and 2 cylinders, zone B also includes storage containers for furnace fuel-oil, gasoline and premium. Zone C is located on the other side of the motorway, south-east of zone B and corresponds to the tanker loading zone.

The butane spheres are spaced 11 m apart and the propane vessels at a distance of 11.8 m. The LPG spheres are filled by 2 corresponding horizontal tanks (or "jet tanks"). All the tanks underwent hydraulic testing in 1964.

SITE DATA:

Location: FEYZIN, FRANCE

Building Air Exchanges Per Hour: 0.65 (unsheltered single storied)

Time: January 4, 1966 0635 hours ST (user specified)

CHEMICAL DATA:

Chemical Name: **BUTANE**

CAS Number: 106-97-8 Molecular Weight: 58.12 g/mol

AEGL-1 (60 min): 5500 ppm AEGL-2 (60 min): 17000 ppm AEGL-3 (60 min): 53000 ppm

LEL: 16000 ppm UEL: 84000 ppm

Ambient Boiling Point: -1.2° C

Vapor Pressure at Ambient Temperature: greater than 1 atm

Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 2.5 meters/second from E at 3 meters

Ground Roughness: open country Cloud Cover: 5 tenths

Air Temperature: 5° C Stability Class: E

No Inversion Height Relative Humidity: 75%

SOURCE STRENGTH:

Leak from short pipe or valve in spherical tank

Flammable chemical escaping from tank (not burning)

Tank Diameter: 62.96 meters Tank Volume: 1.31e+008 liters

Tank contains liquid Internal Temperature: 5° C

Chemical Mass in Tank: 2896000 kilograms

Tank is 3% full

Circular Opening Diameter: 32 inches

Opening is 0 meters from tank bottom

Release Duration: 24 minutes

Max Average Sustained Release Rate: 142,000 kilograms/min

(averaged over a minute or more)

Total Amount Released: 2,896,000 kilograms

Note: The chemical escaped as a mixture of gas and aerosol (two phase flow).

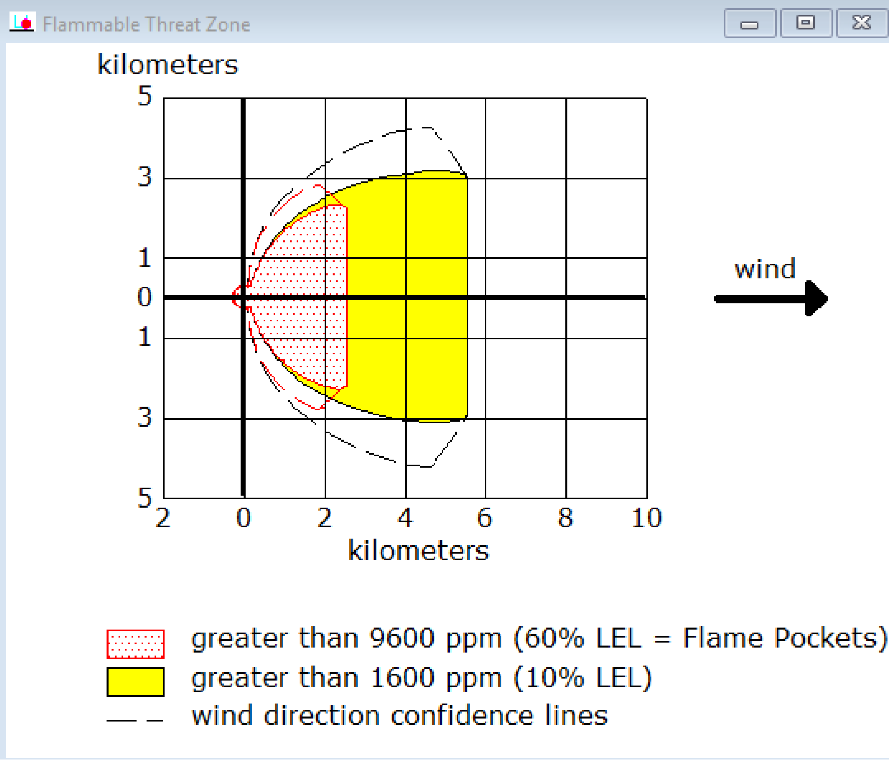


Figure 4.4 Flammable threat zone (Zones that be under danger of fire) (Butane)

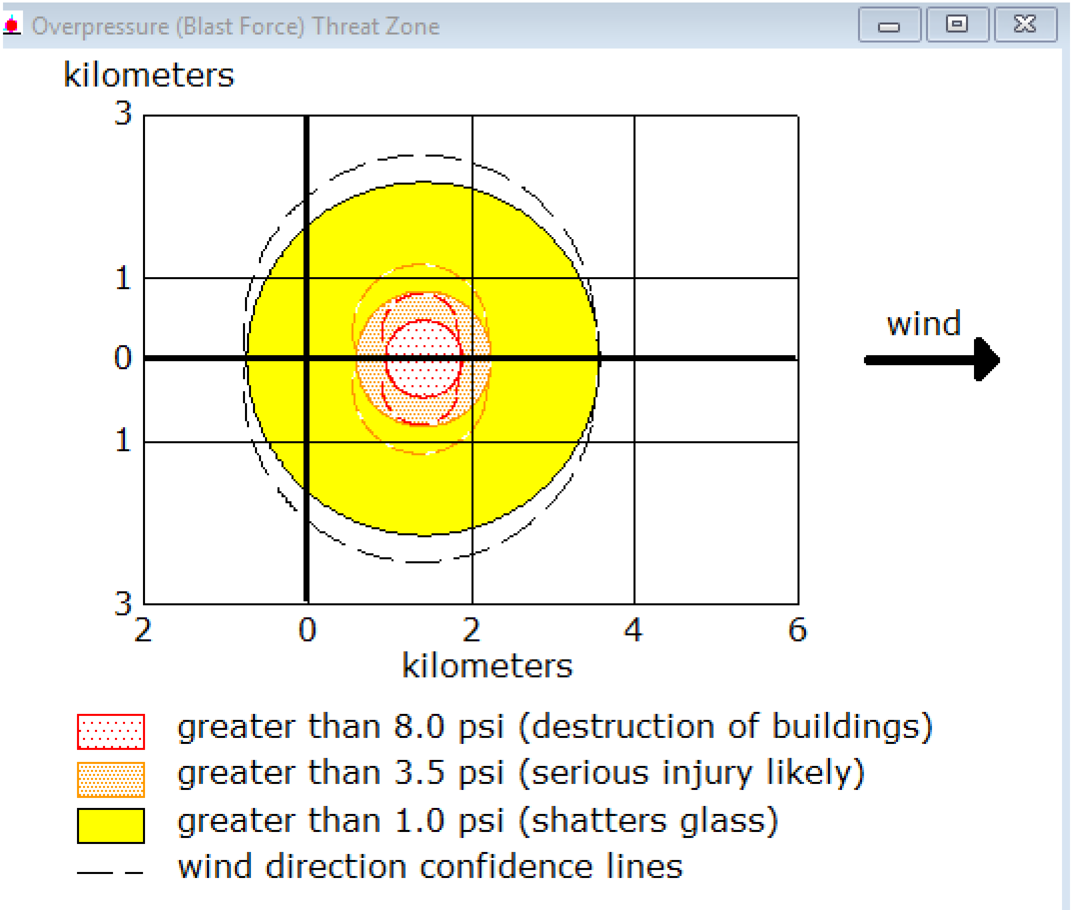


Figure 4.5 Explosion threat zone (Zones that be under danger if it explodes) (Butane)

SITE DATA:

Location: FEYZIN, FRANCE

Building Air Exchanges Per Hour: 0.65 (unsheltered single storied)

Time: January 4, 1966 0635 hours ST (user specified)

CHEMICAL DATA:

Chemical Name: **PROPANE**

CAS Number: 74-98-6   Molecular Weight: 44.10 g/mol

AEGL-1 (60 min): 5500 ppm   AEGL-2 (60 min): 17000 ppm   AEGL-3 (60 min): 33000 ppm

IDLH: 2100 ppm   LEL: 21000 ppm   UEL: 95000 ppm

Ambient Boiling Point: -42.6° C

Vapor Pressure at Ambient Temperature: greater than 1 atm

Ambient Saturation Concentration: 1,000,000 ppm or 100.0%

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: 2.5 meters/second from E at 3 meters

Ground Roughness: open country Cloud Cover: 5 tenths

Air Temperature: 5° C Stability Class: E

No Inversion Height Relative Humidity: 75%

SOURCE STRENGTH:

Leak from short pipe or valve in spherical tank

Flammable chemical escaping from tank (not burning)

Tank Diameter: 53.08 meters Tank Volume: 78,305,337 liters

Tank contains liquid Internal Temperature: 10° C

Chemical Mass in Tank: 9920000 kilograms

Tank is 23% full

Circular Opening Diameter: 24 inches

Opening is 0 meters from tank bottom

Release Duration: 55 minutes

Max Average Sustained Release Rate: 193,000 kilograms/min

(averaged over a minute or more)

Total Amount Released: 9,920,000 kilograms

Note: The chemical escaped as a mixture of gas and aerosol (two phase flow).

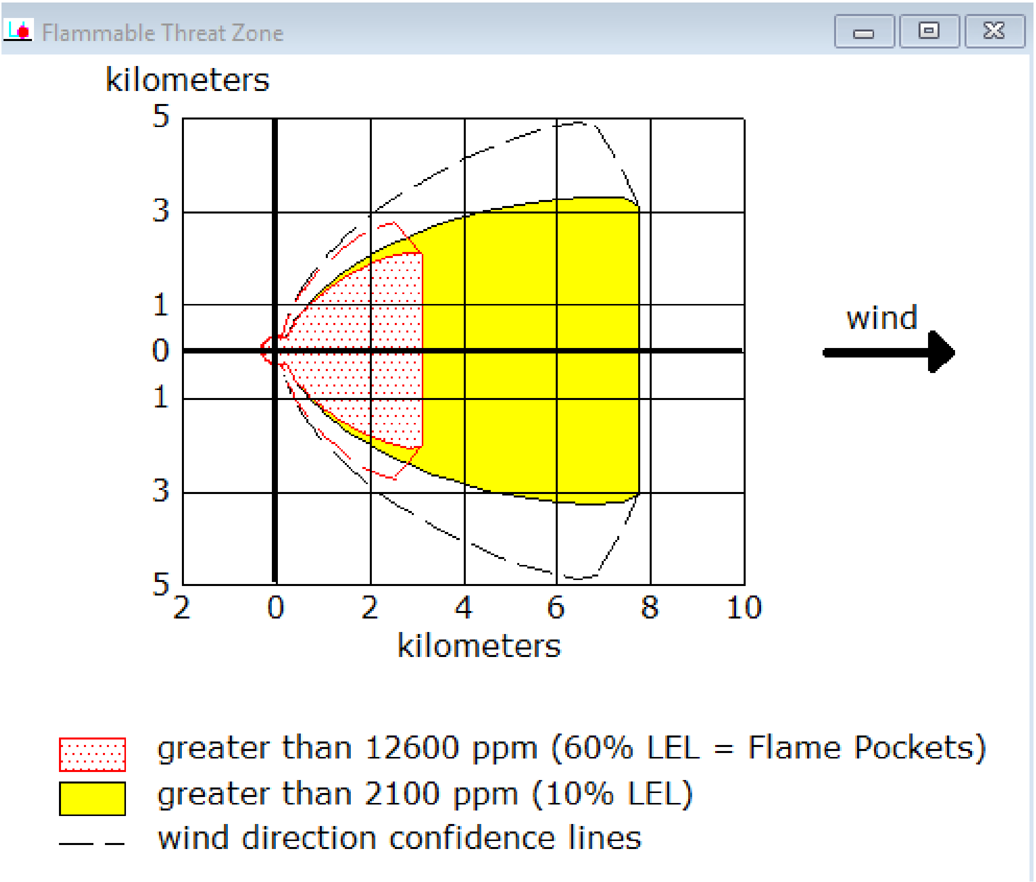


Figure 4.6 Flammable threat zone (Zones that be under danger of fire) (Propane)

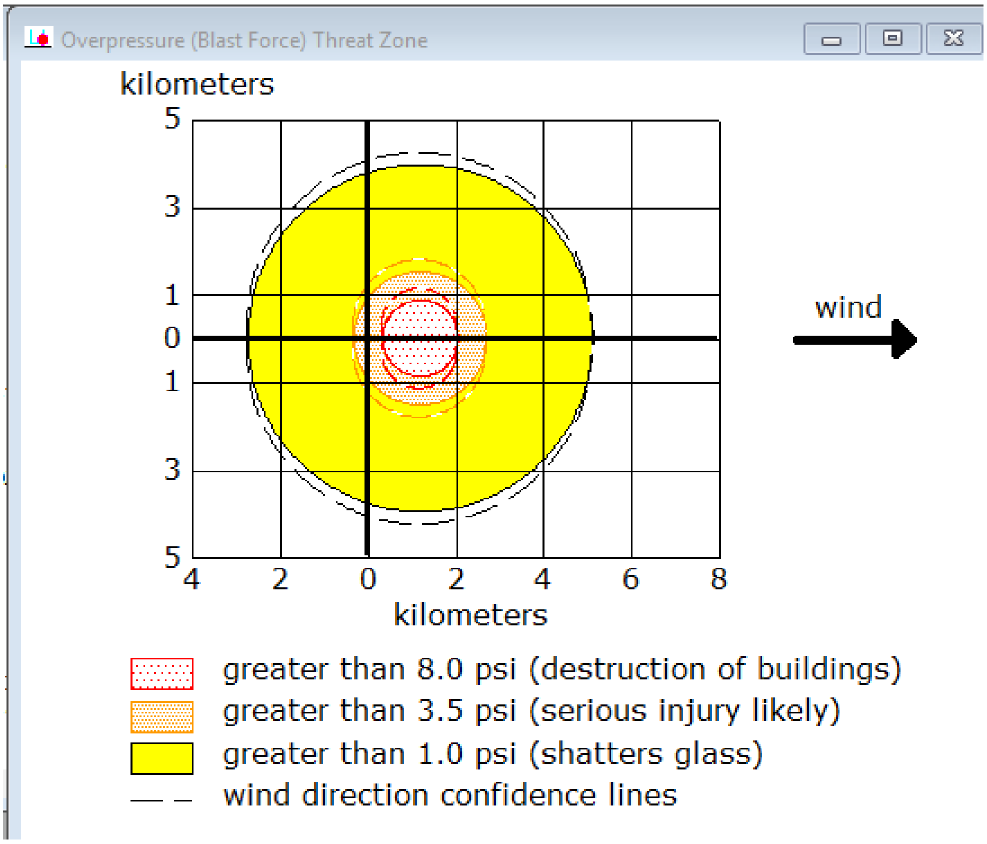


Figure 4.7 Explosion threat zone (Zones that be under danger if it explodes) (Butane)

After 2 real cases, we are going to make a theoretical one to explain the main differences that we can see depending of the compound we analyse. For that we are going to use the same mass, and same conditions to both compounds.

3. Example

***We use the same conditions that for Viareggio train accident.**

****COMMON DATA**

SITE DATA:

Location: VIAREGGIO, ITALY

Building Air Exchanges Per Hour: 0.18 (unsheltered single storied)

Time: July 20, 2017 1920 hours ST (using computer's clock)

ATMOSPHERIC DATA: (MANUAL INPUT OF DATA)

Wind: .54 meters/second from SE at 3 meters

Ground Roughness: urban or forest Cloud Cover: 5 tenths

Air Temperature: 22° C Stability Class: F

No Inversion Height Relative Humidity: 92%

SOURCE STRENGTH:

Leak from hole in horizontal cylindrical tank

Flammable chemical is burning as it escapes from tank

Tank Diameter: 3.04 meters Tank Length: 15.95 meters

Tank Volume: 115,770 liters

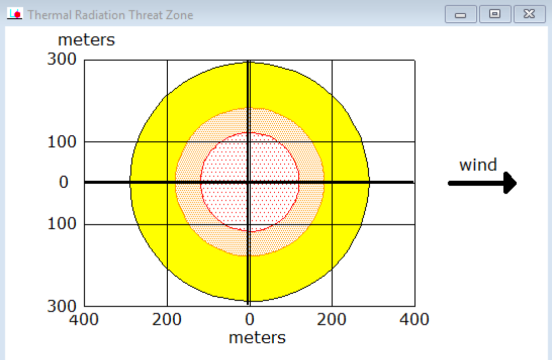
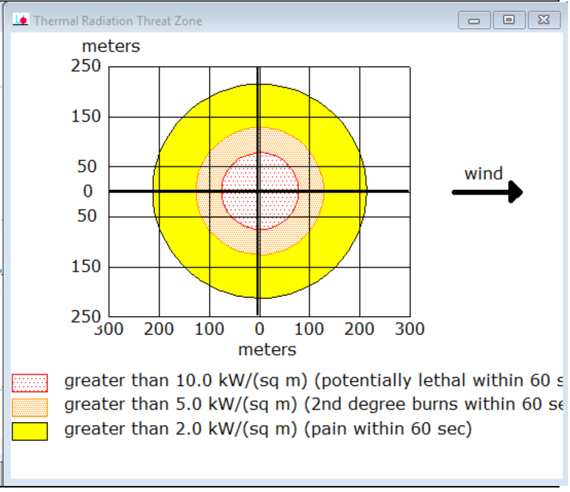
Tank contains liquid Internal Temperature: 22° C

Chemical Mass in Tank: 45000 kilograms

Tank is 78% full

Opening Length: 0.4 meters Opening Width: 0.05 meters

Opening is 0 meters from tank bottom

CHEMICAL DATA: Chemical Name: **PROPANE** CAS Number: 74-98-6 Molecular Weight: 44.10 g/mol AEGL-1 (60 min): 5500 ppm AEGL-2 (60 min): 17000 ppm AEGL-3 (60 min): 33000 ppm IDLH: 2100 ppm LEL: 21000 ppm UEL: 95000 ppm Ambient Boiling Point: -42.0° C Vapor Pressure at Ambient Temperature: greater than 1 atm Ambient Saturation Concentration: 1,000,000 ppm or 100.0%	**CHEMICAL DATA:** Chemical Name: **BUTANE** CAS Number: 106-97-8 Molecular Weight: 58.12 g/mol AEGL-1 (60 min): 5500 ppm AEGL-2 (60 min): 17000 ppm AEGL-3 (60 min): 53000 ppm LEL: 16000 ppm UEL: 84000 ppm Ambient Boiling Point: -0.5° C Vapor Pressure at Ambient Temperature: greater than 1 atm Ambient Saturation Concentration: 1,000,000 ppm or 100.0%
	

What we can observe, directly it’s how thermal radiation changes, being more calorific the propane. That’s due to their different density, that allows to expand (down the air, because it’s heavier) easier to the propane.

5. CONCLUSIONS.

- There is a progressive increase of accidents occurred in the chemical industry and transport of dangerous products with the time since 70’s. This has been attributed both to better access to information on accidents and the development of industrial activity in many countries and the consequent increase of the transporting of hazardous products.

- Regarding the type of accident, there were leak more than 50% of cases, the fire was the most frequent of other accidents, followed by the explosion and gas cloud. According to its origin, most of the accidents occurred in transport, with 39% of cases.

- There are so many type of methods for analysis of risk, been divided into qualitative and quantitative ones.

- In Europe, the Seveso accident in 1976 prompted the adoption of legislation aimed at the prevention and control of major accidents in chemical industry. The resulting 'Seveso' directive now applies to around 10,000 industrial establishments where dangerous substances are used or stored in large quantities.

- LPG is a mixture of organic gases that is used as fuel. It usually be a waste product of obtain of natural gas or oils derivatives from petroleum.

- LPG has characteristic that make it a safety fuel, and a careful environment one.

- Using simulating programs like ALOHA, we can estimate possible consequences of an accident and make more safety our transportation or storage of hazardous products.

6. REFERENCES.

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- [2] https://www.unizar.es/guiar/1/Accident/Seveso.htm
- [3] http://ec.europa.eu/environment/seveso/legislation.htm
- [4] http://www.proteccioncivil.es/documents/20486/57af124e-fa3e-4b6b-a377-8833fbedfaef
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