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FINAL DEGREE THESIS

RISK ANALYSIS FOR THE PRODUCTION OF LEVULINIC ACID FROM BIOMASS

ACADEMIC YEAR: 2017/2018

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1. INTRODUCTION

Every process that involves technology has also got an implicit risk of accident (chemical processes, large scale fuels transport, industrial automatized processes, energy production, etc.).

Since humanity is continuously asking for more energy and technology to develop societies and economies, it is necessary not only to research the development of renewable technologies and pollution reduction treatments, but also the way to make these processes safer for workers, equipments and installations.

With this aim, several quantitative risk assessment (QRA) techniques have been developed, such as Safety review and Check-list analysis (non-structured, i.e. strongly based on experience), What-if analysis, HazId, Failure Modes and Effects Analysis (FMEA), and Hazard and Operability (HazOp) analysis (structured Hazard Identification Techniques). These techniques have been explained during the theoretical lessons.

The procedure applied in this thesis is going to be the **A**ccidental **R**isk **A**ssessment **M**ethodology for **I**ndustrie**s** (ARAMIS) that will be deeply described throughout the thesis developed here.

This thesis has been divided in eight main sections: First, a brief introduction about its aim has been presented. After this, some terms and processes related to fuels and biomass have been explained (since levulinic acid production´s source is biomass). The third part consists in the relatively detailed explanation of the several steps in in which ARAMIS methodology consists. Then, both procedures, MIMAH and MIRAS, will be applied. Basing on the results of the last step, a comparison between the relevant accident scenarios (RAS) derived of the industrial process here presented and the ones detected in a previous study of another industrial process for the production of levulinic acid (these data have been provided, are external to this thesis) is performed. The sixth step will consist on a simplified budget will be discussed and developed. Finally, a brief comment about the acknowledgments and the bibliography in which this work has been based are presented.

2. FUELS, ENERGY CONSUMPTION AND BIOMASS PRODUCTION

2.1 Energy production and consumption

As said in the introduction, and also shown in the figures 2.1 and 2.2, the energetic global consumption is rising every year. Since it is well known that non-renewable resources (petroleum, carbon, natural gas, and nuclear energy obtained from radioactive elements such as uranium-235 and thorium-232) are depletable and also generate great amounts of polluting gases when they are burnt, such as CO2, CH4, N20, etc. (in case of fossil fuels), human beings have been developing different technologies in order to take advantage of other kind of energy resources, such as photovoltaic, eolic, hydro-electrical and biomass (renewable resources).

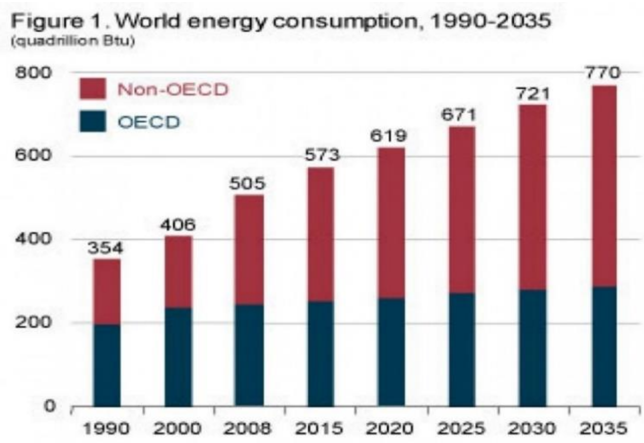


Figure 2.1 [2]

Nevertheless, it is also reflected that non-renewable resources will remain as the main source to obtain energy (figure 2.2).

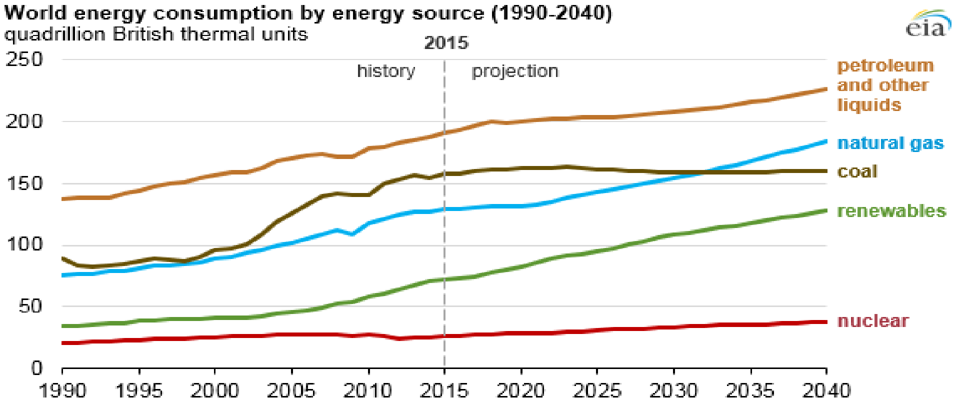
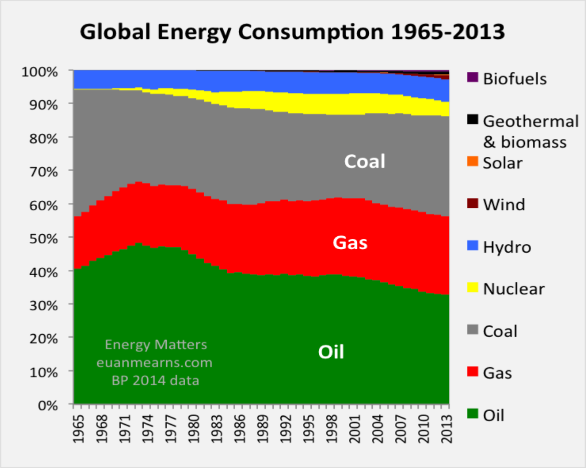
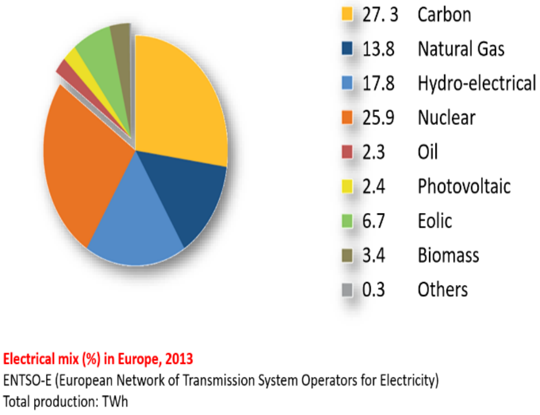


Figure 2.2 [3]

As for biomass, it represents a very small part of the energy resources (figures 2,3 and 2.4).


Global Energy Consumption 1965-2013

Energy Matters
euanmearns.com
BP 2014 data


Electrical mix (%) in Europe, 2013

ENTSO-E (European Network of Transmission System Operators for Electricity)

Total production: TWh

Figure 2.3 [4]

Figure 2.4 [5]

2.2 Biomass concept

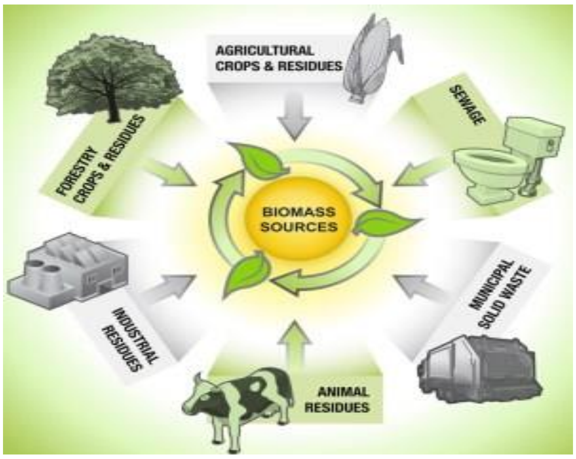
Biomass is any sort of plant matter or animal wastes, based on carbon-hydrogen compounds. Wood remains the world's largest source of biomass and has been traditionally used for energy generation [5]. In figure 2.5 are shown the sources of biomass.

A comparison between biomass and coal:

-Coal contains between 75-90% carbon while biomass carbon content is about 50%: the heating value of biomass is low

-Biomass fuels contain more volatile components and are more reactive than coal: at 500 °C about 85% by weight of the wood material is normally converted into gaseous compounds

-These differences are explained by the O/C and H/C ratios of each fuel, shown in the Van Krevelen diagram (figure 2.6).



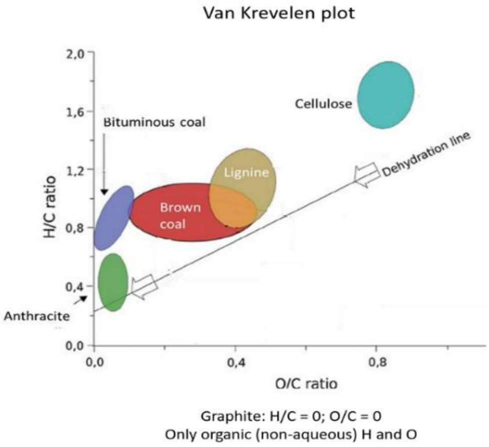


Figure 2.5 [6]

Figure 2.6 [5]

In nature, if biomass is left lying around on the ground it will break down over a long period of time, releasing carbon dioxide and its store of energy slowly. By burning biomass its store of energy is released quickly and often in a useful way. So, converting biomass into useful energy imitates the natural processes but at a faster rate [7].

The main advantages of biomass are [8]:

1.- It is a renewable energy source

Throughout the planet there is the possibility of accessing biomass sources such as crop residues, manure and organic waste. In the course of a year in which all these sources are transformed into biofuels, equivalent amounts are being generated in crops, farms and cities. The rate of transformation resembles the rate of crop growth and harvest and can be as short as a few months in some cases.

2.- Neutral with respect to carbon emissions

This may be the biggest and most important advantage of energy from biomass. Biomass enters fully into the carbon cycle. The carbon in the atmosphere is captured by plants during photosynthesis and becomes part of their structures. When the plant dies or is burned, that carbon returns to the atmosphere. Since it is a cycle, the following crops absorb the carbon again and again, so that a balance is maintained between the amount of carbon that the biomass fuel releases into the atmosphere and the amount that the plants extract from it. For this reason, fuels from biomass do not contribute to global warming, and are considered clean fuels.

3.- Minimum price

The use of the energy contained in the biomass is very economical compared to oil or coal. It usually costs around a third of fossil fuels to get the same result. This means that if your heating depended on biomass, you could save a third of the cost of heating it with diesel oil every year, which is a great saving.

2.3 Types of biofuels

Fuels can be classified into four types, according to the generation they belong to. It is important to note that the structure of the biofuel itself does not change between generations, but the source from which it derives does [44], [45]:

-**First generation biofuels** are produced directly from food crops. The biofuel is ultimately derived from the starch, sugar, animal fats, and vegetable oil that these crops provide. The main sources are the corn, the sugar cane, the soybeans and the vegetable oil.

-In case of **second (or advanced) generation biofuels**, crops are not usually the feedstock on which their production is based. The only time the food crops can act as second generation biofuels is if they have already fulfilled their food purpose. As an example, waste vegetable oil is a second generation biofuel since it has already been used and is no longer fit for human consumption, whereas virgin vegetable oil would be a first generation biofuel. Different technology is normally employed when second generation biofuels are treated, with respect to the one present in the energy extraction processes from first generation biofuels. These kind of biomass is the one employed in the industrial process here studied.

-**Third generation biofuels** refers to those biofuels which derive from algae. Previously, algae were lumped in with second generation biofuels. Algae are characterized for being capable of much higher yields with lower resource inputs than other feedstock. This is the reason why they have nowadays their own category. They are capable to provide several advantages, but at least one major shortcoming that has prevented them from becoming a runaway success: large-scale implementation of algae to produce biofuel will not occur in short nor medium term. Butanol, ethanol and jet fuel are some of the fuels that can be derived from algae.

-Finally, **fourth generation bio-fuels** have a special characteristic: apart from producing sustainable energy, capture and storage of CO_2 takes place during their treatment process. These feedstocks are treated with the same procedures that second generation biofuels for the obtention of fuel, but the difference resides in the fact that at all stages of production the carbon dioxide is captured using processes such as oxy-fuel combustion. The carbon dioxide can then be geosequestered by storing it in old oil and gas fields or saline aquifers.

2.4 Bio-refinery concept

A bio-refinery is a facility that integrates biomass conversion processes and equipment to produce transportation biofuels, power and chemicals from biomass focusing on maximizing the added value. The concept of biorefinery is analogous to that of the oil refinery [9], figure 2.7.

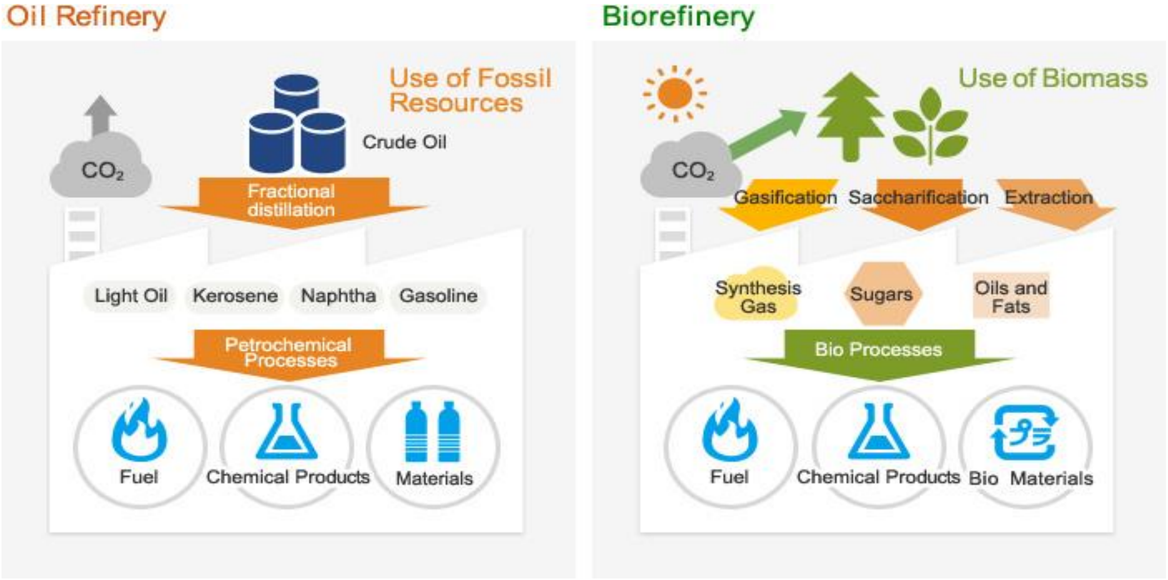


Figure 2.7 [10]

Aside from mechanical biomass cultivation and processing technologies (e.g. harvesting, milling and pressing), there are two main routes for bio-refining.

1) Technologies like a.o. pyrolysis and gasification are so-called thermochemical processes. Here a combination of heat, pressure in the absence of oxygen cause for the chemical breakdown of the biomass feedstock into a number of biocomponents, such as cellulose, hemicellulose, lignin and extractives. These bio-components can then be further processed into commercial products.

2) (Bio)chemical conversion uses chemicals and/or microorganisms (e.g. enzymes) to establish the desired breakdown process of the biomass feedstock into various components. Relevant technologies here are
a.o. hydrolysis, fermentation and anaerobic digestion. These processes require lower temperatures and have lower reaction rates than the thermochemical processes [11].

2.5 The motivation for the QRA in biomass treatment processes

Contrary to what an important part of society thinks, biomass treatment processes are not necessarily safer than those used with oil or coal.

However, as in any process that involves chemical substances and complex industrial processes, accidents can occur.

In fact, as shown in Figures 2.8 and 2.9 [12], over the years the normalized number (with respect to the production of electricity) of major accidents in the biomass sector has grown steadily, while in the case of major accidents in oil refineries, the trend has been the opposite in recent years; this is mainly due to the fact that safety standards and procedures have already been applied in this sector.

For this reason, the application of QRA in this type of processes is essential, in order to improve the safety conditions of workers, equipments and installations.

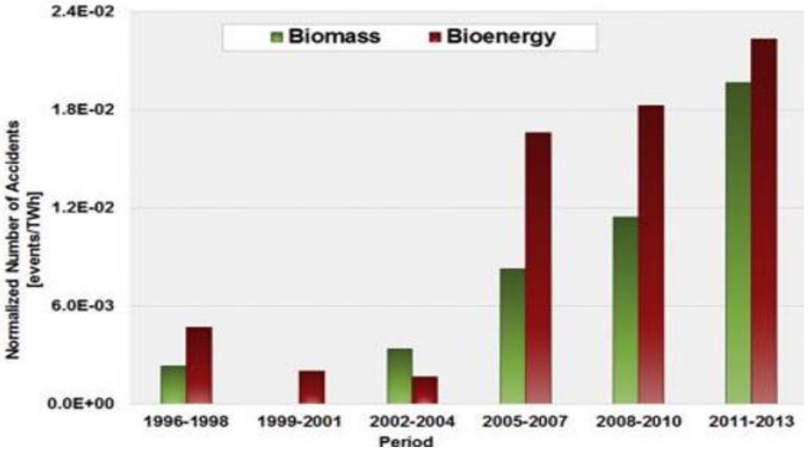


Figure 2.8

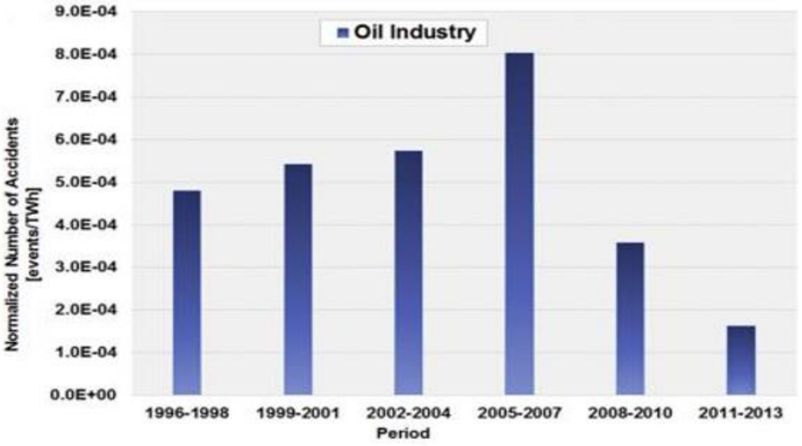


Figure 2.9

3. METHODOLOGY

3.1 The motivation of Quantitative Risk Assessment

The Quantitative Risk Assessment is essential in order to evaluate the risk of several kind of industrial and non-industrial processes and activities, such as the storage of hazardous substances and the transport of fuels. Since the risk is a function that depends on two variables, consequences (damages) and likelihood, QRA has both of them under consideration.

Risk must not be confused either with hazard or with uncertainty. As defined in CCPS [13], the risk is “ a measure of the human injury, environmental damage or economic loss in term of both the incident likelihood and the magnitude of the loss or injury”. Risk already considers the uncertainty (likelihood). As for hazard, in [14] we find hazard defined as “a source of danger.” Risk is the “possibility of loss or injury” and the “degree of probability of such loss.” Hazard, therefore, simply exists as a source. Risk includes the likelihood of conversion of that source into actual delivery of loss, injury, or some form of damage. This idea is symbolically expressed in the form of an equation: $Risk = \frac{Hazard}{Safeguards}$. This equation also brings out the thought that we may make risk as small as we like by increasing the safeguards but may never, as a matter of principle, bring it to zero. Risk is never zero, but it can be small.

3.2 A short view to ARAMIS history and aims

As it is said in [1]: *“In process industries, the identification of possible accident scenarios is a key-point in risk assessment. However, especially in a deterministic approach, mainly worst cases scenarios are considered, often without taking into account safety devices used and safety policy implemented. This approach can lead to an over-estimation of the risk-level and does not promote the implementation of safety systems.*

One of the aims of the ARAMIS project is to develop a methodology able to face this problem. This report describes methods and tools to identify major accidents (without considering safety systems), then to study deeply safety systems, causes of accidents and (qualitative) probabilities, in order to be able to identify Reference Accident Scenarios, which consider safety systems.”

Accidental **R**isk **A**ssessment **M**ethodology for **I**ndustrie**s** (ARAMIS) overall objective is to build up a new Accidental Risk Assessment Methodology for

Industries that combines the strengths of both deterministic and risk-based approaches. Cofounded under the 5th EC Framework Programme, this three-year project started in January 2002, and three years later, the basic methodology was reached and achieved to become a supportive tool to speed up the harmonised implementation of SEVESO II Directive in Europe [15].

3.3 The ARAMIS procedure

In order to achieve the previously mentioned aim, the ARAMIS procedure is performed in several major steps (figure 3.1) [15]:

- Identification of major accident hazards (MIMAH).
- Identification of the safety barriers and assessment of their performances.
- Evaluation of safety management efficiency to barrier reliability.
- Identification of Reference Accident Scenarios (MIRAS).
- Assessment and mapping of the risk severity of reference scenarios.
- Evaluation and mapping of the vulnerability of the plant's surroundings.

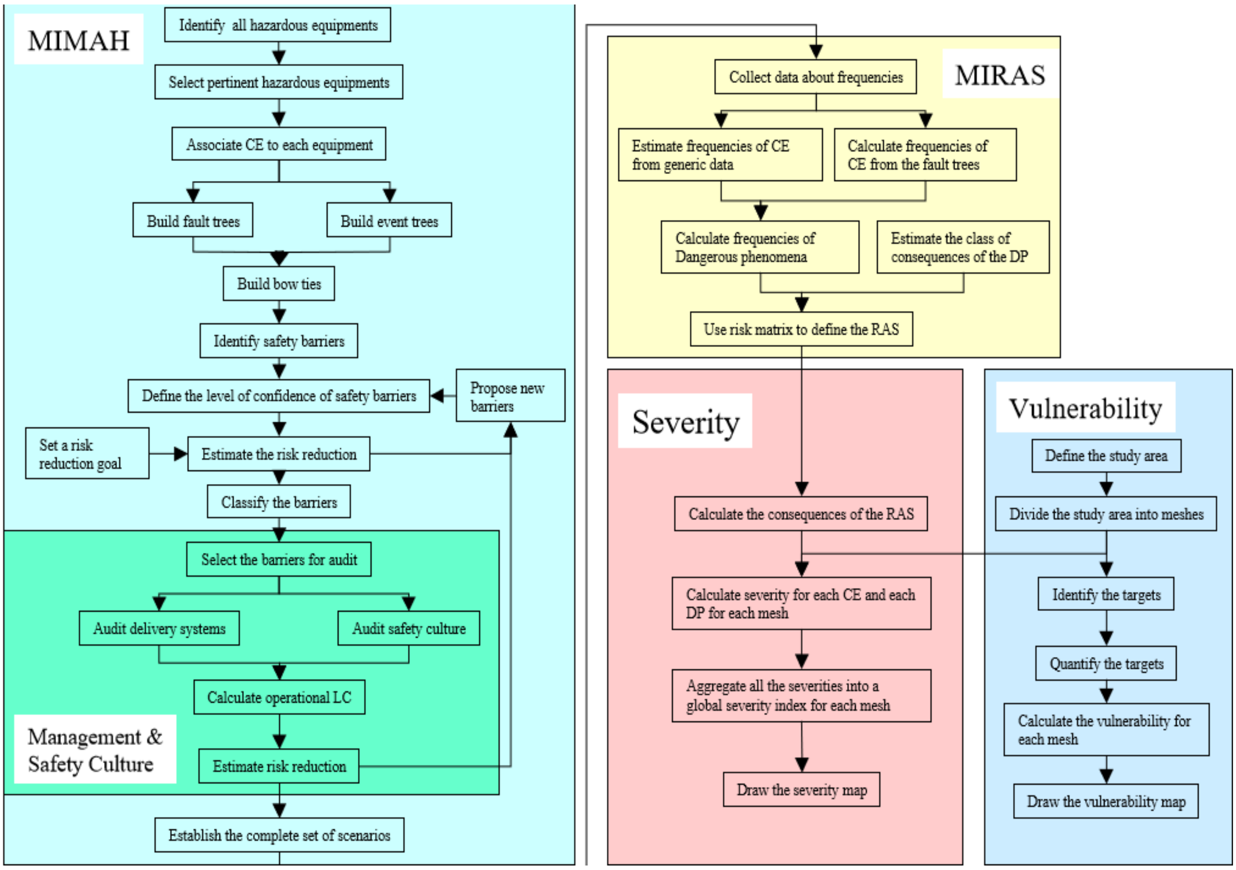


Figure 3.1

There are two main complementary methods applied [1]:

-The first one is the Methodology for the Identification of Major Accident Hazards (MIMAH). It is based mainly on the use of the bow-tie, centred on a critical event and composed of a fault tree on the left and an event tree on the right. The MIMAH methodology defines the maximum hazardous potential of an installation. The term "Major Accident Hazards" must be understood as the worst accidents likely to occur on this installation, assuming that no safety systems (including safety management systems) are installed or that they are ineffective. The major accident hazards identified are only linked with the type of equipment studied and the properties of chemicals handled.

-The second method is called MIRAS (Methodology for the Identification of Reference Accident Scenarios). This method studies the influence of safety devices and policies on scenarios identified by the MIMAH methodology. The deep study of causes of accident, probability levels and safety systems allows to define scenarios more realistic than the Major Accident Hazards. These Reference Accident Scenarios (RAS) represent the real hazardous potential of the equipment, taking into account the safety systems (including safety management system).

3.4 Methodology for the Identification of Major Accident Hazards (MIMAH)

MIMAH is the method for the identification of major accident hazards. It is based mainly on the use of the bow-tie, centred on a critical event and composed of a fault tree on the left and an event tree on the right, as reflected in figure 3.2.

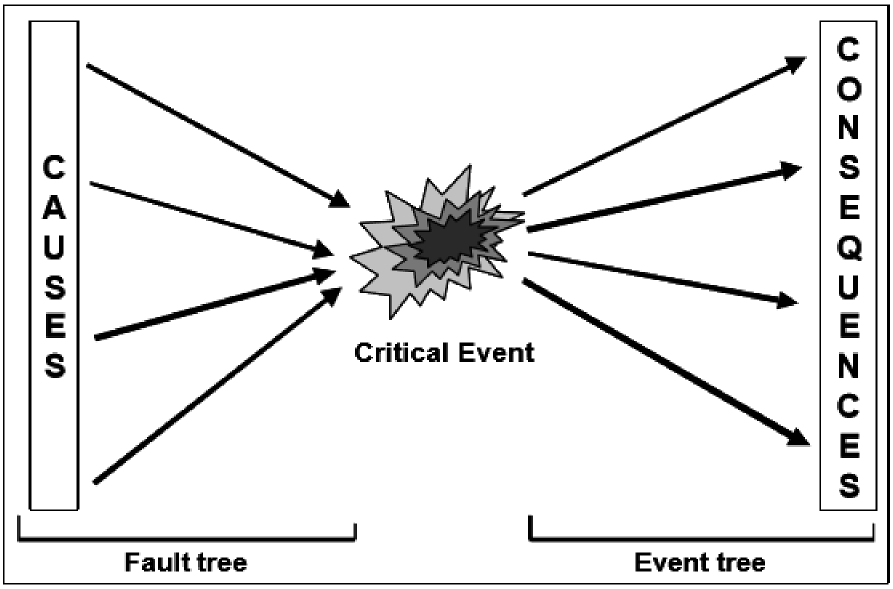


Figure 3.2

It provides a comprehensive methodology to collect the information needed to identify potentially hazardous equipment in the plant and to select relevant hazardous equipments susceptible to generate major accidents [15].

In MIMAH, 7 steps have to be followed:

- Step 1: Collect needed information.
- Step 2: Identify potentially hazardous equipment in the plant.
- Step 3: Select relevant hazardous equipment.
- Step 4: For each selected equipment, associate critical events.
- Step 5: For each critical event, build a fault tree.
- Step 6: For each critical event, build an event tree.
- Step 7: For each selected equipment, build the complete bow-ties.

The procedure is clearly represented in figure 3.3

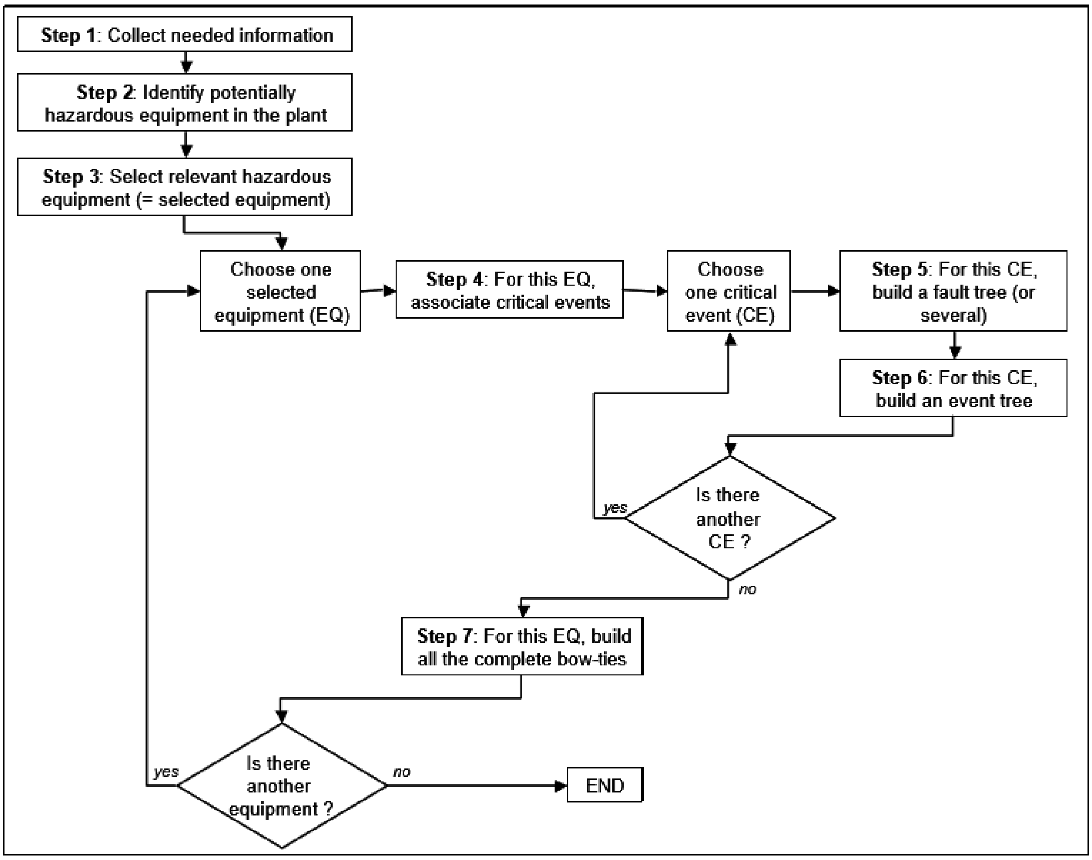


Figure 3.3 [15]

3.4.1 First step of MIMAH procedure: The collection of the needed information

Some information must be collected at the beginning of the MIMAH procedure (general data about the plant in order to have an overview of the plant and of the processes), whereas other data will be being collected as the procedure advances (name, size, handled substances, etc. of the categorized as potentially hazardous equipment).

As for the general data, the required information is the plant layout and a brief description of the processes, the equipment and the pipes, as well as also a list of substances stored or handled in the plant, and the hazardous properties they possess [15].

3.4.2 Second step of MIMAH procedure: The identification of potentially hazardous equipment in the plant

In this second step of MIMAH procedure, a threefold typology (hazardous substances, physical state, equipment) is thus used.

Firstly, a list of the hazardous substances that are present in the plant must be done. These substances may have one (or several) risk phrases that are mentioned in ARAMIS procedure manual. Their classification is performed, in turn, according to the SEVESO II Directive (96/82/EC) and, for each category, risk phrases are associated (namely as defined in the 67/548/EC Directive) (table 3.4).

Category	Risk Phrases
Very toxic	R26, R100
Toxic	R23, R101
Oxidising	R7, R8, R9
Explosive	R1, R2, R3, R4, R5, R6, R16, R19, R44, R102
Flammable	R10, R18
Highly flammable	R10, R11, R17, R30
Extremely flammable	R10, R11, R12
React violently with water	R14, R15, R29, R14/15, R15/29
React violently with another substance	R103, R104, R105, R106
Dangerous for the environment (aquatic)	R50, R51
Dangerous for the environment (non-aq.)	R54, R55, R56, R57, R59

Table 3.4 [15]

Afterwards, it is necessary to draw up a list of the equipment that contains these substances (table 3.5). Four kinds of equipments are defined by ARAMIS procedure:

- Storage unit: unit used for the storage of raw materials, intermediate goods, manufactured products or waste products.

- (Un)loading unit: unit used for inlet and outlet of substances in the establishment, involving transport equipment.

- Pipes networks: piping linking different units are considered as "pipes networks", as well as pipes feeding the flare.

- Process unit: unit used for the processing of substances or for the production of energy used in the establishment.

Finally, it is also necessary to indicate in which physical state the substance can be found in the equipment (solid, liquid, two-phase, gas/vapour).

	Type of equipment
EQ1	Mass solid storage
EQ2	Storage of solid in small packages
EQ3	Storage of fluid in small packages
EQ4	Pressure storage
EQ5	Padded storage
EQ6	Atmospheric storage
EQ7	Cryogenic storage
EQ8	Pressure transport equipment
EQ9	Atmospheric transport equipment
EQ10	Pipe
EQ11	Intermediate storage equipment integrated into the process
EQ12	Equipment involving chemical reactions
EQ13	Equipment devoted to the physical or chemical separation of substances
EQ14	Equipment designed for energy production and supply
EQ15	Packaging equipment
ºEQ16	Other facilities (reboilers, condensers, etc.)

Table 3.5 [15]

As result of this step, a table should be obtained with the following columns:

- Name of the substance

- Hazardous properties of the substance (Risk phrases)

- Name of the equipment in which the substance can be found

- Type of the concerned equipment

- State of the substance in the concerned equipment

This table constitutes the list of potentially hazardous equipment identified on the plant.

It is important to indicate that some equipment could be considered as hazardous one because they are likely to cause a domino effect but do not contain a hazardous substance. These equipments are not considered as potentially hazardous in this methodology [1].

3.4.3 Third step of MIMAH procedure: The selection of relevant hazardous equipment

An equipment containing hazardous substances will be considered as a relevant hazardous equipment if the quantity of hazardous substance that it stores is higher (or at least equal) to a threshold value that depends on the hazardous properties of the substance, as well as its physical state, its possibility of vaporisation and eventually its location with respect to another hazardous equipment in case of possible domino effects.

In the document [16] the method for the selection of relevant hazardous equipments is fully described. This method is based on the “VADE MECUM” methodology used in Walloon Region, in Belgium (DGRNE, 2000).

It is important to highlight that the method must not be applied blindly, since in case that an equipment is dangerous by the presence of a hazardous substance and by the operating conditions inside the equipment, it can be selected as a relevant hazardous equipment and studied according the MIMAH methodology.

These selected equipments will be studied in the following steps of the MIMAH procedure [1].

3.4.4 Fourth step of MIMAH procedure: Association of critical events for each selected equipment

In 3.4 the concept of critical event was mentioned. A critical event can be defined as a Loss of Containment (LOC) or a Loss of Physical Integrity (LPI). On the one hand, LOC definition is quite accurate for fluids, as they usually behave dangerously after release. On the other hand, for solids and more especially for mass solid storage, LPI term, considered as a change of chemical and/or physical state of the substances, is applied.

The document [17] explains deeply the method applied to associate critical events and relevant hazardous equipment. In this method, two matrices are used. One of them crosses the type of equipment and the 12 potentials critical events, whereas the other one crosses the physical state of the substance considered and the 12 potentials critical events. These matrices permit to determine which critical events must be retained for each relevant hazardous equipment.

The mentioned 12 potential critical events considered in the ARAMIS procedure are the following ones (Table 3.6):

	Critical Event	**Description**
CE1	Decomposition	It corresponds to a change of the chemical state of the substance (LPI) by action of an energy/heat source or by reaction with a chemical substance (incompatible reagent). CE1 concerns only solid substances (solid mass storage).
CE2	Explosion	This CE corresponds to a change of physical state of the substance (LPI), either by action of an energy/heat source or a chemical source (incompatible reagent). This change of state implies a combustion of a solid with overpressure generation (or an explosion) due to a violent and spontaneous reaction. CE2 concerns only explosive solid substances (solid mass storage).
CE3	Materials set in motion (entrainment by air)	It refers to a potentially mobile solid (fragmented solid such as dust) exposed to the ambience. This CE takes place in presence of an air vector.
CE4	Materials set in motion (entrainment by a liquid)	Idem to CE3 description, but in this case in presence of a liquid vector.
CE5	Start of fire (LPI)	This CE is associated with substances that have a risk phrase describing a LPI (and also with pyrotechnic substances) and corresponds to the specific reaction between an oxidising substance and a flammable or combustible substance or to the autonomous decomposition of an organic peroxide leading to a fire.
CE6	Breach on the shell in vapour phase	It is a hole with a given diameter on the shell above the liquid level (vapour phase) that can be due to a mechanical stress, e.g., due to external or internal causes. It gives rise to a continuous release.
CE7	Breach on the shell in liquid phase	Idem to CE6 description, but in this case under the liquid level.
CE8	Leak from liquid pipe	It refers to a hole with a diameter that corresponds to a given percentage of the nominal one of the pipe and takes place on pipes that transports a liquid substance.
CE9	Leak from gas pipe	Idem to CE8 description, but in this case transporting a gaseous substance.
CE10	Catastrophic rupture	This CE is the complete failure of the equipment, leading to the absolute and instantaneous release of the stored substance. It is possible that this rupture leads to overpressure and missiles ejection.
CE11	Vessel collapse	The consequence is the same that the one explained in CE10, but in this case the collapse does not lead to overpressure generation nor missiles ejection.
CE12	Collapse of the roof	Finally, this CE may be due to a decrease of the internal pressure in the vessel, leading to the collapse of the mobile roof under the effect of atmospheric pressure

Table 3.6

For CE6, 7, 8 and 9, ARAMIS proposes to consider, by default, sizes for which generic frequencies of critical (Table 3.7) [1]

Size of breach/leak	CE6 and 7: Breaches. Diameter of the breach	CE8 and 9: Leaks Diameter of the leak
Large	100 mm diameter	Full bore rupture
Medium	35 to 50 mm diameter (or diameter of the fitting)	22cto 44% of the pipe diameter
Small	10 mm diameter	10% of the pipe diameter

Table 3.7

3.4.5 Fifth step of MIMAH procedure: The construction of a fault tree for each CE

(I will describe this step briefly since it is not a purpose of my thesis to perform fault trees).

The following step of the MIMAH procedure is the performance of a fault tree, which is constituted by four types of events:

- The Undesirable Events designate the deepest level of causes in the fault trees. The UE are, most of the time, generic events which concern the organisation or the human behaviour, which can always be ultimately considered as a cause of the critical event.

- The Detailed Direct Causes are either the events that can provoke the direct causes or, when the labelling of the direct cause is too generic, the detailed direct cause provides a precision on the exact nature of the direct cause.

- The Direct Causes are the immediate causes of the Necessary and Sufficient Causes (NSC). For a given NSC, the list of direct causes tends to be as most complete as possible.

- The Necessary and Sufficient Causes designate the immediate causes that can give rise to a critical event. For a given critical event, the list of NSC is supposed to be exhaustive.

As seen in the standard structure of a fault tree, represented by figure 3.8, these events are linked by means of AND OR gates.

There are 14 kind of fault trees considered in the ARAMIS procedure (and fully described in [18]) that are linked with the critical events described in 3.4.4 [1].

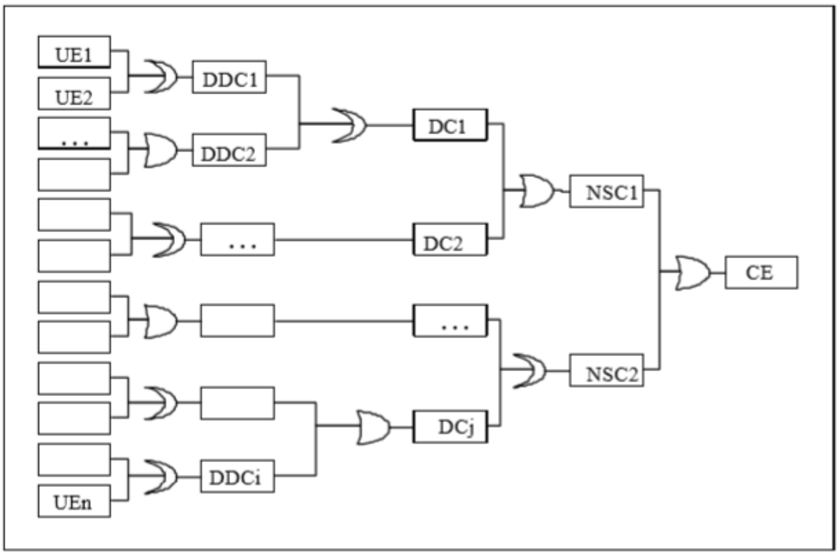


Figure 3.8 [1]

3.4.6 Sixth step of MIMAH procedure: The construction of an event tree for each CE

The penultimate step of MIMAH methodology is the development of an event tree for each CE that has been previously determined. This tree is placed in the right part of the Bow-tie.

As in last step, the typical structure of this kind of tree is shown in figure 3.9. It is important to highlight that AND OR gates are implicitly present in event trees but are not drawn at this stage. Anew, four types of events are found in the tree´s structure:

-Secondary Critical Events (SCE): For example, a pool formation, a jet, a cloud.

-Tertiary Critical Events (TCE): For example, a pool ignited or a pool dispersion.

-Dangerous Phenomena (DP), such as pool fire, tank fire, jet fire, toxic cloud and fireball.

-Major Events (ME) are defined as the significant effects from the identified DP on targets (human beings, structure, environment,…). The possible significant effects are thermal radiation, overpressure, toxic (or eco-toxic in case of effects on the environment instead of on the human beings) effects and missiles.

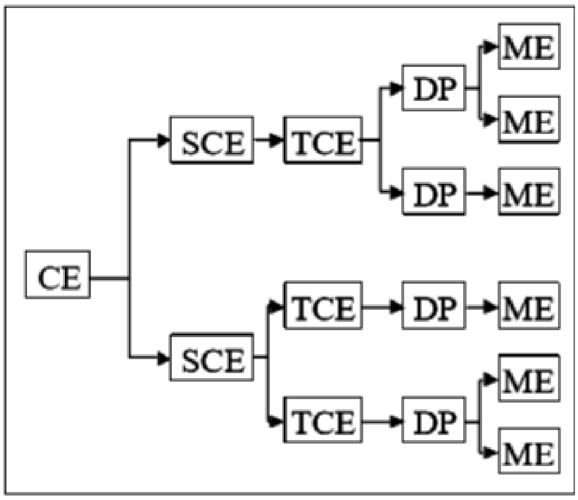


Figure 3.9 [1]

The procedure to build up an event tree in a proper way is explained in detail in document [19]. Anyway, in Figure 3.10 the schematized procedure is reflected.

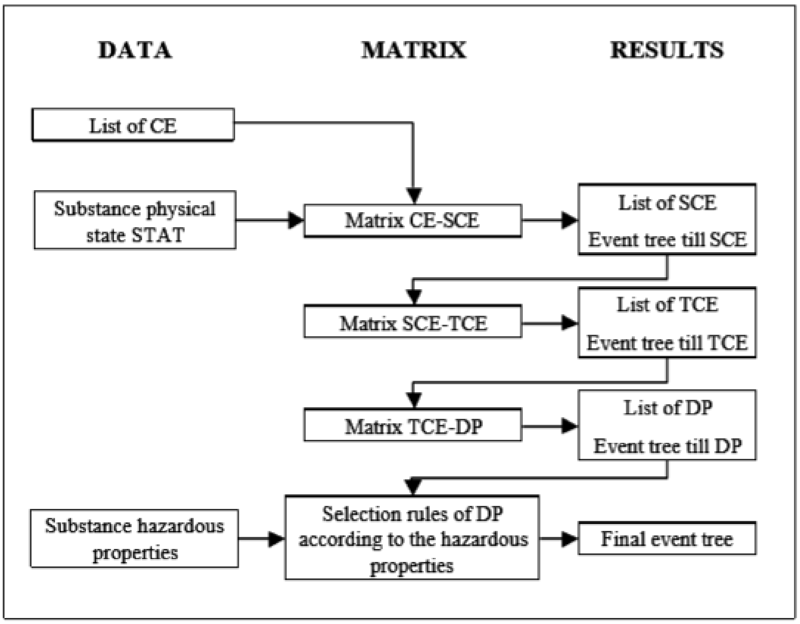


Figure 3.10 [1]

3.4.7 Seventh step of MIMAH procedure: For each selected equipment, build the complete bow-ties.

The final step performed in MIMAH methodology is the construction of complete bow-ties for each selected equipment.

For each selected equipment, the number of bow-ties is equal to the number of fault trees developed. This number can be higher than the number of critical events because, for some critical events, more than one fault tree has to be built.

These bow-ties, result of the whole MIMAH method, are major accident scenarios, assuming that no safety systems (including safety management systems) are installed or that they are ineffective. They are the basis for the application of the MIRAS methodology.

3.5 Methodology for the Identification of Reference Accident Scenarios (MIRAS)

After MIMAH procedure application, it is the turn to implement MIRAS procedure, which aim is to choose Reference Accident Scenarios (RAS) among the Major Accident Hazards identified (MAH) with MIMAH. The Reference Scenarios will be those which have to be modelled to calculate the Severity, which in turn will be compared with the vulnerability of the surroundings of the plant.

To achieve this goal, it is necessary, for each bow-tie built with MIMAH, to obtain the frequency per year of the critical event, either by an analysis of the fault tree or by using generic critical events´ frequencies, as well as identify the possible consequences of the major accident(s), consider the safety systems, the safety management and their effects, and develop the event tree previously performed through MIMAH procedure to consider the safety systems and the "transmission" probabilities.

MIRAS procedure consists in the application and the development of the 8 steps that are indicated below for each bow-tie that has been generated by means of MIMAH methodology [1]:

- Step 1: Collect needed data
- Step 2: **Make a choice** between step 3 or step 4
- Step 3: Calculate the frequency of the critical event by means of the analysis of the fault tree
  - Step 3.A: Estimate initiating events frequencies (or probabilities)
  - Step 3.B: Identify safety functions and safety barriers on the fault tree
  - Step 3.C: Assessment of the performances of safety barriers
  - Step 3.D: Calculate the frequency of the critical event
- Step 4: Estimate the frequency of the critical event by means of generic critical events frequencies
- Step 5: Calculate the frequencies of Dangerous Phenomena
- Step 6: Estimate the class of consequences of Dangerous Phenomena
- Step 7: Use the risk matrix to select Reference Accident Scenarios
- Step 8: Prepare information for the calculation of the Severity

MIMAS procedure is schematically represented in Figure 3.11

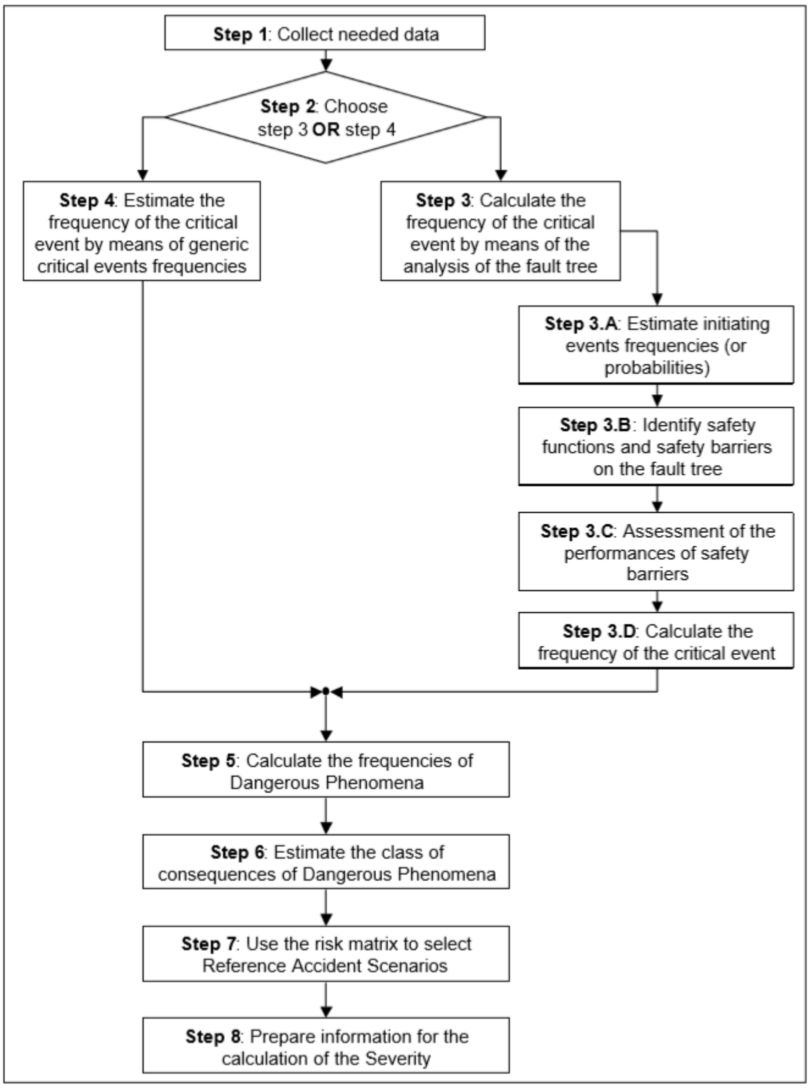


Figure 3.11 [1]

3.5.1 First step of MIRAS procedure: The collection of the needed data

As occurred in MIMAH procedure, the first step of MIRAS procedure consists in the recollection of data that is going to be necessary through the application of this methodology. This data can be collected at the beginning, but it is also possible to keep recollecting it progressively at the same time that the procedure advances [1]

3.5.2 Second step of MIRAS procedure: The selection of the next step

In this step, a decision must be taken: to keep on with MIMAS procedure applicating the Step 3, or applicating the Step 4. Both have the same objective, which is the estimation of the frequency per year of the critical event (CE) considered for each bow-tie built by means of MIRAH methodology application.

The Step 3 consists in carrying out a full analysis of the fault tree built in the fifth step of MIRAH procedure considering the influence of safety barriers in order to calculate the frequency of the CE, whereas the Step 4, which is shorter, estimates the frequency of the CE thanks to the data given in [32]. Step 3 is preferred if data is available, since it takes into account the safety systems present in the plant, what makes it more accurate and reliable [1].

3.5.3 Third step of MIRAS procedure: The calculation of the frequency of the CE through the analysis of the fault tree

If the next step performed in MIRAS methodology is the Step 3 the reader will have to follow four steps.

The first step is Step 3.A, that consists in the determination of the frequencies (or probabilities) of the initiating events that must be placed at the beginning of the fault tree. An initiating event can be an undesirable event, a detailed event cause, a direct cause or a necessary and sufficient cause (depending on the level of development of the fault tree) since it is defined as the first cause upstream of each branch leading to de critical event. Even though [29] provides a general point of view of the available data about the frequencies of these initiating events, it is important to take under consideration that it is advisable to apply the specific data of the plant (if it is available) or try to estimate them with the plant staff if it is possible.

Secondly, the reader must identify the safety functions and safety barriers on the fault tree (Step 3.B). A check-list, given in [30], helps the reader to identify the functions and barriers associated with each type of event which can be found in the generic fault and event trees. On the one hand, a safety function is a technical or organisational action (not an object or a physical system) that must be carried out to avoid (make the event impossible to occur), prevent (to hinder its occurrence) or to control or to limit (reduce the magnitude) its occurrence. In the fault tree, the different possible actions of safety functions are to prevent the occurrence of an event and reduce the probability of an event, whereas in the case of the event tree they are to avoid, prevent or reduce the consequences of the critical event and to mitigate its effects on the surroundings of the equipment. On the other hand, a safety barrier can be a physical system, such as an emergency control system or a prevention system, or a human action. Safety barriers help the safety functions to be achieved since they are the “how” to implement them. They can be classified into passive (permanently functioning), activated (must be automated or activated manually), human (the knowledge of the operator is essential for its effectiveness) and symbolic barriers (need to be interpreted). In order to identify these safety barriers, each event of a tree, branch per branch, must be examined and the following question should be asked: "Is there a safety barrier which avoids, prevents or controls this event ?". If yes, this safety barrier must be placed upstream of an event if it avoids or prevents the occurrence of the event, whereas it must be placed downstream if it controls it.

After that, an assessment of the performance of safety barriers (Step 3C) must be carried out. This performance must obey to three parameters: the level of confidence (LC), defined as the probability of failure of a safety barrier considering a certain safety function, effectiveness and response time previously imposed; the effectiveness (E), which is the ability to perform a safety function for a determined period (it can be expressed in percentage) in a non-degraded mode, and the response time (RT), which is the duration between the beginning of the safety barrier and the complete achievement of the safety function that it carries out. The way to assess these parameters is explained in [31]. It is important to highlight that the level of confidence of the performance of a safety barrier may decrease over time.

The last step (Step3D) consists in the calculi of the frequency of the CE associated to the analysed fault tree. Since the gate-to-gate method applied with this purpose is quite complex, some rules and advices must be followed [1].

3.5.4 Fourth step of MIRAS procedure: The estimation of the frequency of the CE through generic CE frequencies

If the reader chooses this step instead of the previously mentioned Step 3 because it is not possible to calculate the frequency of the CE through the analysis of the fault tree, he (or she) will have to determine it by means of generic critical event frequencies.

In this sense, the document [32] provides the results of a bibliographic review of published data related to this theme. However, the reader must be conscious to the fact that these frequencies are totally **generic**, since they are given for a standard security level, which is not specified, and the age, the state and the number of safety barriers are unknown. That is the reason why the available data must be carefully handled, and this step performed with attention.

3.5.5 Fifth step of MIRAS procedure: The calculation of the frequencies of Dangerous Phenomena

The output of this step consists in a list of dangerous phenomena (DP) associated to each CE determined by means of MIMAH procedure, and which contains the frequencies of these dangerous phenomena.

In order to obtain these frequencies, the frequencies of the critical events obtained by means of MIMAH procedure, the transmission probabilities and the AND OR gates present (no explicitly represented) that link the events of the event tree must be combined. As shown in Figure 3.12, AND gates are placed between an event and its **simultaneous** consequences, which have the same frequencies as it is seen, whereas OR gates are placed between an event and its consequent events, with the difference that in this case one of the consequent events may occur, but not the others (i.e. these events linked by the OR gate are mutually exclusive), what is shown in Figure 3.13. The frequency of each event downstream the OR gate is the result of the multiplication of the upstream event frequency, and the correspondent transmission (conditional) probability (Pi).

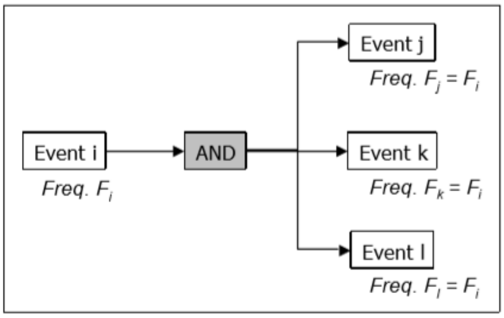


Figure 3.12

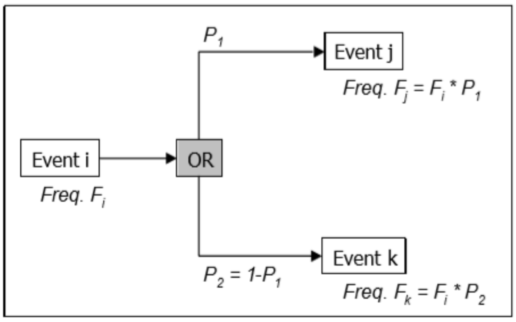


Figure 3.13

Of course, the presence of safety barriers has an important influence. The method applied to identify them is identical to the one used for the fault tree and explained in 3.5.3 section. This identification can be made with the industrialists, with the help of "process and instrumentation diagrams" and "flow diagrams" or with any other existing documentation. After that, and as in 3.5.3, the reader will have to assess the performance of this safety barriers as explained in [31]. Depending in the type of barrier (“prevent”, “control” or “limit” barrier), a specific method must be used to take the barrier into account in the event tree.

3.5.6 Sixth step of MIRAS procedure: The estimation of the class of consequences of Dangerous Phenomena

Because the selection of Reference Accident Scenarios (RAS) is based on the study and the evaluation of the frequency of DP, as well as their potential consequences, now it becomes necessary the obtention of these consequences. The evaluation of the consequences is qualitative, so the quantitative analysis is performed in the ARAMIS procedure **after** the selection of RAS.

This qualitative assessment is based on the classification that MIRAS procedure makes about the possible consequences of the dangerous phenomena, which is reflected in the following Table 3.14.

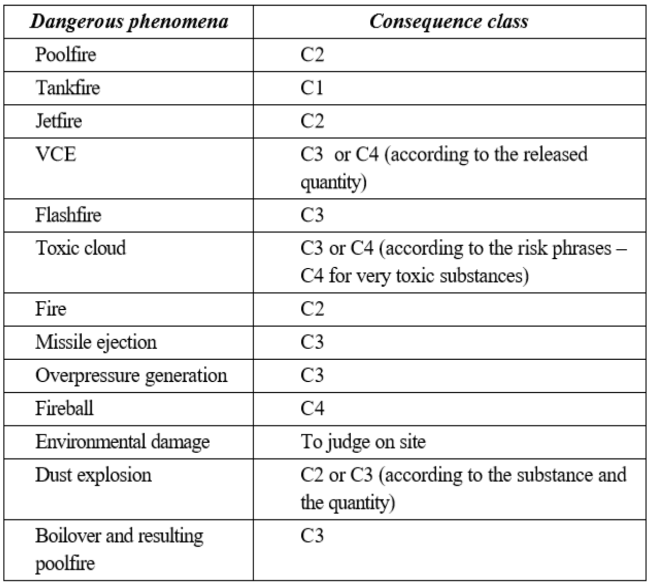
CONSEQUENCES		**CLASS**
Effects on humans	**Effects on the environment**	**Ranking**
No injury or slight injury with no stoppage or work	No action necessary, just watching	C1
Injury leading to a hospitalisation > 24 hours	Serious effects on environment, requiring local means of intervention	C2
Irreversible injuries or death inside the site, Reversible injuries outside the site	Effects on environment outside the site, requiring national means	C3
Irreversible injuries or death outside the site	Irreversible effects on environment outside the site, requiring national means	C4

Table 3.14 [1]

These classes are defined according to the environmental effects on humans and the environment, as well as the domino effect, which consists in that if a dangerous phenomenon induces another one, and this last one has a higher class of consequence that the triggering phenomenon, then the class of consequence of the triggering one will be raised to the class of the triggered dangerous phenomenon. A class of consequence must be assigned to each dangerous phenomenon obtained in the development of the event trees.

Depending on the presence of safety barriers, dangerous phenomenon can be classified into “fully developed” if no safety system is present (no mitigation of effects), “limited effects” if the barrier acts in the event tree, but not directly after the CE, and “limited source term” when the consequences are limited by a safety barrier applied after the CE.

If there is a “limited effects” or “limited source term” DP, the class of consequence may be decreased, whereas if there is a “fully developed” one, the consequence class and DP are linked as shown in Table 3.15. Here, DP correspond to a specific class of consequence in which the intensity level does not influence.



Dangerous phenomena	*Consequence class*
Poolfire	C2
Tankfire	C1
Jetfire	C2
VCE	C3 or C4 (according to the released quantity)
Flashfire	C3
Toxic cloud	C3 or C4 (according to the risk phrases – C4 for very toxic substances)
Fire	C2
Missile ejection	C3
Overpressure generation	C3
Fireball	C4
Environmental damage	To judge on site
Dust explosion	C2 or C3 (according to the substance and the quantity)
Boilover and resulting poolfire	C3

Table 3.15 [1]

As described in 4.2.5, in the present study this step is complemented and enhanced by means of the use of an informatic tool, the DNV-GL Phast, in order to tackle the study of the classes of consequences in a quantitative way.

3.5.7 Seventh step of MIRAS procedure: The use of the risk matrix to select Reference Accident Scenarios

The frequency of each dangerous phenomenon was calculated in step 5, and thanks to step 6, a class of consequence is associated to each dangerous phenomenon found in the event trees. So, after performing these steps, the seventh one allows to evaluate the Reference Accident Scenarios (RAS) that will be modelled to calculate the severity.

This aim is performed by means of a Risk Matrix, which aspect is reflected in the Figure 3.16. The X axis contains the four classes of consequences previously mentioned, whereas the Y axis reflects the frequency of the Dangerous Phenomena.

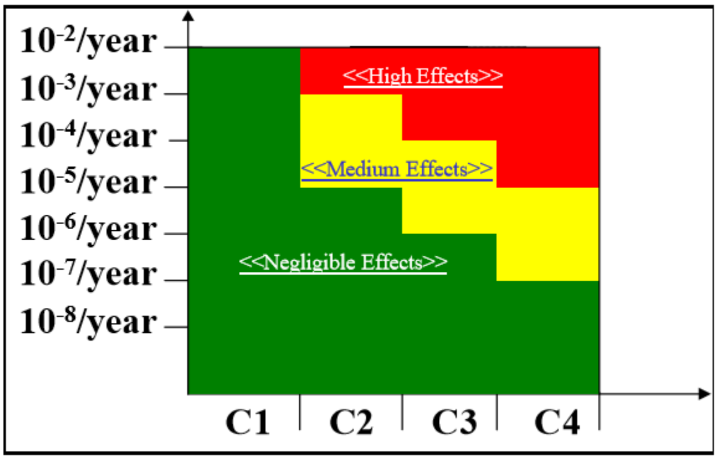


Figure 3.16 [1]

As seen in the Figure 3.16, three different zones can be differentiated:

-The green one, called “Negligible effects” zone corresponds to dangerous phenomena with a low enough frequency and/or consequence to consider that they will have no effects on the severity.

-As for the yellow zone (“Medium effects” zone), dangerous phenomena that will probably affect the severity (and so selected to be modelled afterwards) are placed here. So, these DP are considered as RAS.

-Finally, the red zone, known as “High effects” zone, corresponds to those dangerous phenomena that will have undoubtedly effects on the severity, so they are obviously selected to me modelled for the severity calculations, and correspond to Reference Accident Scenarios.

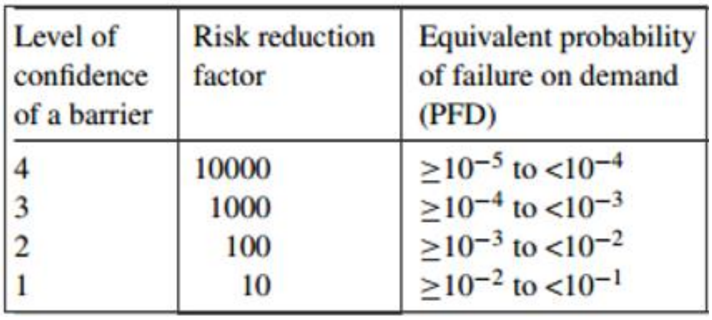
The document [33] provides the necessary information to build a Risk Matrix. It is necessary to highlight that a Risk Matrix cannot be used blindly, since if the reader considers that a dangerous phenomenon placed in the green zone must be modelled, then it can be done.

3.5.8 Eighth step of MIRAS procedure: The preparation of the information for the calculation of the Severity

This last step consists in the collection of the necessary information about every reference accident scenario (i.e. those dangerous phenomena that were considered to probably affect the severity, and so placed in the “medium effects” zone, or considered as determinant to the severity, and so placed in the “high effects” zone) for the severity calculi.

This collected information must refer to different aspects, such as the equipment type, the properties of the hazardous substance, the temperature and pressure conditions inside the equipment, the critical event, the wind rose, the characteristics of the safety barriers (if they are present) and the description of the surroundings of the plant (for example, if there are schools or hospitals nearby).

Moreover, ARAMIS procedure contemplates a useful tool that can be used in order to determine the level of confidence of the safety barriers that is required to have an assumable risk level. Each level of confidence has a linked risk reduction. The relation among them is shown in Figure 3.16.



Level of confidence of a barrier	Risk reduction factor	Equivalent probability of failure on demand (PFD)
4	10000	$\geq 10^{-5}$ to $< 10^{-4}$
3	1000	$\geq 10^{-4}$ to $< 10^{-3}$
2	100	$\geq 10^{-3}$ to $< 10^{-2}$
1	10	$\geq 10^{-2}$ to $< 10^{-1}$

Figure 3.16

The previously mentioned tool is known as Risk Graph, and its way of application is deeply described in the document [34]. This is a helpful tool, especially in the design phase. It was finally not performed in the present study.

The reason is that, as being a process that is found at its design stage and not at its operating stage, only a limited information is provided. So, it was finally decided not to elaborate the risk graphs that would result from the performance of this step.

4. ARAMIS PROCEDURE APPLICATION TO THE LEVULINIC ACID OBTAINMENT PROCESS

4.1 Furfural as a solvent in a 3-distillation column: MIMAH procedure application

4.1.1 MIMAH procedure: first step

The feed mixture and the furfural solvent are introduced into the extractor (F-EX) to generate a water-rich phase as the top stream and solvent-rich phase containing mainly furfural, LA and formic acid as the bottom stream. The solvent-rich phase is then fed to the F-C1 to deliver the light boiling azeotrope of furfural and water as the overhead whereas the bottom stream contains formic acid, furfural and LA. The overhead of F-C1 is condensed and naturally split into two liquid phases, aqueous and furfural, by a decanter (Dec). The furfural phase is recycled back to the F -C1. The bottom of F-C1 is then introduced into the F-C2 to collect formic acid as the distillate, whereas the bottom stream, that is composed by furfural and LA, is fed into the F-C3. The function of F-C3 is to separate LA as the bottom product and furfural as the top product.

Interestingly, in this process, furfural, which is one of the products, was used as the extraction solvent. Furthermore, the formation of only two azeotropes means the furfural system is less complicated than others, such as the octanol and MIBK processes, which have five azeotropes, and it requires a lower amount of energy. However, the LA extraction ability of furfural is lower than that of MIBK and octanol, what results in a higher amount of furfural required than the amount required for MIBK and octanol.

This industrial process is fully represented by Figure 4.1. The considered biomass inlet mass flow is 2500 tons per day (TPD) in order to make a comparison with available data provided by the professor. So, the Figure 4.1 basically shows the process schematized, but mass flow numbers differ from the ones applied in this work

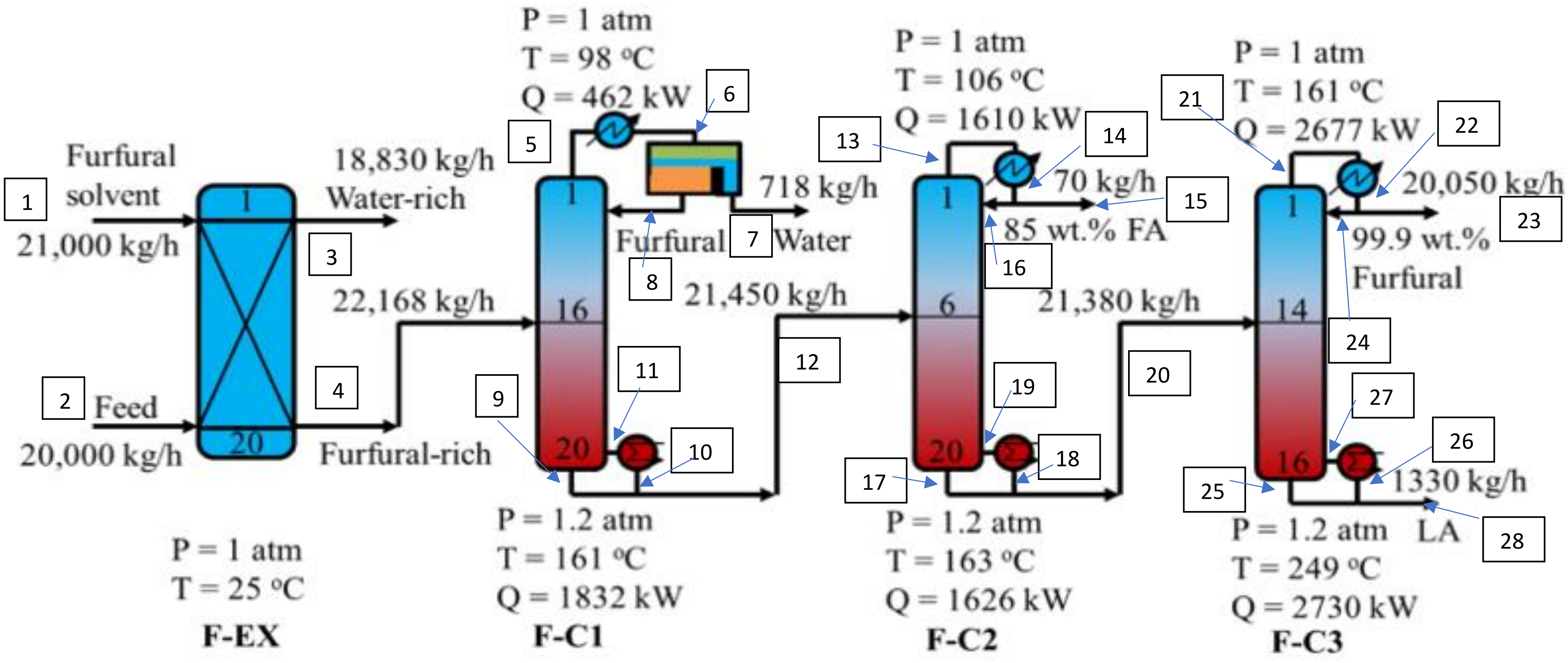

P = 1 atm
T = 98 °C
Q = 462 kW
P = 1 atm
T = 106 °C
Q = 1610 kW
P = 1 atm
T = 161 °C
Q = 2677 kW
Furfural solvent
21,000 kg/h
18,830 kg/h
Water-rich
22,168 kg/h
Feed
20,000 kg/h
Furfural-rich
718 kg/h
Furfural
Water
21,450 kg/h
70 kg/h
85 wt.% FA
21,380 kg/h
20,050 kg/h
99.9 wt.%
Furfural
1330 kg/h
LA
1
20
1
16
20
1
6
20
1
14
16
P = 1 atm
T = 25 °C
F-EX
P = 1.2 atm
T = 161 °C
Q = 1832 kW
F-C1
P = 1.2 atm
T = 163 °C
Q = 1626 kW
F-C2
P = 1.2 atm
T = 249 °C
Q = 2730 kW
F-C3
1
2
3
4
5
6
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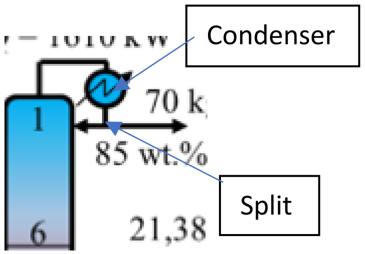
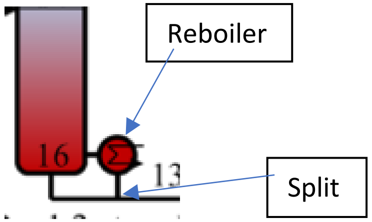
Figure 4.1 [20]


1610 kW
Condenser
70 k
1
85 wt.%
Split
6
21,38


Reboiler
16
13
Split

In the following table 4.2 the industrial equipment is summarized, as well as temperature and pressure conditions, outlet mass flow rate and the composition of the outlet stream:

Nº	Unit	State	Temperature (ºC)	Pressure (atm)	Outlet mass flow rate (kg/h)	Composition of the outlet stream (%)
1	Pipe 1	Liquid	25	1	109375 (Furfural solvent)	---
2	Pipe 2	Liquid (triturated solid biomass with water)	25	1	104166,67 (Biomass)	---
EX	Extractor	Liquid	25	1	98083,33 (Water-rich) 115484,33 (Furfural-rich, of which 104427,08 is Furfural, 364,58 is FA 6927,083 LA and 3739,58 is Water)	Water = 46 Furfural-rich = 54 (Water=1,75 FA=0,17 LA=3,25 Furfural=48,90)
3	Pipe 3	Liquid	25	1	98083,33 (Water-rich)	---
4	Pipe 4	Liquid	25	1	111718,75 (Furfural-rich, of which 104427,08 is Furfural, 364,58 is FA and 6927,083 LA), 3739.58 (Water)	Water= 3,24 Furfural-rich= 96,76 (FA= 0,316 LA= 6 Furfural= 90,44)
DC1	First distillation column	Vapour/Liquid	161	1,2	104427,08 (Furfural, of which 520,83 go to pipe 5), 364,58 (FA), 6927,083 (LA) and 3739,58 (Water to pipe 5),	Water= 3,24 Furfural-rich= 96,76 (FA= 0,316 LA= 6 Furfural= 90,44)
5	Pipe 5	Vapour	161	1,2	3739,58 (Water) and 520,83 (Furfural)	Water= 87,78 Furfural= 12,22
Condenser 1	Condenser 1	Vapour→Liquid	161→98	1	3739,58 (Water) and 520,83 (Furfural)	Water= 87,78 Furfural= 12,22
6	Pipe 6	Liquid	98	1	3739,58 (Water) and 520,83 (Furfural)	Water= 87,78 Furfural= 12,22
DEC	Decanter	Liquid	98	1	3739,58 (Water) and 520,83 (Furfural)	Water (87,78) and furfural, 12,22)
7	Pipe 7	Liquid	98	1	3739,58 (Water, out of the process)	Water=100
8	Pipe 8	Liquid	98	1	520,83 (Furfural, recirculated)	Furfural=100
9	Pipe 9	Liquid	161	1,2	104427,08 (Furfural), 364,58 (FA), 6927,083 (LA)	FA=0,326 LA=6,20 Furfural= 93,47

10	Pipe 10	Liquid	161	1,2	---	---
Reboiler 1	Reboiler 1	Liquid→Vapour	161→165	1,2	---	---
11	Pipe 11	Vapour	165	1,2	---	---
12	Pipe 12	Liquid	161	1,2	104427,08 (Furfural), 364,58 (FA), 6927,083 (LA)	FA=0,326 LA=6,20 Furfural= 93,47
DC2	Second distillation column	Vapour/Liquid	163	1,2	104427,09 (Furfural, of which 1041,67 go to the pipe 13), 364,58 (FA) and 6927,08 (LA)	FA = 0,326 LA= 6,20 Furfural= 93,47
13	Pipe 13	Vapour	163	1,2	1041,67 (Furfural) 364,58 (FA)	Furfural= 74,07 FA= 25,93
Condenser 2	Condenser 2	Vapour→Liquid	163→106	1	1041,67 (Furfural) 364,58 (FA)	Furfural= 74,07 FA= 25,93
14	Pipe 14	Vapour/Liquid	106	1	1041,67 (Furfural) 364,58 (FA)	Furfural= 74,07 FA= 25,93
15	Pipe 15	Vapour	106	1	364,58 (FA, out of the process)	FA= 100
16	Pipe 16	Liquid	106	1	1041,67 (Furfural, recirculated)	Furfural= 100
17	Pipe17	Liquid	163	1.2	104427,08 (Furfural) 6927,08 (LA)	Furfural= 93,78 LA= 6,22
18	Pipe 18	Liquid	163	1.2	---	---
Reboiler 2	Reboiler 2	Liquid→Vapour	163→170	1,2	---	---
19	Pipe 19	Vapour	170	1,2	---	---
20	Pipe 20	Liquid	163	1,2	104427,08 (Furfural) 6927,083 (LA)	Furfural= 93,78 LA= 6,22
DC3	Third distillation column	Vapour/Liquid	249	1,2	104427,08 (Furfural) 6927,083 (LA, of which 260,417 go to the pipe 21)	Furfural= 93,78 LA= 6,22
21	Pipe 21	Vapour	249	1,2	104427,08 (Furfural), 260,417 (LA)	Furfural= 99,75 LA= 0,25
Condenser 3	Condenser 3	Vapour→Liquid	249→161	1	104427,08 (Furfural), 260,417 (LA)	Furfural= 99,75 LA= 0,25
22	Pipe 22	Liquid	161	1	104427,08 (Furfural), 260,417 (LA)	Furfural= 99,75 LA= 0,25
23	Pipe 23	Liquid	161	1	104427,08 (Furfural, end of process)	Furfural= 100
24	Pipe 24	Liquid	161	1	260,417 (LA, recirculated)	LA= 100
25	Pipe 25	Liquid	249	1,2	6927,083 (LA)	LA= 100
26	Pipe 26	Liquid	249	1,2	---	---
Reboiler 3	Reboiler 3	Liquid→Vapour	249→260	1,2	---	---
27	Pipe 27	Vapour	260	1,2	---	---
28	Pipe 28	Liquid	249	1,2	6927,0833 (LA)	LA=100

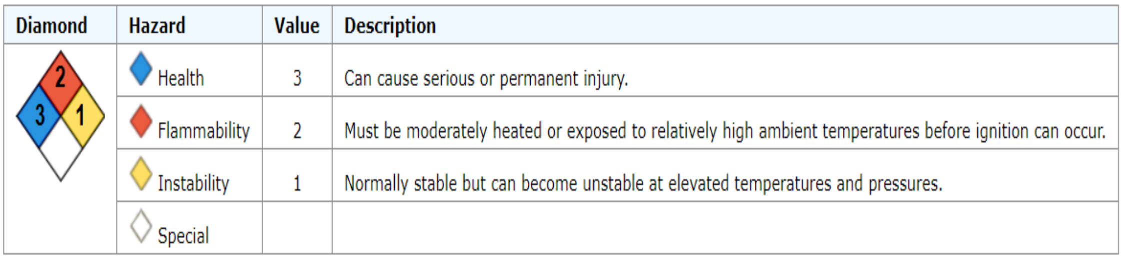
Table 4.2 [20] and [21]

4.1.2 MIMAH procedure: second step

Following the indications given in the point 3.4.2, after collecting the data showed in the 4.1.1 a table must be performed to identify the potentially hazardous equipment in the plant.

Next, I will describe some properties of the hazardous substances that are handled in the process:

1. Furfural ($C_5H_4O_2$): It is a colourless, oily liquid that turns yellow to brown on exposure to air and light and resinifies. Its molecular weight is 96.085 g/mole. There is inadequate evidence in humans for the carcinogenicity of furfural, so it is not classifiable as to its carcinogenicity to humans (but it is confirmed as animal carcinogen). It causes generally throat and eye irritation, depending on the concentration, and it is especially dangerous for persons with chronic respiratory, skin diseases. It also gives rise to skin irritation. LC50 Rat inhalation value is 756 mg/cu m (189 ppm) /1 hour, and LD50 Dog oral value is 950 mg/kg. The boiling point is 161.7°C, whereas the melting point is -38,1°C. The LFL is 2.1% by volume, and the UFL is 19.3% by volume. It is a flammable liquid. Its ingestion is very harmful. The flash point temperature is 60°C (closed cup), and the autoignition temperature is 316°C. An exothermic polymerization of almost explosive violence can occur upon contact with strong mineral acids or alkalis, and it can react with oxidizing materials. The value of the lethal concentration is $LC_{50} = 1{,}63\ ppm\ (mg/l)$ on rats and after 4h of exposure [42],whereas the value of the IDLH is 100 ppm [24]. The density is 1160 kg/m^3at 25°C and 1 atm, whereas the molecular weight is 96,08 g/mol. Its soil mobility is estimated as 40(SRC), what means a very high mobility in soil [23].



Diamond	Hazard	Value	Description
	Health	3	Can cause serious or permanent injury.
	Flammability	2	Must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.
	Instability	1	Normally stable but can become unstable at elevated temperatures and pressures.
	Special		

Figure 4.3[24]

The hazardous properties of this substance are:

-H226: Flammable liquid and vapour. (R10)

-H301: Toxic if swallowed. (R25)

-H312: Harmful in contact with skin. (R21)

-H315: Causes skin irritation. (R38)

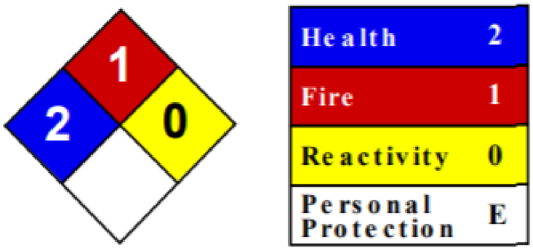
-H319: Causes serious eye irritation. (R36)

-H331: Toxic if inhaled. (R23)

-H335: May cause respiratory irritation. (R37)

-H351: Suspected of causing cancer. (R45)

2. Levulinic Acid ($C_5H_8O_3$): Its molecular weight is 116.12 g/mole. It is very hazardous in case of skin contact (irritant), of eye contact (irritant), while hazardous in case of ingestion (it is important not to induce vomiting) or inhalation. Inflammation of the eye is characterized by redness, watering, and itching. Skin inflammation is characterized by itching, scaling, reddening, or, occasionally, blistering. The autoignition temperature value is not available, as well as neither its flammable limits. Its flash point is at 137°C (closed cup). It is compulsory to keep it in a cool and dry place. The LD50 value is 1850mg/kg (on Rats). The density is 1140 kg/m^3at 25°C and 1 atm, whereas the molecular weight is 116,11 g/mol. The boiling point and the melting point are 245°C and 34°C, respectively [25], [26].



Health	2
Fire	1
Reactivity	0
Personal Protection	E

Figure 4.4 [25]

The hazardous properties of this substance are:

-H302: Harmful if swallowed. (R22)

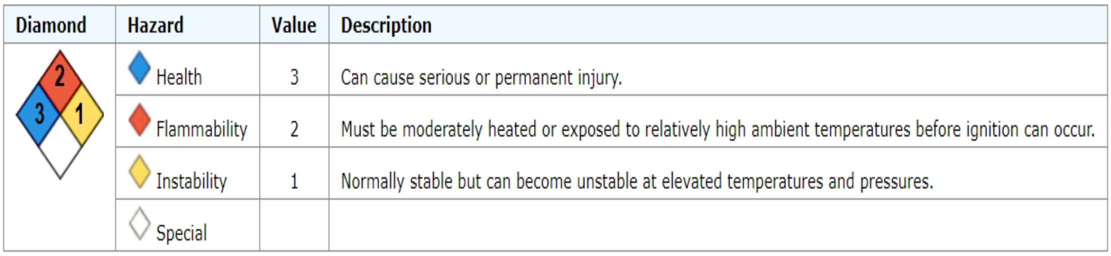
-H314: Causes severe skin burns and eye damage. (R35-R41)

-H319: Causes serious eye irritation. (R36)

-H332: Harmful if inhaled. (R20)

3. Formic Acid (CH_2O_2): It is described as a colourless liquid with a pungent, penetrating odor. The molecular weight of this chemical compound is 46 g/mole. Swallowing formic acid is very hazardous and usually causes death.

The symptoms include salivation, vomiting, burning sensation in the mouth, bloody vomiting, diarrhoea, and pain. Skin contact and inhalation are also very hazardous. Fire may produce irritating, corrosive and/or toxic gases. The LFL value is 18% (90% solution), whereas the UFL value is 57% (90% solution) [27]. Its boiling point is at 101°C, whereas its melting point is at 8.3 °C. The value of flash point temperature is 50°C (closed cup). The value of the lethal concentration is $LC_{50} = 7{,}4\, ppm\ (mg/l)$ on rats and after 4h of exposure, [42], whereas the value of the IDLH is 30 ppm [24]. The density is 1218,3 kg/m^3at 25°C and 1 atm, whereas the molecular weight is 46,03 g/mol. Its autoignition temperature is around 520°C [23].



Diamond	Hazard	Value	Description
	◆ Health	3	Can cause serious or permanent injury.
	◆ Flammability	2	Must be moderately heated or exposed to relatively high ambient temperatures before ignition can occur.
	◆ Instability	1	Normally stable but can become unstable at elevated temperatures and pressures.
	◇ Special		

Figure 4.5 [24]

The hazardous properties of this substance are:

-H226: Flammable liquid and vapour. (R10)

-H301: Toxic if swallowed. (R25)

-H314: Causes severe skin bums and eye damage. (R35-R41)

-H331: Toxic if inhaled. (R23)

After identifying the hazardous substances, it is necessary to classify the equipment into the categories indicated in the Table 3.5, at point 3.4.2.:

-Storage units (EQ1-EQ7): No units of this kind are found at the plant layout.

-(Un)loading units (EQ8-EQ9): No units of this kind are found at the plant layout.

-Pipes networks (EQ10): Represented in the following Table 4.6:

Pipe	Connection
Pipe 1	Beginning of the process-Extractor (Furfural)
Pipe 2	Beginning of the process-Extractor (Biomass)
Pipe 3	Extractor-Outside of the process (Water)

Pipe 4	Extractor-C1 (Furfural-rich)
Pipe 5	C1-Condenser1 (Furfural and Water)
Pipe 6	Condenser1-DEC (Furfural and Water)
Pipe 7	DEC-Outside of the process (Water)
Pipe 8	DEC-C1 (Furfural)
Pipe 9	C1-Split1 (Furfural, LA and FA)
Pipe 10	Split1-Reboiler1 (Furfural, LA and FA)
Pipe 11	Reboiler1-C1 (Furfural, LA and FA)
Pipe 12	Split1-C2 (Furfural, LA and FA)
Pipe 13	C2-Condenser2 (FA)
Pipe 14	Condenser2-Split2 (FA)
Pipe 15	Split2-Outside of the process (FA)
Pipe 16	Split2-C2 (FA)
Pipe 17	C2-Split3 (Furfural and LA)
Pipe 18	Split3-Reboiler2 (Furfural and LA)
Pipe 19	Reboiler2-C2 (Furfural and LA)
Pipe 20	Split3-C3 (Furfural and LA)
Pipe 21	C3-Condenser3 (Furfural and LA)
Pipe 22	Condenser3-Split4 (Furfural and LA)
Pipe 23	Split4-Outside of the process (Furfural)
Pipe 24	Split4-C3 (LA)
Pipe 25	C3-Split5 (LA)
Pipe 26	Split5-Reboiler3 (LA)
Pipe 27	Reboiler3-C3 (LA)
Pipe 28	Split5-Outside of the process (LA)

Table 4.6

-Process units (EQ11-EQ16): As for the equipment devoted to the physical or chemical separation of substances (EQ13), in the plant the three distillation columns (C1, C2 and C3) and the decanter (DEC) are found. As for the equipment involving chemical reactions (EQ12), the extractor (EX) is in this category. Finally, as for other facilities (EQ16), three condensers and three reboilers are present at the plant.

Finally, the result of the application of this step gives rise to the following Table 4.7 where all the needed information is summarized:

Equipment	Type of equipment	Substance	Hazardous properties [28]	State of the substance
Pipe 1	EQ10	Furfural (solvent)	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Extractor	EQ12	Furfural (rich), Biomass and Water (rich)	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 4	EQ10	Furfural (rich)	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Distillation column 1	EQ13	Furfural, LA, FA and Water	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Vapour (Water with small amount of Furfural)/Liquid (mainly Furfural, LA, FA)
Pipe 5	EQ10	Furfural and Water	-R10, R21, R23, R25, R36, R37, R38, R45	Vapour
Condenser 1	EQ16	Furfural and Water	-R10, R21, R23, R25, R36, R37, R38, R45	Vapour/Liquid
Pipe 6	EQ10	Furfural and Water	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Decanter	EQ13	Furfural and Water	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 8	EQ10	Furfural	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 9	EQ10	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Liquid
Pipe 10	EQ10	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Liquid
Reboiler 1	EQ16	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Vapour

			-R10, R23, R25, R35, R41	
Pipe 11	EQ10	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Vapour
Pipe 12	EQ10	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Liquid
Distillation column 2	EQ13	Furfural, LA and FA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41 -R10, R23, R25, R35, R41	Vapour (FA)/Liquid (mainly Furfural, LA)
Pipe 13	EQ10	FA and Furfural	-R10, R23, R25, R35, R41	Vapour
Condenser 2	EQ16	FA and Furfural	-R10, R23, R25, R35, R41	Vapour/Liquid
Pipe 14	EQ10	FA and Furfural	-R10, R23, R25, R35, R41	Vapour/Liquid
Pipe 15	EQ10	FA	-R10, R23, R25, R35, R41	Vapour
Pipe 16	EQ10	FA	-R10, R23, R25, R35, R41	Liquid
Pipe 17	EQ10	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Liquid
Pipe 18	EQ10	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Liquid
Reboiler 2	EQ16	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Vapour
Pipe 19	EQ10	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Vapour
Pipe 20	EQ10	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Liquid
Distillation column 3	EQ13	Furfural and LA	-R10, R21, R23, R25, R36, R37, R38, R45 -R20, R22, R35, R36, R41	Liquid (LA)/Vapour (Furfural)

Pipe 21	EQ10	Furfural (and some LA)	-R10, R21, R23, R25, R36, R37, R38, R45	Vapour
Condenser 3	EQ16	Furfural (and some LA)	-R10, R21, R23, R25, R36, R37, R38, R45	Vapour/Liquid
Pipe 22	EQ10	Furfural (and some LA)	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 23	EQ10	Furfural	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 24	EQ10	LA	-R10, R21, R23, R25, R36, R37, R38, R45	Liquid
Pipe 25	EQ10	LA	-R20, R22, R35, R36, R41	Liquid
Pipe 26	EQ10	LA	-R20, R22, R35, R36, R41	Liquid
Reboiler 3	EQ16	LA	-R20, R22, R35, R36, R41	Vapour
Pipe 27	EQ10	LA	-R20, R22, R35, R36, R41	Vapour
Pipe 28	EQ10	LA	-R20, R22, R35, R36, R41	Liquid

Table 4.7

*Pipes 2, 3 and 7 have not been mentioned since they mainly transport non-hazardous substances.

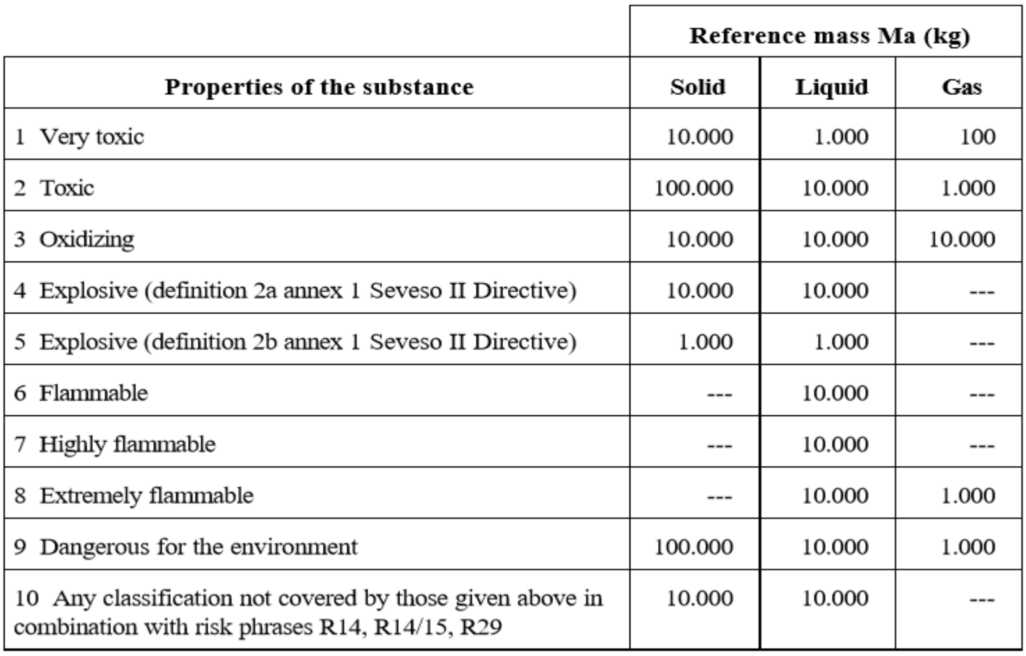
**Non-hazardous substances.

***Risk phrases not included in the Table 2: Typology of hazardous substances in [1], and so not finally considered as significant at determining the potentially hazardous equipment. In this sense, Pipes 24-28 and Reboiler 3 are not considered as potentially hazardous equipment (together with pipes 2,3 and 7). Thus, the considered substances in the analysis are the Furfural and the Formic Acid, but not the Levulinic Acid.

So, from the 39 initial equipments or sections of the installation, 30 are considered as potentially hazardous.

4.1.3 MIMAH procedure: third step

The first is to assign a reference mass (Ma, in kg) according to the physical state of the substance and its hazardous properties, as shown in the Table 4.8 [16]:



	Reference mass Ma (kg)		
Properties of the substance	**Solid**	**Liquid**	**Gas**
1 Very toxic	10.000	1.000	100
2 Toxic	100.000	10.000	1.000
3 Oxidizing	10.000	10.000	10.000
4 Explosive (definition 2a annex 1 Seveso II Directive)	10.000	10.000	---
5 Explosive (definition 2b annex 1 Seveso II Directive)	1.000	1.000	---
6 Flammable	---	10.000	---
7 Highly flammable	---	10.000	---
8 Extremely flammable	---	10.000	1.000
9 Dangerous for the environment	100.000	10.000	1.000
10 Any classification not covered by those given above in combination with risk phrases R14, R14/15, R29	10.000	10.000	---

Table 4.8

Since our considered substances (furfural and formic acid) are considered both as toxic and flammable, and they are both found in liquid but also in gas state in the industrial process (Table 4.9):

Substance	Risk Phrase	State	Reference mass Ma(kg)
Furfural	R10 (Flammable)	Liquid	10000
		Gas	1000
	R23 (Toxic)	Liquid	10000
		Gas	1000
Formic Acid	R10 (Flammable)	Liquid	10000
		Gas	1000
	R23 (Toxic)	Liquid	10000
		Gas	1000

Table 4.9

It is necessary to indicate that, in addition to the parts of the installation that have been previously discarded as containing mostly non-hazardous substances (pipes 2,3 and 7), or for having risk phrases that are not considered by the ARAMIS procedure (pipes 24-28, reboiler 3), to continue with the MIMAH procedure the following parts are added, since a negligible mass flow and therefore do not pose a relevant danger: pipe 10, pipe 11, reboiler 1, pipe 18, pipe 19 and reboiler 2. Thus, now, from the 30 equipments finally considered as potentially hazardous, 24 of them are candidates for becoming relevant hazardous equipments.

As for **liquid state substances**, the reference mass must be corrected by means of a "S" coefficient: $Mb = \frac{Ma}{S}$. S is the sum of S_1 and S_2 (Table 4.10), where $S1 = 10^{\frac{T_p - T_{eb}}{100}}$ (T_p is the service temperature in °C and T_{eb} is the boiling temperature in °C at atmospheric conditions).

Equipment	**Serivice temp.(Tp. in °C)**		**S1**		**S2**		**S**	
	Furfural	Formic Acid	Furfural	Formic Acid	Furfural	Formic Acid	Furfural	Formic Acid
Pipe 1	25	---	0,0430	---	0	0	0,1	---
Extractor	25	25	0,0430	0,1738	0	0	0,1	0,1738
Pipe 4	25	25	0,0430	0,1738	0	0	0,1	0,1738
Dist. column 1	161	161	0,9840	3,9811	0	0	0,9840	3,9811
Condenser 1	98	---	0,2307	---	0	0	0,2307	---
Pipe 6	98	---	0,2307	---	0	0	0,2307	---
Decanter	98	---	0,2307	---	0	0	0,2307	---
Pipe 8	98	---	0,2307	---	0	0	0,2307	---
Pipe 9	161	161	0,9840	3,9811	0	0	0,9840	3,9811
Pipe 12	161	161	0,9840	3,9811	0	0	0,9840	3,9811
Dist. column 2	163	---	1,0304	---	0	0	1,0304	---
Condenser 2	106	106	0,2773	1,1220	0	0	0,2773	1,1220
Pipe 14	106	106	0,2773	1,1220	0	0	0,2773	1,1220
Pipe 16	106	---	0,2773	---	0	0	0,2773	---
Pipe 17	163	---	1,0304	---	0	0	1,0304	---
Pipe 20	163	---	1,0304	---	0	0	1,0304	---
Condenser 3	161	---	0,9840	---	0	0	0,9840	---
Pipe 22	161	---	0,9840	---	0	0	0,9840	---
Pipe 23	161	---	0,9840	---	0	0	0,9840	---

Table 4.10

The value of S in case of Furfural in the Extractor and pipes 1 and 4 has been corrected to 0,1 since this parameter $S \in [0{,}1; 10]$.

Now, the corrected value of Mb (in kg) is calculated and showed in Table 4.11, as well as the equipment finally regarded as relevant hazardous. Worth noting is that, as highlighted in 3.4.3, if a specific equipment can be dangerous due to the presence of a hazardous substance and/or by the operating conditions inside the equipment, it can be selected as a relevant hazardous one even though its threshold value is bigger than the mass of hazardous substance.

Following this criterion, it has been considered that those equipments which $\frac{M}{Mb} \geq 60\%$ are finally estimated as relevant hazardous.

Equipment	**Mb**	**M**	**Relevant hazardous. eq.**	**M/Mb (%)**	**Finally considered**
Pipe 1	100000	18229,167	NO	18,229	NO
Extractor	157543,994	8732,639	NO	5,543	NO
Pipe 4	157543,994	17465,278	NO	11,086	NO
Dist. column 1 (L)	12674,373	8732,639	NO	68,900	SI
Dist. column 1 (V)	1000	4,340	NO	0,434	NO
Pipe 5	1000	86,805	NO	8,681	NO
Condenser 1 (L)	43351,088	43,403	NO	0,100	NO
Condenser 1 (V)	1000	4,340	NO	0,434	NO
Pipe 6	43351,088	86,805	NO	0,200	NO
Decanter	43351,088	43,403	NO	0,100	NO
Pipe 8	43351,088	86,805	NO	0,200	NO
Pipe 9	12674,373	17465,278	SI	137,800	SI
Pipe 12	12674,373	17465,278	SI	137,800	SI
Dist. column 2 (L)	9705,100	8702,258	NO	89,667	SI
Dist. column 2 (V)	2000	11,719	NO	0,586	NO
Pipe 13	2000	234,375	NO	11,719	NO
Condenser 2 (L)	36057,864	86,806	NO	0,241	NO
Condenser 2 (V)	2000	11,719	NO	0,586	NO
Pipe 14 (L)	36057,864	173,612	NO	0,481	NO
Pipe 14 (V)	1000	60,763	NO	6,076	NO
Pipe 15	1000	60,763	NO	6,076	NO
Pipe 16	36057,864	173,612	NO	0,481	NO
Pipe 17	9705,100	17404,515	SI	179,333	SI
Pipe 20	9705,100	17404,515	SI	179,333	SI
Dist. column 3 (V)	1000	870,226	NO	87,023	SI
Pipe 21	1000	17404,515	SI	1740,452	SI
Condenser 3 (L)	10162,487	8702,258	NO	85,631	SI
Condenser 3 (V)	1000	870,225	NO	87,023	SI
Pipe 22	10162,487	17404,515	SI	171,262	SI
Pipe 23	10162,487	17404,515	SI	171,262	SI

Table 4.11

For distillation columns and condensers, the considered time of residence has been of 5 min for liquid phase and of 0,5 min for vapour phase. According to Table 4.11, **11 equipments are finally considered as relevant hazardous** as result the performance of the third step of MIMAH procedure.

4.1.4 MIMAH procedure: fourth step

As explained before, this step consists in the association of critical events (CE) to each one of the equipments that has been considered as relevant hazardous according to the criteria contemplated in the ARAMIS methodology.

According to [17] the different types of equipments have associated specific CE. These CE are fully described in Table 3.6. Since in the industrial process under analysis, EQ10, 12, 13 and 16 are present, the associated CE are shown in the following Table 4.12:

Equipments (EQ)	**Associated critical events (CE)**					
Type	CE5	CE6	CE7	CE8	CE9	CE10
EQ10	X			X	X	
EQ12	X	X	X	X	X	X
EQ13	X	X	X	X	X	X
EQ16	X	X	X	X	X	X

Table 4.12

Thus, taking into account the equipments that have been regarded as relevant hazardous in the previous MIMAH´s procedure step (together with the state in which the substances flow through them), as well as the sizes of breaches and leaks contemplated by ARAMIS methodology and indicated in Table 3.7, and the CE that may be associated with the equipments according to their type (Table 4.12), Table 4.13 is performed:

Equipment	**Associated critical events**												
	CE6			CE7			CE8			CE9			CE10
	S	M	L	S	M	L	S	M	L	S	M	L	
Pipe 9							X	X	X				
Pipe 12							X	X	X				
Pipe 17							X	X	X				
Pipe 20							X	X	X				
Pipe 22							X	X	X				
Pipe 23							X	X	X				
Pipe 21										X	X	X	
Distillation c.1				X	X	X							X
Distillation c. 2				X	X	X							X
Distillation c. 3	X	X	X										X
Condenser 3	X	X	X	X	X	X							X

Table 4.13

This table is the first one obtained by means of the application of the current step. As shown, 40 CE have been considered.

For a liquid release from a hole of diameter d in a pipe or vessel (considering that the difference in height from the liquid layer to the hole is negligible), the equation that provides the discharge rate is:

$\dot{m} = \rho A\, u = c_D A\sqrt{2P_{rel} \cdot \rho}$, where:

$\dot{m}$ = Liquid discharge rate (kg/s)

ρ= Liquid density (kg/m^3)

A= Hole cross-section area (m^2). Since circular holes are considered, $A = \frac{\pi d^2}{4}$

u= Liquid velocity (m/s)

c_D= Discharge coefficient (dimensionless)

P_{rel}= Relative pressure (Pa)

A discharge coefficient c_D = 1 has been considered in this equation, although other authors use a 0.8 value.

As for the equation that provides the gas discharge rate when a gas out flow takes place through a hole:

$\dot{m} = A \cdot P_0 \sqrt{\frac{\gamma M}{R \cdot T_0} \cdot \left(\frac{2}{1+\gamma}\right)^{\frac{\gamma+1}{\gamma-1}}}$, where:

$\dot{m}$ = Liquid discharge rate (kg/s)

A= Hole cross-section area (m^2). Since circular holes are considered, $A = \frac{\pi d^2}{4}$

P_0= Inner pressure (Pa)

γ= Heat capacity ratio "c_p/c_v"

M= Molecular weight (kg/kmol)

R= Gas constant (8314 J/($kmol \times K$))

T_0= Inner temperature (K)

Once determined the values of the discharge rates of all equipments, the mass of substance released by every one of them in 10 minutes is determined. In order to establish the release classification of the different releases into continuous, quasi-instantaneous and instantaneous, the released mass in 10 minutes is compared to the inventory of the considered equipment, according to the document [37]. This is indicated in the table below (Table 4.14). It is also important to indicate that for the equipments “Condenser 3, Pipe 22 and Pipe 23” a pressure of 1,2 atm has been considered **in this step** in order to have a certain difference between the internal and external pressures (otherwise, theoretically no liquid release would take place).

Equipment	**Critical event**	**ṁ (kg/s)**	**m (kg)**	**Release classification**
Dist. column 1	Small breach in liquid phase	0,545	327,126	Continuous
	Medium breach in liquid phase	13,630	8178,150	Quasi-instantaneous
	Large breach in liquid phase	54,521	32712,600	Quasi-instantaneous
	Catastrophic rupture	---	8732,639	Instantaneous
Pipe 9	Small leak in liquid phase	1,859	1115,358	Continuous
	Medium leak in liquid phase	35,989	21593,331	Quasi-instantaneous
	Large leak in liquid phase	185,893	111535,800	Quasi-instantaneous
Pipe 12	Small leak in liquid phase	1,859	1115,358	Continuous
	Medium leak in liquid phase	35,989	21593,331	Quasi-instantaneous
	Large leak in liquid phase	185,893	111535,800	Quasi-instantaneous
Dist. column 2	Small breach in liquid phase	0,539	323,118	Continuous
	Medium breach in liquid phase	13,463	8077,950	Quasi-instantaneous
	Large breach in liquid phase	53,853	32311,800	Quasi-instantaneous
	Catastrophic rupture	---	8702,258	Instantaneous
Pipe 17	Small leak in liquid phase	1,831	1098,702	Continuous
	Medium leak in liquid phase	35,451	21270,871	Quasi-instantaneous
	Large leak in liquid phase	183,117	109870,200	Quasi-instantaneous
Pipe 20	Small leak in liquid phase	1,831	1098,702	Continuous
	Medium leak in liquid phase	35,451	21270,871	Quasi-instantaneous
	Large leak in liquid phase	183,117	109870,200	Quasi-instantaneous
Dist. column 3	Small breach in vapour phase	0,031	18,462	Continuous
	Medium breach in vapour phase	0,769	461,550	Continuous
	Large breach in vapour phase	3,077	1846,200	Quasi-instantaneous
	Catastrophic rupture	---	870,226	Instantaneous
Pipe 21	Small leak in vapour phase	4,212	2527,014	Continuous
	Medium leak in vapour phase	81,538	48922,991	Quasi-instantaneous
	Large leak in vapour phase	421,169	252701,400	Quasi-instantaneous
Condenser 3	Small breach in vapour phase	0,031	18,462	Continuous
	Medium breach in vapour phase	0,769	461,550	Continuous
	Large breach in vapour phase	3,077	1846,200	Quasi-instantaneous
	Small leak in liquid phase	0,539	323,118	Continuous
	Medium leak in liquid phase	13,463	8077,950	Quasi-instantaneous
	Large leak in liquid phase	53,853	32311,800	Quasi-instantaneous
	Catastrophic rupture	---	8702,2575+870,226	Instantaneous
Pipe 22	Small leak in liquid phase	1,720	1031,826	Continuous
	Medium leak in liquid phase	33,294	19976,151	Quasi-instantaneous
	Large leak in liquid phase	171,971	103182,600	Quasi-instantaneous
Pipe 23	Small leak in liquid phase	1,714	1028,364	Continuous
	Medium leak in liquid phase	33,182	19909,127	Quasi-instantaneous
	Large leak in liquid phase	171,394	102836,400	Quasi-instantaneous

Table 4.14

In case of medium breaches, a 50 mm diameter has been considered, whereas in case of medium leaks, the criterion has been to consider 44% of the pipe diameter. These considerations have been taken to establish a more conservative procedure.

Bearing in mind that it is possible to assume that those critical events whose release is almost instantaneous behave as catastrophic events from the point of view of the release classification (instantaneous), it is possible to reduce the initial number of critical events from 40 to 18 (those placed in orange cells).

4.1.5 MIMAH procedure: fifth step

Considering the critical events detected through the previous step, it should time to build the corresponding fault trees. Since they are generic fault trees, they are not specific of the plant where the risk performance is being carried out, but can be used as a first tool to build the left part of the bow-tie. Obviously, it would be necessary to apply the critical events provided by Appendix 4 [18] with a critical vision, adding or deleting branches according to specifications and characteristics of the equipments previously regarded as relevant hazardous.

However, since this present work is focused on an industrial process that is found at its design stage instead of its operating stage, only a limited information is provided. This information is not enough to elaborate the fault trees in an accurate and rigorous way. So, this case of study will be specially focused in the consequences (event tree) of the established CE instead of on their causes (fault trees).

4.1.6 MIMAH procedure: sixth step

It is possible to identify the potential consequences of the critical events by the construction of an event tree through the application of the matrices proposed in the Appendix 5 of the ARAMIS methodology [19]. These matrices consider a number of different incidents outcomes which depend on if ignition occurs, as well as when it takes place and on its consequence.

In first instance, two matrices considering the type of equipment, the CE and the physical state of the evaluated substance have been applied to detect the secondary critical events (SCE) that, as previously shown in Figure 3.9, are those ones which are found immediately after the CE in the event tree. In the present study, the following SCE have been detected:

-Catastrophic rupture in the Condenser 3, leads to another “catastrophic rupture” (SCE2), pool formation (SCE3) and aerosol puff (SCE8).

-Catastrophic rupture in the Dist. column 3 leads to another “catastrophic rupture” (SCE2) and gas puff (SCE6).

-Catastrophic rupture in the Dist. column 1 and 2 leads to another “catastrophic rupture” (SCE2) and pool formation (SCE3).

-Breaches in vapour phase lead to gas jet (SCE5) take place in Dist. column 3 and Condenser 3, as well as also do leak in vapour phase in Pipe 21.

-Breaches and leaks in liquid phase lead to pool formation (SCE3) in case of Dist. column 1 and 2, as well as in Pipe 9, 12, 17, 20, 22 and 23, respectively. In case of Condenser 3, a breach in liquid phase leads to pool formation (SCE3) and two-phase jet (SCE7).

It is necessary to highlight, to prevent bewilderments, that when the transition Catastrophic rupture to SCE2 (another catastrophic rupture) is indicated, it means that this event does not lead to any other SCE.

After the application of the first matrix, another one is used in order to associate the potential tertiary critical events (TCEs) with the SCEs that have been previously established. Basing on the information provided in [19], these TCEs are represented in the following Table 4.15:

	TCE2	**TCE4**	**TCE5**	**TCE7**	**TCE8**	**TCE9**	**TCE10**	**TCE11**
SCE2	X							
SCE3		X	X					X
SCE5			X	X				
SCE6			X		X			
SCE7			X			X		
SCE8			X				X	

Table 4.15

Where the TCE2, TCE4, TCE5, TCE7, TCE8, TCE9, TCE10 and TCE11 are catastrophic rupture, pool ignited, gas dispersion, gas jet ignited, gas puff ignited, two-phase jet ignited, aerosol puff ignited and pool not ignited/pool dispersion, respectively.

Finally, it is necessary to build a matrix that shows the relation between the TCEs previously determined and their corresponding dangerous phenomena (DP):

	DP1	DP3	DP4	DP5	DP6	DP8	DP9	DP10	DP11
TCE2						X	X		
TCE4	X				X				X
TCE5			X	X	X				X
TCE7		X			X				X
TCE8					X			X	X
TCE9		X			X				X
TCE10					X			X	X
TCE11									X

Table 4.16

Where the DP1, DP3, DP4, DP5, DP6, DP8, DP9, DP10 and DP11 are pool fire, jet fire, vapour cloud explosion (VCE), flashfire, toxic cloud, missiles ejection, overpressure generation, fireball and environmental damage.

Finally, the event trees related to each equipment according to its considered critical events (CEs) must be represented.

A. Distillation column 1

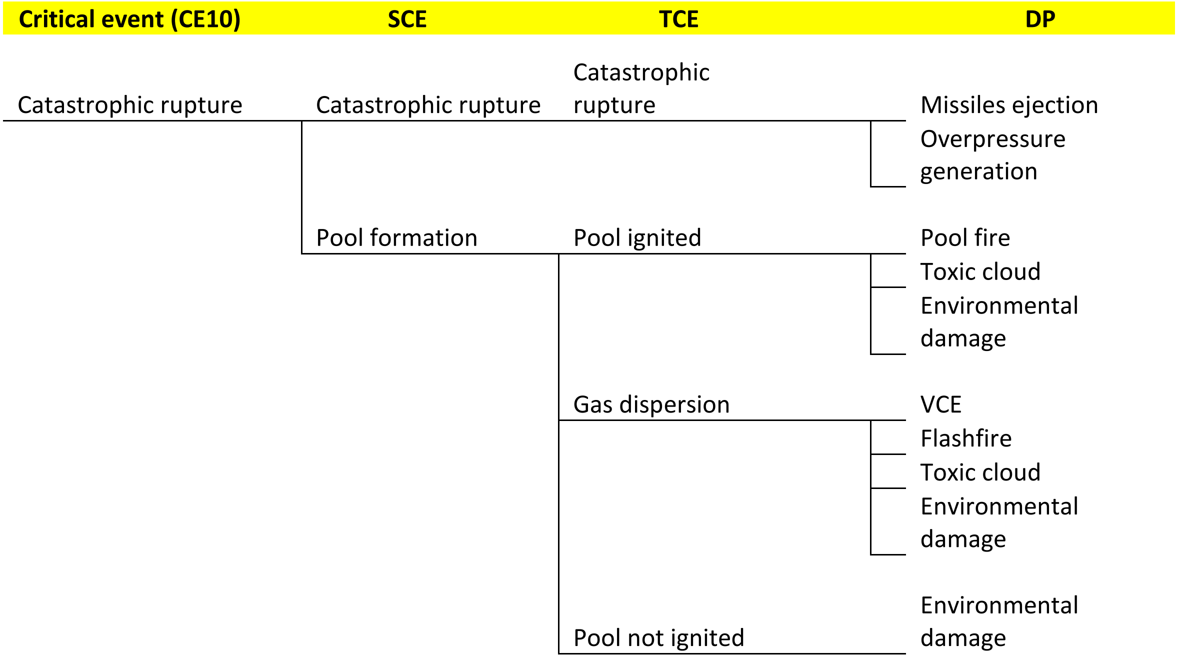


Figure 4.17- Event tree for the catastrophic rupture of the DC1

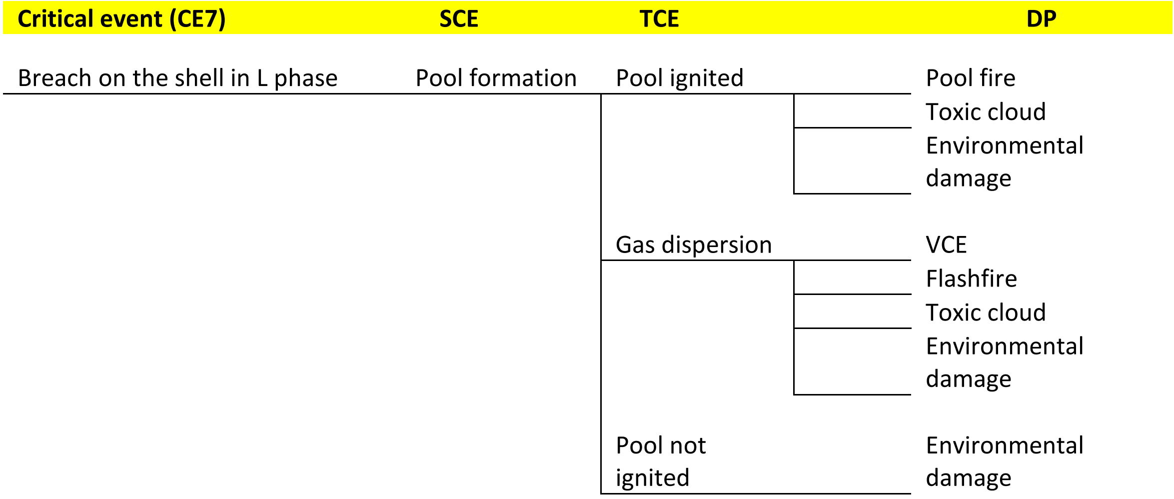


Figure 4.18- Event tree for the small breach in liquid phase on the shell of the DC1

B. Pipe 9

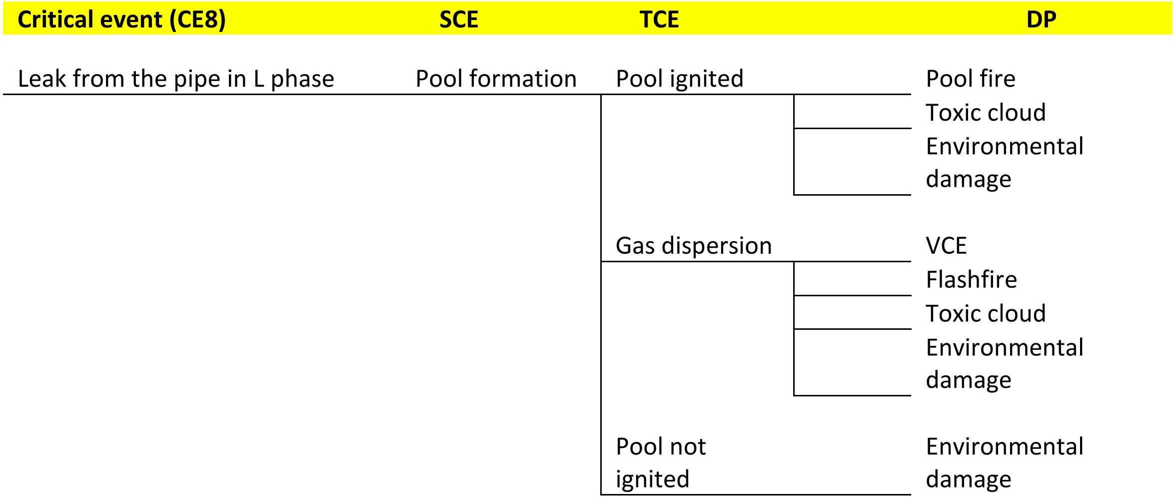


Figure 4.19- Event tree for the small leak in liquid phase from the Pipe 9

C. Pipe 12

The event tree is identical to the one of the Pipe 9

D. Distillation column 2

The event trees are the same ones that those of the Distillation column 1

E. Pipe 17

The event tree is identical to the one of the Pipe 9

F. Pipe 20

The event tree is identical to the one of the Pipe 9

G. Distillation column 3

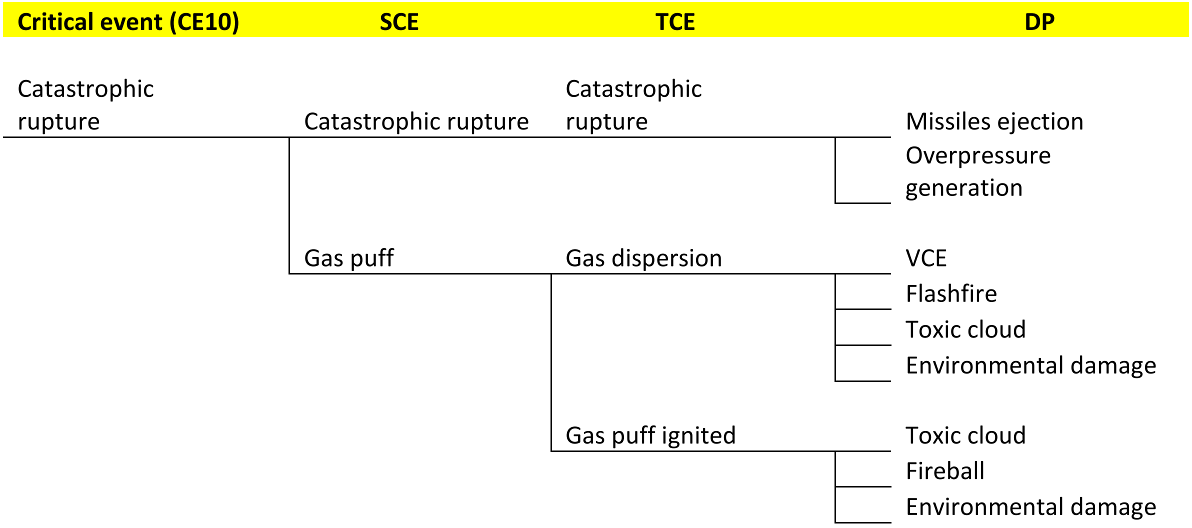


Figure 4.20- Event tree for the catastrophic rupture of the DC3

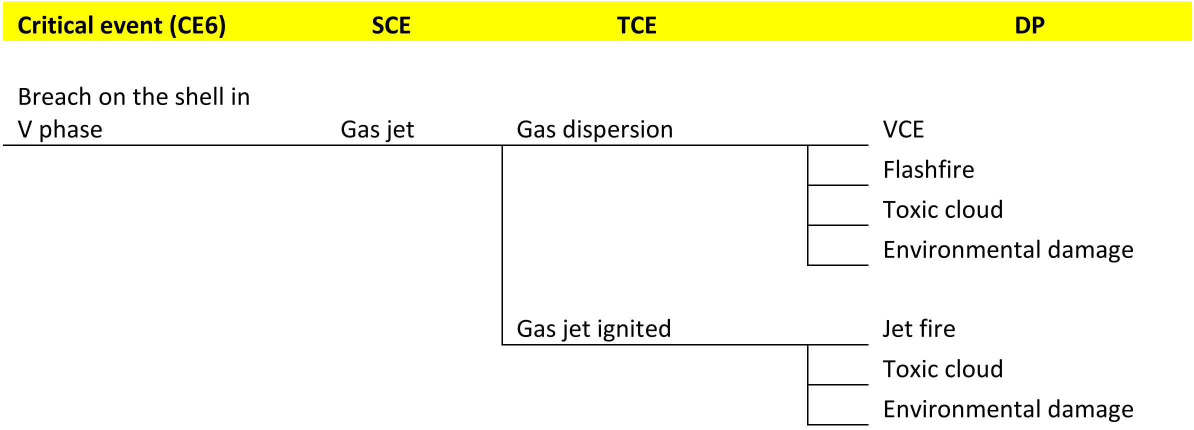


Figure 4.21- Event tree for the small and medium breach in vapour phase on the shell of the DC3

H. Pipe 21

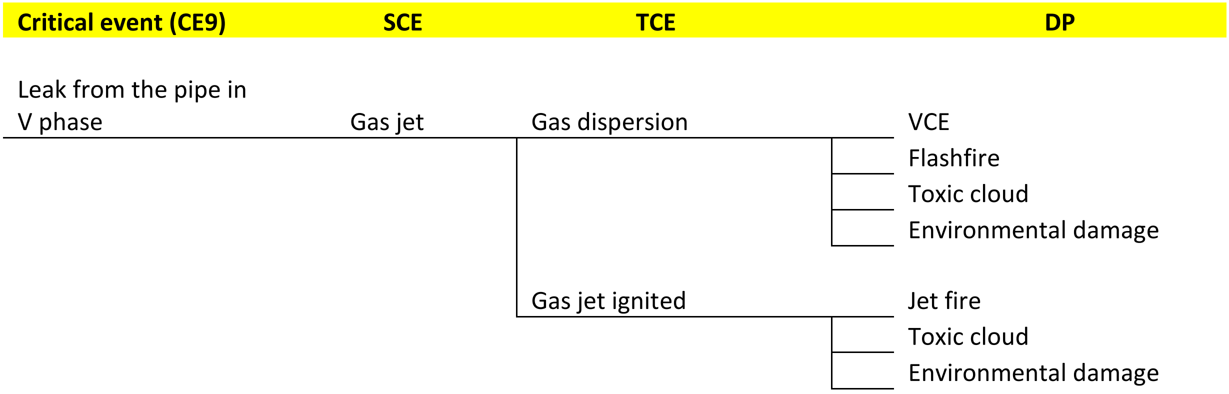


Figure 4.22- Event tree for the small leak in vapour phase from the Pipe 21

I. Condenser 3

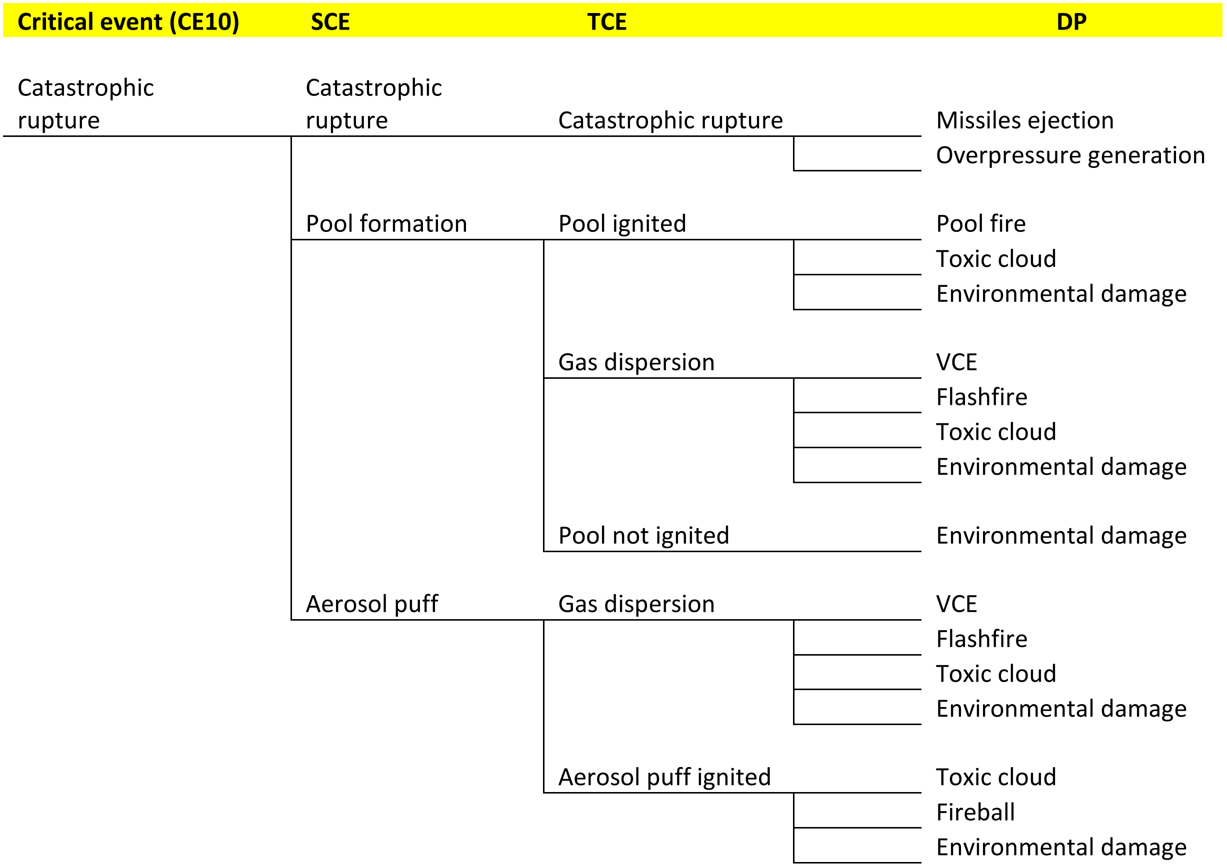


Figure 4.23- Event tree for the catastrophic rupture of the Condenser 3

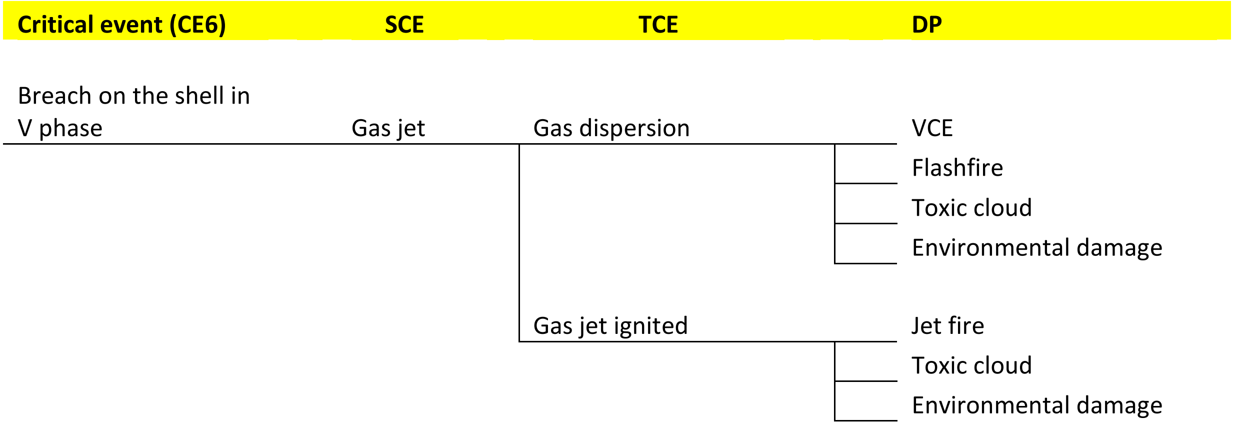


Figure 4.24- Event tree for the small and medium breach in vapour phase on the shell of the Condenser 3

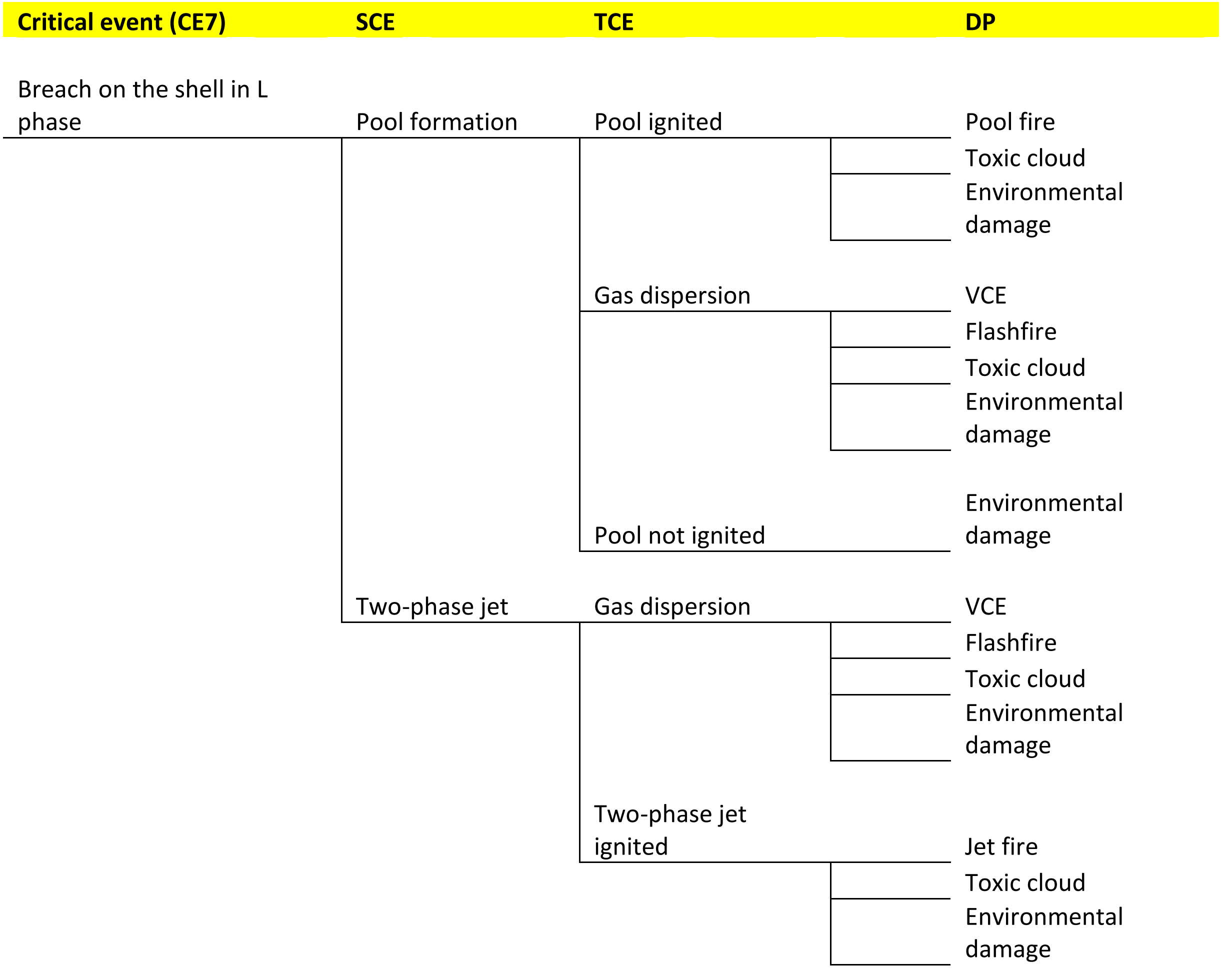


Figure 4.25- Event tree for the small breach in liquid phase on the shell of the Condenser 3

J. Pipe 22

The event tree is identical to the one of the Pipe 9

K. Pipe 23

The event tree is identical to the one of the Pipe 9

4.1.7 MIMAH procedure: seventh step

As said before, the performance of this step has been omitted, since as the fifth step was not developed, this one would only consist in the representation of the characteristic event trees, and they have already been represented in the previous step.

4.2 Furfural as a solvent in a 3-distillation column: MIRAS procedure application

4.2.1 MIRAS procedure: first step

This step, as the first step of MIMAH procedure, consists in the collection of data that are required for the performance of the following steps. These data are the results of MIMAH. No extra data are necessary here.

4.2.2 MIRAS procedure: second step

As explained in 3.5.2, this step consists in deciding which will be the next step to be performed between the step 3 and step 4. Both have the same objective, which is the estimation of the frequency per year of the critical event (CE) considered for each bow-tie built by means of MIRAH methodology application.

Even though step 3 is preferred due to it has a higher level of reliability and accuracy, in the present work the step 4 will be chosen since there is not an available source of historical data about failure frequencies related to this process, because it is relatively new.

4.2.3 MIRAS procedure: fourth step

The aim of this step is to define the frequencies for the considered critical events, according to the kind of equipment they are associated to. It is fully detailed in [32], which is based on diverse bibliographical sources that provide generic frequencies for the critical events, such as the Handboek Kanscijfers [35], the

Canvey report [36] and the "Purple book" [37], and. Most of these are issued from countries where QRA serves as a decision support for land use planning.

Equipment	**Small leak**
Pipes 9,12,17,20,21,22,23 (Dn>150mm)	$1{,}75 \times 10^{-6}$

Table 4.26

The previous Table 4.26 shows the generic frequencies provided by [32] for a leak from a pipe. In case of pipelines, the frequencies are provided in failures per year and per meter, so the total failure frequency of a pipeline is determined by multiplying the failure frequency by its total length. Regarding to the length, it has been decided to consider a length of 4 meters for every pipe. As result, a frequency of 7×10^{-6} failures per year is obtained.

Table 4.27 contains the generic frequencies for breaches and catastrophic ruptures of the three DC and the Condenser3. In this case, frequencies are given in failures per year. Worth noting is that, due to the values correspond to the type of equipment 13 (equipment devoted to the physical or chemical separation of substance) and the Condenser 3 has been categorized as equipment 16 (other facilities), its values for the generic frequencies have been taken from [37] since no data is provided in the Appendix 10. Specifically, the values for the condenser come from the "Table 3.11, pag.50".

Equipment	**Small breach**	**Medium breach**	**Catastrophic rupture**
Dist. column 1	1×10^{-4}	→	1×10^{-5}
Dist. column 2	1×10^{-4}	→	1×10^{-5}
Dist. column 3	1×10^{-4}	5×10^{-5}	5×10^{-6}
Condenser 3 (L)	1×10^{-3}	→	5×10^{-5}
Condenser 3 (V)	1×10^{-3}	5×10^{-5}	5×10^{-5}

Table 4.27

All of these frequencies are given for a standard security level, which is not specified in the literature. That is the reason why these generic frequencies of critical events will be used only if it is not possible to obtain the frequency of the critical event from the fault tree (as in this case study). It is necessary to mention that **the value of the probability of catastrophic rupture of the DC3 has been changed, from 1×10^{-5} to 5×10^{-6}**, according to the criteria established by the tutor.

4.2.4 MIRAS procedure: fifth step

Starting from the frequency of critical events obtained in the previous step, it is possible to define now the frequencies of the last level of the event trees: the dangerous phenomena.

This step is performed taking into account the different branches of the event trees obtained before, as well as certain tables provided by the Appendix 12 of ARAMIS methodology [39] and which in turn, as mentioned in the references of the document, are based on the results of several sources of study, such as [36], [37] and [38]. In consequence, the following tables are built. They contain values of probabilities based on several aspects (class of source and the state of the substance) that will be lately assigned to the branches of the built event trees.

Source		Substance	
Continuous (CE6,CE7,CE8,CE9)	**Instantaneous (CE10)**	**K1-Liquid $P_{im.ig\ (L)}$**	**Gas average/ high reactive $P_{im.ig\ (G)}$**
< 10 kg/s	< 1000 kg	0,065	0,2
10 - 100 kg/s	1000 - 10000 kg	0,065	0,5
> 100 kg/s	> 10000 kg	0,065	0,7

Table 4.28

The previous table is obtained from the data shown in *"Table 4.5 Probability of direct ignition for stationary installations"*, page 75 of document [37]. Since Appendix 12 proposes, for liquids, the value of 0,9 as the one of the most unfavourable case, this value will be taken into consideration instead of 0.065 in order to establish a more conservative criterion.

Regarding to the other events which probabilities are shown in [39], the proposed values are the following ones:

-Probability of delayed ignition of a gas dispersion: 0,8 (process units, since they are present in the plant layout, whereas storage and loading/unloading units are not). Defined as $P_{del.ig}$

-Probability of vapour cloud explosion (VCE): 0,5 (medium obstruction). Defined as P_{VCE}

Finally, the tables containing the failure frequencies (failures/year) of the DP according to the CE they come from can be developed basing on the event trees of the different equipments and the probabilities established just before, as previously explained.

A. Distillation column 1

	Equation	**Frequency**
Missiles ejection	FCE	1×10^{-5}
Overpressure generation	FCE	1×10^{-5}
Pool fire	$FCE \times P_{im.ig\ (L)}$	9×10^{-6}
Toxic cloud	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times (1 - P_{del.ig})$	$9{,}2 \times 10^{-6}$
Environmental damage	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times \left(1 - P_{del.ig}\right) + FCE \times (1 - P_{im.ig\ (L)})$	$10{,}2 \times 10^{-6}$
VCE	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times P_{VCE}$	4×10^{-7}
Flashfire	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times (1 - P_{VCE})$	4×10^{-7}

Table 4.29- Failure frequencies of DP for the catastrophic rupture of the DC1

	Equation	**Frequency**
Pool fire	$FCE \times P_{im.ig\ (L)}$	9×10^{-5}
Toxic cloud	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times (1 - P_{del.ig})$	$9{,}2 \times 10^{-5}$
Environmental damage	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times \left(1 - P_{del.ig}\right) + FCE \times (1 - P_{im.ig\ (L)})$	$10{,}2 \times 10^{-5}$
VCE	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times P_{VCE}$	4×10^{-6}
Flashfire	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times (1 - P_{VCE})$	4×10^{-6}

Table 4.30– Failure frequencies of DP for the small breach in liquid phase on the shell of the DC1

B. Pipe 9

	Equation	**Frequency**
Pool fire	$FCE \times P_{im.ig\ (L)}$	$6{,}3 \times 10^{-6}$
Toxic cloud	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times (1 - P_{del.ig})$	$6{,}44 \times 10^{-6}$
Environmental damage	$FCE \times P_{im.ig\ (L)} + FCE \times (1 - P_{im.ig\ (L)}) \times \left(1 - P_{del.ig}\right) + FCE \times (1 - P_{im.ig\ (L)})$	$7{,}14 \times 10^{-6}$
VCE	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times P_{VCE}$	$2{,}8 \times 10^{-7}$
Flashfire	$FCE \times (1 - P_{im.ig\ (L)}) \times P_{del.ig} \times (1 - P_{VCE})$	$2{,}8 \times 10^{-7}$

Table 4.31– Failure frequencies of DP for the small leak in liquid phase from Pipe 9

C. Pipe 12

Table 4.32– Failure frequencies of DP for the small leak in liquid phase from Pipe 12 is equal to Table 4.31

D. Distillation column 2

Table 4.33- Failure frequencies of DP for the catastrophic rupture of the DC2 is equal to Table 4.29

Table 4.34– Failure frequencies of DP for the small breach in liquid phase on the shell of the DC2 is equal to Table 4.30

E. Pipe 17

Table 4.35– Failure frequencies of DP for the small leak in liquid phase from Pipe 17 is equal to Table 4.31

F. Pipe 20

Table 4.36– Failure frequencies of DP for the small leak in liquid phase from Pipe 2 is equal to Table 4.31

G. Distillation column 3

	Equation	**Frequency**
Missiles ejection	FCE	5×10^{-6}
Overpressure generation	FCE	5×10^{-6}
Toxic cloud	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	1.8×10^{-6}
Fireball	$FCE \times P_{im.ig\,(G)}$	1×10^{-6}
VCE	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$1,6 \times 10^{-6}$
Flash fire	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$1,6 \times 10^{-6}$
Environmental damage	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	1.8×10^{-6}

Table 4.37- Failure frequencies of DP for the catastrophic rupture of the DC3

	Equation	**Frequency**
VCE	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$3,2 \times 10^{-5}$
Flash fire	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$3,2 \times 10^{-5}$
Toxic cloud	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$3,6 \times 10^{-5}$
Environmental damage	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$3,6 \times 10^{-5}$
Jet fire	$FCE \times P_{im.ig\,(G)}$	2×10^{-5}

Table 4.38– Failure frequencies of DP for the small breach in vapour phase on the shell of the DC3

	Equation	Frequency
VCE	$FCE \times (1 - P_{im.ig\ (G)}) \times P_{del.ig} \times P_{VCE}$	$1{,}6 \times 10^{-5}$
Flash fire	$FCE \times (1 - P_{im.ig\ (G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$1{,}6 \times 10^{-5}$
Toxic cloud	$FCE \times P_{im.ig\ (G)} + FCE \times (1 - P_{im.ig\ (G)}) \times (1 - P_{del.ig})$	$1{,}8 \times 10^{-5}$
Environmental damage	$FCE \times P_{im.ig\ (G)} + FCE \times (1 - P_{im.ig\ (G)}) \times (1 - P_{del.ig})$	$1{,}8 \times 10^{-5}$
Jet fire	$FCE \times P_{im.ig\ (G)}$	1×10^{-5}

Table 4.39– Failure frequencies of DP for the medium breach in vapour phase on the shell of the DC3

H. Pipe 21

	Equation	Frequency
VCE	$FCE \times (1 - P_{im.ig\ (G)}) \times P_{del.ig} \times P_{VCE}$	$2{,}24 \times 10^{-6}$
Flash fire	$FCE \times (1 - P_{im.ig\ (G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$2{,}24 \times 10^{-6}$
Toxic cloud	$FCE \times P_{im.ig\ (G)} + FCE \times (1 - P_{im.ig\ (G)}) \times (1 - P_{del.ig})$	$2{,}52 \times 10^{-6}$
Environmental damage	$FCE \times P_{im.ig\ (G)} + FCE \times (1 - P_{im.ig\ (G)}) \times (1 - P_{del.ig})$	$2{,}52 \times 10^{-6}$
Jet fire	$FCE \times P_{im.ig\ (G)}$	$1{,}4 \times 10^{-6}$

Table 4.40– Failure frequencies of DP for the small leak in vapour phase from Pipe 21

I. Condenser 3

	Equation	Frequency
Missiles ejection	FCE	5×10^{-5}
Overpressure generation	FCE	5×10^{-5}
Pool fire	$FCE \times P_{im.ig\,(L)}$	$4{,}5 \times 10^{-5}$
Toxic cloud	$FCE \times P_{im.ig\,(L)} + FCE \times (1 - P_{im.ig\,(L)}) \times \left(1 - P_{del.ig}\right) + FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$6{,}4 \times 10^{-5}$
Environmental damage	$FCE \times P_{im.ig\,(L)} + FCE \times (1 - P_{im.ig\,(L)}) \times \left(1 - P_{del.ig}\right) + FCE \times (1 - P_{im.ig\,(L)}) + FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$6{,}9 \times 10^{-5}$
VCE	$FCE \times (1 - P_{im.ig\,(L)}) \times P_{del.ig} \times P_{VCE} + FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$1{,}8 \times 10^{-5}$
Flashfire	$FCE \times (1 - P_{im.ig\,(L)}) \times P_{del.ig} \times (1 - P_{VCE}) + FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$1{,}8 \times 10^{-5}$
Fireball	$FCE \times P_{im.ig\,(G)}$	1×10^{-5}

Table 4.41- Failure frequencies of DP for the catastrophic rupture of the Condenser 3

	Equation	Frequency
VCE	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$3{,}2 \times 10^{-4}$
Flash fire	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$3{,}2 \times 10^{-4}$
Toxic cloud	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$3{,}6 \times 10^{-4}$
Environmental damage	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$3{,}6 \times 10^{-4}$
Jet fire	$FCE \times P_{im.ig\,(G)}$	2×10^{-4}

Table 4.42– Failure frequencies of DP for the small breach in vapour phase on the shell of the Condenser 3

	Equation	Frequency
VCE	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$1{,}6 \times 10^{-5}$
Flash fire	$FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$1{,}6 \times 10^{-5}$
Toxic cloud	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$1{,}8 \times 10^{-5}$
Environmental damage	$FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$1{,}8 \times 10^{-5}$
Jet fire	$FCE \times P_{im.ig\,(G)}$	1×10^{-5}

Table 4.43– Failure frequencies of DP for the medium breach in vapour phase on the shell of the Condenser 3

	Equation	Frequency
Pool fire	$FCE \times P_{im.ig\,(L)}$	9×10^{-4}
Toxic cloud	$FCE \times P_{im.ig\,(L)} + FCE \times (1 - P_{im.ig\,(L)}) \times \left(1 - P_{del.ig}\right) + FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$1{,}28 \times 10^{-3}$
Environmental damage	$FCE \times P_{im.ig\,(L)} + FCE \times (1 - P_{im.ig\,(L)}) \times \left(1 - P_{del.ig}\right) + FCE \times \ (1 - P_{im.ig\,(L)}) + FCE \times P_{im.ig\,(G)} + FCE \times (1 - P_{im.ig\,(G)}) \times (1 - P_{del.ig})$	$1{,}38 \times 10^{-3}$
VCE	$FCE \times (1 - P_{im.ig\,(L)}) \times P_{del.ig} \times P_{VCE} + FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times P_{VCE}$	$3{,}6 \times 10^{-4}$
Flashfire	$FCE \times (1 - P_{im.ig\,(L)}) \times P_{del.ig} \times (1 - P_{VCE}) + FCE \times (1 - P_{im.ig\,(G)}) \times P_{del.ig} \times (1 - P_{VCE})$	$3{,}6 \times 10^{-4}$
Jet fire	$FCE \times P_{im.ig\,(G)}$	2×10^{-4}

Table 4.44– Failure frequencies of DP for the small breach in liquid phase on the shell of the Condenser 3

J. Pipe 22

Table 4.45– Failure frequencies of DP for the small leak in liquid phase from Pipe 22 is equal to Table 4.31

K. Pipe 23

Table 4.46– Failure frequencies of DP for the small leak in liquid phase from Pipe 23 is equal to Table 4.31

4.2.5 MIRAS procedure: sixth step

The next step consists in the consequence analysis. ARAMIS establishes four classes of consequences that provide qualitative information, since they do not take into account the intensity of the dangerous phenomena.

In this sense, the software tool DNV-GL Phast is used in order to evaluate in a quantitative way these four classes of consequences of dangerous phenomena. This software enables the calculation of damage distances of each dangerous phenomenon. Damage distances are defined as the maximum distance where, at a fixed height, the physical effects of the scenario provided as model outputs by the DNV-GL Phast (thermal radiation, overpressure or concentration) reach a threshold value [40]. In the present work, the fixed height is of 1 m. According to their value, the damage distances determine the class of consequence.

The threshold values proposed in document [41] are going to be used for the calculation of damage distances. The following Table 4.48 shows these values, also considering the four classes of consequences contemplated in ARAMIS methodology and previously described in Table 3.14 (3.5.6).

Accident scenario	**Reversible injuries**	**Irreversible injuries**	**Beginning fatalities (lethality)**	**High fatalities (lethality)**
	C1	C2	C3	C4
Fire (stationary thermal radiation, Jet fire/ Pool fire)	3 kW/m^2	5 kW/m^2	7 kW/m^2	12,5 kW/m^2
BLEVE / Fireball (radiation variable thermal)	125 kJ/m^2	200 kJ/m^2	350 kJ/m^2	Fireball beam
Flash-fire (thermal radiation instant)	$\frac{1}{10}LFL$ *Not indicated in [36]. Taken for this study.	$\frac{1}{4}LFL$ *Not indicated in [36]. Taken for this study.	$\frac{1}{2}LFL$	LFL (Lower Flammability Limit)
VCE (overpressure of peak)	0,03 bars	0,07 bars	0,14 bars	0,3 bars
Toxic release (dose absorbed)	$\frac{1}{10}IDLH$ *Not indicated in [36]. Taken for this study.	IDLH Immediately Dangerous to Live and Health		LC_{50} (30 min, hmn) Concentration of toxic substance capable to cause the death of 50% of persons exposed within 30 min of exposure

Table 4.47

In order to establish which class of consequence corresponds to a DP resulting from a specific CE, basing on the obtained damage distances, the following criteria have been adopted:

1. If the hazardous distance that corresponds to irreversible injuries is lower than a threshold value, the corresponding class of consequence is C1. This threshold distance has been regarded of 10 m.
2. The class of consequence assigned to the DP will be C2 if the hazardous distance that corresponds to irreversible injuries is higher than the threshold value, but the damage distance corresponding to reversible injuries remains within the plant boundaries (is not placed beyond the specific dimension of the site). In this sense, since no information about the plant layout is provided, the site-specific dimension has been assumed of 100 meters.
3. The corresponding class of consequence will be C3 in case that the damage distance corresponding to reversible injuries exceeds the plant´s size, whereas the damage distance that corresponds to irreversible injuries still remains inside the boundary of the plant.
4. The worst case is that in which the class C4 is assigned to the DP. This happens if both damage distances exceed the plant boundaries.

Since PHAST software develops the consequence modelling by considering only pure substances, in those situations in which the releases contain more than one hazardous substance (furfural and formic acid) it is necessary to assume that only one of them is released. Hence, even though the current industrial process for the obtention of LA is characterized by a much higher flow rate of furfural than of formic acid, it would be rational to consider that only formic acid is released in those cases, since it is regarded as the most dangerous one. However, there is a particular situation in these equipments (Dist. column 1, pipes 9 and 12): Considering both substances together (as they flow through them), formic acid is regarded to be in liquid state, since even though the boiling point is significantly lower than the temperature of the equipments, the mass of furfural is much higher and it flows in liquid state (and so the formic acid which it is mixed with). That is why the tables with the frequencies of DP and the event trees of these equipments contain the “pool fire” and not “jet fire”. The problem is that, if only formic acid is considered, the Phast indicates that its state is vapour, not liquid, due to the lower boiling point. So, it has been decided to model these equipments with furfural instead of formic acid, and when the radius of the pool fire is obtained, use it to model a pool fire with the mass of formic acid.

As seen in the following tables that relate dangerous phenomena with damage distances and classes of consequences, missiles ejection and environmental damage are not shown. This is due to modelling does not include these DP. Their class of consequence, according to Table 3.15, are C3 and C1 (since furfural and formic acid do not represent a hazard for the environment if released). It is also possible to observe that the classification of the DP according to the criteria of ARAMIS (Table 3.15) is usually more conservative (higher levels of damage).

It is also necessary to highlight that it has been considered that all the equipments are placed at the centre of the plant, as well as due to PHAST database of the version used for the consequence analysis (6.4) does not contain the properties of formic acid and furfural, the values of the properties of these hazardous substances have been provided by members of the department in which the current study has been developed.

Regarding to weather conditions, Phast 6.4 contemplates three different scenarios: a wind speed of 1,5 m/s and F stability, a wind speed of 1,5 m/s and D stability and a wind speed of 5 m/s and D stability. In order to consider the most conservative situation, the first situation will be regarded in the present study. Otherwise, the volume of results would have been excessively large.

A. Distillation column 1

Dangerous phenomena	**Damage distances (m)**				**Class of consequence**
	Reversible injuries	**Irreversible injuries**	**Beginning fatalities**	**High fatalities**	
Overpressure generation	Not reached	Not reached	Not reached	Not reached	C1
Pool fire	Not reached	47	35	23	C2
Toxic cloud	2400	350	-	-	C4
VCE	19,8	17,2	12,7	11,5	C2
Flashfire	85	65	50	40,5	C2

Table 4.48 Damage distances and classes of consequences for the DP of the catastrophic rupture of the DC1

Dangerous phenomena	**Damage distances (m)**				**Class of consequence**
	Reversible injuries	**Irreversible injuries**	**Beginning fatalities**	**High fatalities**	
Pool fire	Not reached	23,8	20,5	16,7	C2
Toxic cloud	40	20	-	-	C2
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	9,6	7,3	3,5	3	C1

Table 4.49 Damage distances and classes of consequences for the DP of the small breach in liquid phase on the shell of the DC1

B. Pipe 9

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	Not reached	30,5	28	19,7	C2
Toxic cloud	100	40	-	-	C3 (for being more conservative)
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	13,8	10,6	8,7	4,3	C2

Table 4.50 Damage distances and classes of consequences for the DP of the small leak in liquid phase from Pipe 9

C. Pipe 12

The same table than the previous one

D. Distillation column 2

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Overpressure generation	27	14	8.7	5,6	C2
Pool fire	60	46	37,2	22,7	C2
Toxic cloud	4300	650	-	-	C4
VCE	50	37	21,44	16	C2
Flashfire	136	98	87	62,5	C3

Table 4.51 Damage distances and classes of consequences for the DP of the catastrophic rupture of the DC2

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	29	24	21,5	17	C2
Toxic cloud	40	20	-	-	C2
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	10	7,5	3,4	2,7	C1

Table 4.52 Damage distances and classes of consequences for the DP of the small breach in liquid phase on the shell of the DC2

E. Pipe 17

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	40	32,5	28	19,5	C2
Toxic cloud	100	45	-	-	C3 (for being more conservative)
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	14,2	10,8	8,8	4,3	C2

Table 4.53Damage distances and classes of consequences for the DP of the small leak in liquid phase from Pipe 17

F. Pipe 20

The same table than the previous one

G. Distillation column 3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Overpressure generation	42	22	14,2	8,8	C2
Toxic cloud	2200	600	-	-	C4
Fireball	-	-	-	27,62	C2
VCE	46,2	35,4	20,2	15,8	C2
Flashfire	36	32	27,5	22	C2

Table 4.54 Damage distances and classes of consequences for the DP of the catastrophic rupture of the DC3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	4,3	2,6	1,43	0,75	C1
Toxic cloud	75	25	-	-	C2
Jet fire	Not reached	3,5	3,23	Not reached	C1

Table 4.55 Damage distances and classes of consequences for the DP of the small breach in vapour phase on the shell of the DC3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	16	10,4	6,6	3,6	C2
Toxic cloud	145	52	-	-	C3
Jet fire	Not reached	19	18	16,4	C2

Table 4.56 Damage distances and classes of consequences for the DP of the medium breach in vapour phase on the shell of the DC3

H. Pipe 21

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
VCE	13,8	12,8	11,1	10,5	C2
Flashfire	28	22,5	16	8	C2
Toxic cloud	285	60	-	-	C3
Jet fire	44,5	40,8	38,7	35,8	C2

Table 4.57 Damage distances and classes of consequences for the DP of the small leak in vapour phase from Pipe 21

I. Condenser 3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Overpressure generation	42	22	14,2	8,8	C2
Pool fire	60	47	37,9	23,1	C2
Toxic cloud	2200	600	-	-	C4
VCE	46,2	35,4	20,2	15,8	C2
Flashfire	36	32	27,5	22	C2
Fireball	-	-	-	27,62	C2

Table 4.58 Damage distances and classes of consequences for the DP of the catastrophic rupture of the Condenser 3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	4,3	2,6	1,43	0,75	C1
Toxic cloud	75	25	-	-	C2
Jet fire	Not reached	3,5	3,23	Not reached	C1

Table 4.59 Damage distances and classes of consequences for the DP of the small breach in vapour phase on the shell of the Condenser 3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	16	10,4	6,6	3,6	C2
Toxic cloud	145	52	-	-	C3
Jet fire	Not reached	19	18	16,4	C2

Table 4.60 Damage distances and classes of consequences for the DP of the medium breach in vapour phase on the shell of the Condenser 3

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	28,5	23,8	21	16.7	C2
Toxic cloud	38	22	-	-	C2
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	9,2	7,1	3,4	2,6	C1
Jet fire	-	18,3	Not reached	Not reached	C2

Table 4.61 Damage distances and classes of consequences for the DP of the small breach in liquid phase on the shell of the Condenser 3

J. Pipe 22

Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	40	32,2	27,8	19,3	C2
Toxic cloud	102	40	-	-	C3
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	12,6	10,1	8,3	4,3	C2

Table 4.62 Damage distances and classes of consequences for the DP of the small leak in liquid phase from Pipe 22

K. Pipe 23

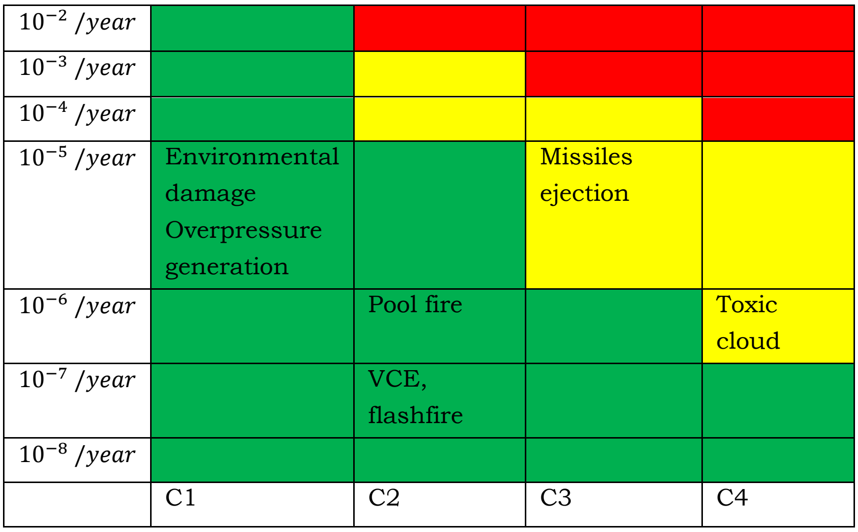
Dangerous phenomena	Damage distances (m)				Class of consequence
	Reversible injuries	Irreversible injuries	Beginning fatalities	High fatalities	
Pool fire	39,5	32,1	27,7	19,2	C2
Toxic cloud	100	38	-	-	C3 (for being more conservative)
VCE	Not reached	Not reached	Not reached	Not reached	C1
Flashfire	12,3	10	8,2	4,2	C2 (for being more conservative)

Table 4.63 Damage distances and classes of consequences for the DP of the small leak in liquid phase from Pipe 22

4.2.6 MIRAS procedure: seventh step

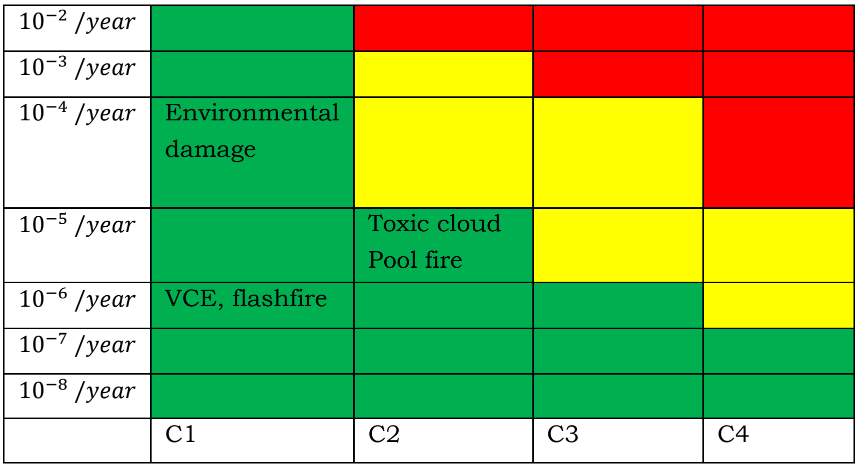
Since it is necessary at this moment to evaluate the Reference Accident Scenarios (RAS) that will be modelled to calculate the severity, the risk matrixes of every critical event must be built for each selected equipments. As explained before (3.5.7), each risk matrix relates the frequencies and the classes of consequences of the dangerous phenomena that result from the critical events detected for the equipments. Dangerous phenomena located in the yellow or the red zone are considered as RAS.

A. Distillation column 1



$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩 Environmental damage Overpressure generation	🟩	🟨 Missiles ejection	🟨
$10^{-6}\ /year$	🟩	🟩 Pool fire	🟩	🟨 Toxic cloud
$10^{-7}\ /year$	🟩	🟩 VCE, flashfire	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.1 Risk matrix for the catastrophic rupture of the DC1



$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩 Environmental damage	🟨	🟨	🟥
$10^{-5}\ /year$	🟩	🟩 Toxic cloud Pool fire	🟨	🟨
$10^{-6}\ /year$	🟩 VCE, flashfire	🟩	🟩	🟨
$10^{-7}\ /year$	🟩	🟩	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.2 Risk matrix for the small breach in liquid phase on the shell of the DC1

B. Pipe 9

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩	🟩	🟨	🟨
$10^{-6}\ /year$	🟩 Environmental damage	🟩 Pool fire	🟩 Toxic cloud	🟨
$10^{-7}\ /year$	🟩 VCE	🟩 Flash fire	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.3 Risk matrix for the small leak in liquid phase from Pipe 9

C. Pipe 12

Has the same risk matrix that the one of pipe 9

D. Distillation column 2

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩 Environmental damage	🟩 Overpressure generation	🟨 Missiles ejection	🟨
$10^{-6}\ /year$	🟩	🟩 Pool fire	🟩	🟨 Toxic cloud
$10^{-7}\ /year$	🟩	🟩 VCE	🟩 Flashfire	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.4 Risk matrix for the catastrophic rupture of the DC2

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩 Environmental damage	🟨	🟨	🟥
$10^{-5}\ /year$	🟩	🟩 Toxic cloud Pool fire	🟨	🟨
$10^{-6}\ /year$	🟩 VCE, flashfire	🟩	🟩	🟨
$10^{-7}\ /year$	🟩	🟩	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.5 Risk matrix for the small breach in liquid phase on the shell of the DC2

E. Pipe 17

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩	🟩	🟨	🟨
$10^{-6}\ /year$	🟩 Environmental damage	🟩 Pool fire	🟩 Toxic cloud	🟨
$10^{-7}\ /year$	🟩 VCE	🟩 Flashfire	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.6 Risk matrix for the small leak in liquid phase from Pipe 17

F. Pipe 20

Has the same risk matrix that the one of pipe 17

G. Distillation column 3

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩	🟩	🟨	🟨
$10^{-6}\ /year$	🟩 Environmental damage	🟩 Overpressure generation VCE, flashfire Fireball	🟩 Missiles ejection	🟨 Toxic cloud
$10^{-7}\ /year$	🟩	🟩	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.7 Risk matrix for the catastrophic rupture of the DC3

$10^{-2}\ /year$	🟩	🟥	🟥	🟥
$10^{-3}\ /year$	🟩	🟨	🟥	🟥
$10^{-4}\ /year$	🟩	🟨	🟨	🟥
$10^{-5}\ /year$	🟩 Environmental damage VCE, flashfire Jet fire	🟩 Toxic cloud	🟨	🟨
$10^{-6}\ /year$	🟩	🟩	🟩	🟨
$10^{-7}\ /year$	🟩	🟩	🟩	🟩
$10^{-8}\ /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.8 Risk matrix for the small breach in vapour phase on the shell of the DC3

$10^{-2} /year$	🟩	🟥	🟥	🟥
$10^{-3} /year$	🟩	🟨	🟥	🟥
$10^{-4} /year$	🟩	🟨	🟨	🟥
$10^{-5} /year$	🟩 Environmental damage VCE	🟩 Flashfire Jet fire	🟨 Toxic cloud	🟨
$10^{-6} /year$	🟩	🟩	🟩	🟨
$10^{-7} /year$	🟩	🟩	🟩	🟩
$10^{-8} /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.9 Risk matrix for the medium breach in vapour phase on the shell of the DC3

H. Pipe 21

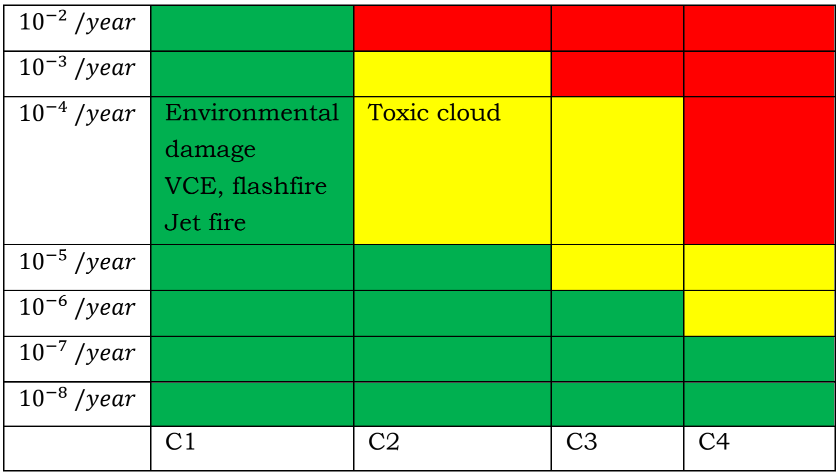
$10^{-2} /year$	🟩	🟥	🟥	🟥
$10^{-3} /year$	🟩	🟨	🟥	🟥
$10^{-4} /year$	🟩	🟨	🟨	🟥
$10^{-5} /year$	🟩	🟩	🟨	🟨
$10^{-6} /year$	🟩 Environmental damage	🟩 VCE, flashfire Jet fire	🟩 Toxic cloud	🟨
$10^{-7} /year$	🟩	🟩	🟩	🟩
$10^{-8} /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.10 Risk matrix for the small leak in vapour phase from Pipe 21

I. Condenser 3

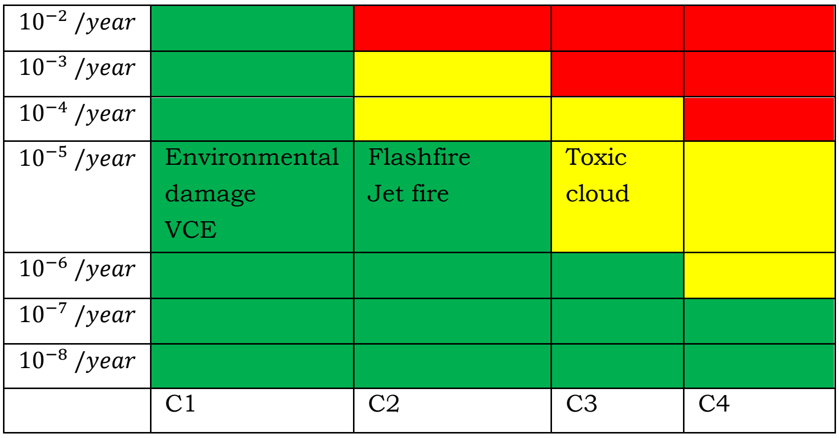
$10^{-2} /year$	🟩	🟥	🟥	🟥
$10^{-3} /year$	🟩	🟨	🟥	🟥
$10^{-4} /year$	🟩	🟨	🟨	🟥
$10^{-5} /year$	🟩 Environmental damage	🟩 Overpressure Pool fire VCE, flashfire Fireball	🟨 Missiles ejection	🟨 Toxic cloud
$10^{-6} /year$	🟩	🟩	🟩	🟨
$10^{-7} /year$	🟩	🟩	🟩	🟩
$10^{-8} /year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.11 Risk matrix for the catastrophic rupture of the Condenser 3



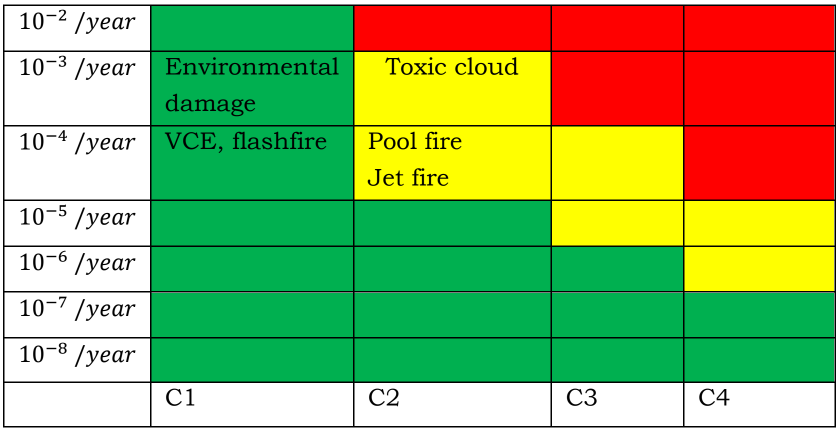
$10^{-2}\,/year$	🟩	🟥	🟥	🟥
$10^{-3}\,/year$	🟩	🟨	🟥	🟥
$10^{-4}\,/year$	🟩 Environmental damage VCE, flashfire Jet fire	🟨 Toxic cloud	🟨	🟥
$10^{-5}\,/year$	🟩	🟩	🟨	🟨
$10^{-6}\,/year$	🟩	🟩	🟩	🟨
$10^{-7}\,/year$	🟩	🟩	🟩	🟩
$10^{-8}\,/year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.12 Risk matrix for the small breach in vapour phase on the shell of the Condenser 3



$10^{-2}\,/year$	🟩	🟥	🟥	🟥
$10^{-3}\,/year$	🟩	🟨	🟥	🟥
$10^{-4}\,/year$	🟩	🟨	🟨	🟥
$10^{-5}\,/year$	🟩 Environmental damage VCE	🟩 Flashfire Jet fire	🟨 Toxic cloud	🟨
$10^{-6}\,/year$	🟩	🟩	🟩	🟨
$10^{-7}\,/year$	🟩	🟩	🟩	🟩
$10^{-8}\,/year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.13 Risk matrix for the medium breach in vapour phase on the shell of the Condenser 3



$10^{-2}\,/year$	🟩	🟥	🟥	🟥
$10^{-3}\,/year$	🟩 Environmental damage	🟨 Toxic cloud	🟥	🟥
$10^{-4}\,/year$	🟩 VCE, flashfire	🟨 Pool fire Jet fire	🟨	🟥
$10^{-5}\,/year$	🟩	🟩	🟨	🟨
$10^{-6}\,/year$	🟩	🟩	🟩	🟨
$10^{-7}\,/year$	🟩	🟩	🟩	🟩
$10^{-8}\,/year$	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.14 Risk matrix for the small breach in liquid phase on the shell of the Condenser 3

J. Pipe 22

10^{-2} /year	🟩	🟥	🟥	🟥
10^{-3} /year	🟩	🟨	🟥	🟥
10^{-4} /year	🟩	🟨	🟨	🟥
10^{-5} /year	🟩	🟩	🟨	🟨
10^{-6} /year	🟩 Environmental damage	🟩 Pool fire	🟩 Toxic cloud	🟨
10^{-7} /year	🟩 VCE	🟩 Flashfire	🟩	🟩
10^{-8} /year	🟩	🟩	🟩	🟩
	C1	C2	C3	C4

Figure 4.15 Risk matrix for the small leak in liquid phase from Pipe 22

K. Pipe 23

Has the same risk matrix that the one of pipe 22

5. Comparison of the results of two different industrial processes for the obtention of levulinic acid

After the ARAMIS procedure application to the industrial process whose scheme and performance are explained and detailed in 4.1.1, and as mentioned in the introduction, a comparison of the results of this study with those of a previous analysis of another process for the same production of levulinic acid, whose data and results are provided, is carried out in order to evaluate which should be the safest alternative for the production of levulinic acid. As a result, a conclusion is obtained at this point.

The scheme with the components of the industrial process analysed in the other study, different from the one of the present thesis, is shown below, whereas the following table contains the damage distances and the corresponding classes of consequences to these equipments, according to the dangerous phenomena, that result from the application of the ARAMIS procedure.

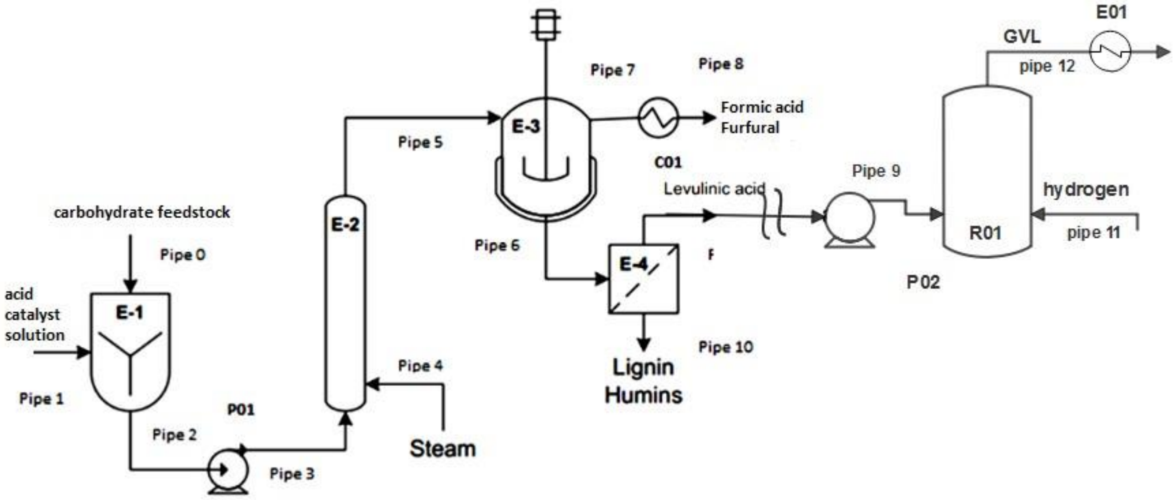


Figure 4-1.. Biofine Process Scheme. E-1: mixer; P01: feeding pump; E-2: PFR; E-3: CSTR; C01: condenser; E-4: Filter press. Pipe 0: Biomass; Pipe 1: solution of H_2SO_4; Pipe 2: Mixer outlet; Pipe 3: PFR inlet; Pipe 4: Steam; Pipe 5: CSTR inlet; Pipe 6: Filter press inlet; Pipe 7: FA+F hot stream; Pipe 8: FA+F cold stream; Pipe 9: LA and solution of catalyst; Pipe 10: Char. Catalytic hydrogenation process scheme to GVL. P02: feeding pump; R01: catalytic hydrogenation reactor; Pipe 9: LA and solution of catalyst; Pipe 11: Hydrogen; Pipe 12: GVL and solution of acid catalyst before cooling; E01: heat exchanger.

	Equipment	Critical events	Dangerous phenomena	Reversible injuries (m)	Irreversible injuries (m)	Beginnning fatalities (m)	High fatalities (m)	Position in the risk matrix
BIOFINE PROCESS	CSTR	Catastrophic rupture	Overpressure generation	44	24	15	9,4	C2
			Toxic cloud	25000	860	/	101	C4
			Fireball	/	/	/	52	C2
			VCE	44	28	21,5	17,3	C2
			Flash fire	33	22,5	17,5	14	C2
		Small breach in vapour phase	Jet fire	5	Not reached	Not reached	Not reached	C1
			Toxic cloud	3200	873	/	36	C4
			VCE	Not reached	Not reached	Not reached	Not reached	C1
			Flash fire	16	6	2,2	0,8	C2
		Medium breach in vapour phase	Jet fire	12	11	10	Not reached	C2
			Toxic cloud	413	250	/	42	C4
			VCE	11,4	10,7	10,5	10,4	C2
			Flash fire	26	21	14	5	C2
	CONDENSER	Catastrophic rupture	Overpressure generation	5,6	3,1	1,9	0,7	C1
			Toxic cloud	3816	987	/	42	C4
			Fireball	/	/	/	6,55	C1
			VCE	Not reached	Not reached	Not reached	Not reached	C1
			Flash fire	11	4,9	3,6	3	C1
			Pool fire	8,2	7	6	Not reached	C1
	Pipe 7	Small leak in vapour phase	Jet fire	4	2,3	0,8	Not reached	C1
			Toxic cloud	5500	1400	/	55	C4
			VCE	Not reached	Not reached	Not reached	Not reached	C1
			Flash fire	24	8,8	3,7	1,3	C1
		Medium leak in vapour phase	Jet fire	7	5,7	4,9	Not reached	C1
			Toxic cloud	14250	3187	/	160	C4
			VCE	Not reached	Not reached	Not reached	Not reached	C1
			Flash fire	45	17	8,36	2,8	C2
HYDROGENATION PROCESS	HYDR. REACTOR	Catastrophic rupture	Overpressure generation	300	164	101	62	C4
			Flash fire	140	100	54	35	C4
			VCE	318	187	128	92	C4
			Fireball	76	59	42,5	25,6	C2
		Small breach in vapour phase	Jet fire	2,5	1,9	Not reached	Not reached	C1
			VCE	23	> 10	13,4	12,6	C2
			Flash fire	10	4,6	3	2	C1
		Medium breach in vapour phase	Jet fire	12,7	11	9,7	7,8	C2
			VCE	43	28	21,4	17,3	C2
			Flash fire	38	18	11,6	7,6	C2
	Pipe 11	Small leak in vapour phase	Jet fire	3,7	3,1	2,6	1,8	C1
			VCE	38,5	> 10	24,8	23,7	C2
			Flash fire	15	7,3	4,7	3,4	C1
		Medium leak in vapour phase	Jet fire	8	7	6,5	5,4	C1
			VCE	40	> 10	18	16	C2
			Flash fire	30	15	9,2	6,2	C2

There are four substantial differences between the industrial process I analysed in this study (A) and the one shown just before (B):

-The first one is the relevant difference in the existing proportion between formic acid and furfural. In B the absolute and relative quantities (%w/w) were quite close (I did not include the chart where the equipments, the state, temperature and pressure of the substances, as well as the mass flow rate and the composition of the streams of each equipment to prevent the document to lengthen in excess), but in A, and as it is possible to check in Table 4.2, the relative quantity of furfural is much higher than the one of formic acid in the main equipments (distillation columns and many pipes), and the flowrate of formic acid only represents 0.34% of the one of furfural.

-Secondly, there is another important difference: B includes hydrogen (H_2), whereas A does not use this element. The boiling temperature of hydrogen is 253°C, whereas the auto-ignition temperature, LFL and UFL are 566 °C, 4% and 75% respectively [24]. The H-statements are H280 (contains gas under pressure; may explode if heated) and **H220 (extremely flammable gas)** [43]. It is an advantage A has with respect to B, since the use of hydrogen entails risks due to the large flammability range.

-Moreover, is worth noting that A has more components and equipments (39) than B (25), so more dangerous phenomena are likely to occur, what is a disadvantage.

-Finally, the following Table 4.64 illustrates the number of RAS of both industrial processes:

Number of RAS	Industrial process A	Industrial process B
Green zone (Negligible effects zone, nor really RAS)	86	32
Yellow zone (Medium effects zone)	13	11
Red zone (High effects zone)	0	0

Table 4.64

So, even though the number of equipments is considerably higher in case of A, the number of RAS is only a little higher. It is due to, in case of B, the pressure is several times the one employed in the equipments of A (1,2 atm, whereas B has about 5 atm).

6. Final comments and conclusions

The complexity of industrial processes is currently growing, what leads to the necessity of evaluating several scenarios that can result from catastrophic events by means of increasingly modern and specialized software.

Indeed, the purpose of the study previously carried out has been to obtain, analyse and use the data of an specific industrial process for the obtention of levulinic acid from biomass for the later application of ARAMIS methodology, enhanced through the employment of the Phast software tool for the obtention of damage distances, what has allowed to assess the risks from which can derive.

Other industrial processes for the obtention of levulinic acid were initially contemplated, evaluated and their performance understood, but finally discarded, either for being “too simple” (having few equipments to be analysed), or for providing limited information that would not have allowed to conclude with a sufficiently accurate and rigorous risk analysis. In fact, and as mentioned in other paragraphs of this study, the information was not complete enough to apply the 100% of ARAMIS methodology, but enough to carry out a reliable analysis and results that were finally employed in a comparison with another industrial process risk analysis results.

In the same way, there were several software tools that could have been used instead of Phast. One of them is ALOHA. Nevertheless, Phast was finally chosen for consequence modelling and the obtention of damage distances, further converted to ARAMIS consequence classes to quantify the consequences of the considered scenarios and leading to more realistic results than the ones which would have been obtained through the direct use of the classes of consequences proposed by ARAMIS, since it is showing more effect distances compared to ALOHA. The reason is that Phast software considers more inputs on atmospheric data and geometric measures of chemical inventories; hence PHAST results are more realistic. However, it is necessary to mention that the installation and the lately use of this software led to some difficulties.

Even though some considerations were taken in order to finally perform the study, the results are regarded as acceptably rigorous. Finally, it is worth noting that in the comparison between the number of RAS done in the fifth section, the industrial process B also included equipments (those which involved hydrogen) for the upgrading of levulinic acid to γ-valerolactone. If industrial process A had included the equipments for this upgrading, the number of RAS would have undoubtedly increased, so the difference in the number of RAS would rise.

7. Budget

For the elaboration of the budget of the present study, the required time is the essential factor. The employed time for the performance of this document has been considered to be about 85 h for an engineer with relative experience, so about 30% of the time that has been required for me, since I had no experience with the computer tool applied for the obtention of results (I had to learn how to use it) and the application of some steps of ARAMIS procedure presented difficulties and uncertainties that had to be discussed and analysed.

So, considering an average salary of an engineer here in Bologna for this kind of jobs (100 €/h), the cost of the elaboration of this document would be around 8500€. Considering the time that I have consumed, it would rise to 28300€. much more expensive. Furthermore, if the cost of the installation of the informatic tool is included (I had access to it and did not have to pay), the budget needed would rise to 20.000 € extra for a company. Since in my case, the tool was provided to a university, the price is only 2000€. Then, in my case, the price rises to 30300€ if the tool had to be bought, whereas for an engineer in a company would be of 28500€.

8. Acknowledgements

First of all, and above all, I must thank both my university centre in Spain (UPV) and my parents, since they have been, each one on its own way, the two main pillars that have made it possible for me to study the last semester of my degree in engineering in industrial technologies in a foreign country, and therefore to finish my university academic training, also acquiring the experience of developing myself and acquiring knowledge in a different language and educational system. This formation on the abroad is experiencing a growing relevance for companies nowadays. It has been one of the reasons why I decided to enrol the current semester in the Erasmus+ program, and I am grateful for the opportunity I have had to complete my formation.

Secondly, of course I must thank the effort, patience and dedication that my final degree thesis tutors have had with me throughout these months, since without them I would not have been able to carry out this work successfully. I must also thank them, as well as other engineers of the "Dipartamento di Ingegneria Civile, Ambientale e dei Materiali" (DICAM) for their instructions in the use of the computer tool used to enhance the performance of ARAMIS methodology (DNV-GL Phast), as well as the time they spent with me until the mentioned program could be finally installed successfully, since many problems arose during its installation. I cannot finish this thesis without mentioning that the help of other staff of the department of chemical engineering has also been crucial for the development of the study.

9. Bibliography

[1]- ARAMIS_deliverable_D1C: Faculté Polytechnique de Mons, Major Risk Research Centre, Prof. C. Delvosalle, Ir C. Fiévez, Ir A. Pipart.presip

[2]- https://visual.ly/community/infographic/economy/world-energy-consumption-1990-2035-quadrillion-btu.

[3]- U.S Energy Information Administration: https://www.eia.gov/todayinenergy/detail.php?id=26212.

[4]https://www.reddit.com/r/energy/comments/28y7az/global_energy_consumption_19652013/.

[5]- Industrial Ecology, theme 1: Ernesto Salzano, Unibo.

[6]- https://www.cleantechloops.com/an-introduction-to-biomass-energy/.

[7]- https://www.bioenergyconsult.com/biomass-energy-introduction/.

[8]- http://www.energiasrenovablesinfo.com/biomasa/biomasa-ventajas-desventajas/.

[9]http://www.cenipalma.org/sites/default/files/files/Cenipalma/Magistral_Biorefineriaalternativamanejobiomasa%20residual_opt.pdf.

On the other hand, this website cites another website, the National Renewable Energy Laboratory: https://www.nrel.gov.

[10]- http://www.viaspace.com/biochemicals_bio_plastics.php.

[11]- http://www.climatetechwiki.org/technology/bioref.

[11]- http://naukas.com/2017/10/24/por-que-necesitamos-energia-nuclear/.

[12]- V. Moreno and V. Cozzani: “Major accident hazard in bioenergy production”, Journal of loss prevention in the process industries, vol. 35, pages 135-144, 2015.

[13]- CCPS, Guidelines for Chemical Process Quantitative Risk Assessment, The Hage, Netherlands: Committee for the Prevention of Disasters, 1999.

[14]- Websterk New Collegiate Dictionary (G. & C. Merriam Co., Springfield, 1977).

[15]- H.Andersen, J.Casal, A.Dandrieux, B. Debray, V.De Dianous, N.J.Duijm, C.Delvosalle, C.Fievez, L.Goossens, R.T.Gowland, A.J.Hale, D.Hourtolou,

B.Mazzarotta, A.Pipart, E.Planas, F.Prats, O.Salvi, J.Tixier, “ARAMIS Final User Guide”, December 2004

[16]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 2 - Methodology for the selection of equipment to be studied,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[17]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 3 - Method to associate critical events and relevant hazardous equipment,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[18]- Debray B., Piatyszek E., Cauffet F., Londiche H., “ARAMIS. Appendix 4 - Generic fault trees,” Armines, Ecole Nationale Supérieure de Mines de Saint Etienne (France).

[19]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 5 - Methodology for the building of generic event trees (MIMAH),”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[20]- Report Schemes LA production V2 (Valerian´s folder).

[21]- Excel file: Exploitation of flowrates (LA production) (Valerian´s folder).

[22]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 10 - Generic frequencies data for the critical events,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[23]- Toxicology Data Network (TOXNET) Website.

[24]- Cameo Chemicals Website.

[25]- Science Lab Website.

[26]- Wikipedia Website

[27]- Centers for Disease Control and Prevention (CDC) Website; National Institute for Occupational Safety and Health (NIOSH).

[28]- https://www.sigmaaldrich.com/content/dam/sigma-aldrich/docs/promo_NOT_INDEXED/General_Information/1/h_overview.pdf

[29]- Debray B., Piatyszek E., Cauffet F., Londiche H., “ARAMIS. Appendix 7 – Frequencies and probabilities data for the fault tree,” Armines, Ecole Nationale Supérieure de Mines de Saint Etienne (France).

[30]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 8 - Checklists of safety functions and barriers,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[31]- de Dianous V., Hourtolou D., Bernuchon E., "APPENDIX 9- Assessment of the performances of safety barriers”, INERIS, Accidental Risk Division (France).

[32]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 10 - Generic frequencies data for the critical events,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[33]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 13 – Risk Matrix,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[34]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 10 - Generic frequencies data for the critical events,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[35]- Handboek Kanscijfers, Ministerie van de Vlaamse Gemeenschap, Departement Leefmilieu en Infrastructuur, AMINAL, Brussel, 1994.

[36]- Canvey: an investigation of potential hazards from operations in the Canvey Island/Thurrock area. Health and Safety Executive, HMSO, 1978

[37]- The "Purple book" - Committee for the Prevention of Disasters. Guidelines for quantitative risk assessment. CPR 18 E. 1999.

[38]- S. Carol, J.A. Vilchez, J. Casal, Using major hazard database systems to develop event trees for flammable materials. Universitat Politècnica de Catalunya, CERTEC, Barcelona

[39]- C. Delvosalle, C. Fiévez and A. Pipart, “ARAMIS. Appendix 12 - Probabilistic aspects in the event tree,”, Faculté Polytechnique de Mons, Major Risk Research Centre (Belgium), 2004.

[40]- A. Tugnoli, V. Cozzani and G. Landucci, “A Consequence Based Approach to the Quantitative Assessment of Inherent Safety,” AIChE Journal, vol. 53, no. 12, pp. 3171-3182, 2007.

[41]- Decreto del ministerio dei lavori pubblici, “Requisiti minimi di sicurezza in materia di pianificazione urbanistica e territoriale per le zone interessate da stabilimenti a rischio di incidente rilevante”, D. M. LL.PP. 9 maggio 2001

[42]- SIGMA-ALDRICH website

[43]- Praxair website

[44]- Biofuel.org.UK website

[45]- “Energy from waste and good” website