

A PROPOSAL OF GENERIC EVENT TREES AND PROBABILITIES FOR THE RELEASE OF DIFFERENT TYPES OF HAZARDOUS MATERIALS

Juan A. Vilchez*, Vicenç Espejo* and Joaquim Casal**

**TIPs. Barcelona, Spain*

Llenguadoc 10. 08030-Barcelona, Spain

***Centre for Studies on Technological Risk (CERTEC)*

*Department of Chemical Engineering, Universitat Politècnica de Catalunya
Diagonal 647. 08028-Barcelona, Spain*

Abstract: In quantitative risk analysis usually generic hypothesis concerning the loss of containment initiating events are applied, in order to simplify the analysis. For example, for the loss of containment from a storage tank: instantaneous release of the complete inventory, continuous release of the complete inventory in 10 min and continuous release from a hole with a diameter of 10 mm. Once these initiating events specified, it is necessary to develop the corresponding event trees to establish which are the different sequences –depending on the properties of the released material, the existing safety barriers, etc.– leading from each initiating event to the diverse final outcomes or accident scenarios. In this communication a set of generic short event trees are proposed for the main cases which can be found, as a function of the type of hazardous material released. Values for the corresponding intermediate probabilities (immediate ignition, delayed ignition, flame front acceleration, BLEVE, etc.) are also proposed, following both a literature survey and expert judgment.

Keywords: risk analysis, event tree, accidental sequence, probability

1. INTRODUCTION

After a loss of containment event (the collapse of a tank, a hole in a pipe, etc.) takes place, the incident can follow diverse sequences depending on the circumstances: the properties and condition of the released material, the existence of one or more safety barriers, etc. Each one of these sequences will lead to a final accidental scenario with a severity which will range between “no outcome” (no consequences or negligible consequences) and a major accident such as an explosion, a large fire, etc.

When the quantitative risk analysis of a given plant is performed, usually generic hypothesis concerning the initiating events to be taken into account are applied. Thus, for example, for the loss of containment from a storage tank the following three loss of containment events are considered: instantaneous release of the complete inventory, continuous release of the complete inventory in 10 min and continuous release from a hole with a diameter of 10 mm (each one with the corresponding associated frequency). Then, following each initiating event, the incident can evolve in different ways; therefore, the corresponding event trees must be constructed to know the diverse final outcomes or accident scenarios, and b) the frequencies associated to each one of these final scenarios.

In the same way that generic hypothesis on the initiating events are assumed, generic event trees following these events can also be assumed for the most frequent cases, as a function of the type of hazardous material involved. The inclusion in these events trees of the intermediate probabilities associated to the diverse circumstances or safety barriers (immediate ignition, delayed ignition, flame front acceleration, BLEVE, etc.) will allow establishing the frequencies expected for the different outcomes or accidental scenarios. This will help in performing systematic

quantitative risk analysis. Of course, if a specific risk analysis must be performed on a given unit, specific initiating loss of containment events and events trees should be better considered, but for ordinary analysis the aforementioned approach would be a useful tool.

In this communication a set of generic short event trees are proposed for the main cases which can be found, as a function of the type of hazardous material released. Values for the corresponding intermediate probabilities are also proposed, following both a literature survey and expert judgment. Examples of petroleum fractions or representative chemicals are included for each tree.

2. PROPOSED EVENT TREES

2.1. Flammable, low volatility liquid materials

For example, kerosene or chemicals with $21 \leq T_f \leq 55$ °C at room temperature, equivalent to *R10* flammable substances (according to EC labeling directives). The following event tree should be considered:

<i>Initiating event</i>	<i>Ignition</i>	<i>Final scenario</i>
Liquid spill f	Yes $P_1 = 0.01$	Pool fire
	No $\bar{P}_1 = 0.99$	No consequences

For substances with $T_f > 55$ °C the ignition probability is very low, and usually it is not considered in QRA studies. In some cases, if T_f is close to 55 °C (i.e. diesel oil) the same ignition probability can be considered: $P_1 = 1\%$. Delayed ignition is neglected because, due to the low volatility, flammable clouds are not generated (Ronza et al., 2007).

2.2. Toxic and flammable, low volatility liquid materials

For example, allyl alcohol (at room temperature). This event tree for toxics is not used in a regular manner, and often it can be neglected in QRA analysis.

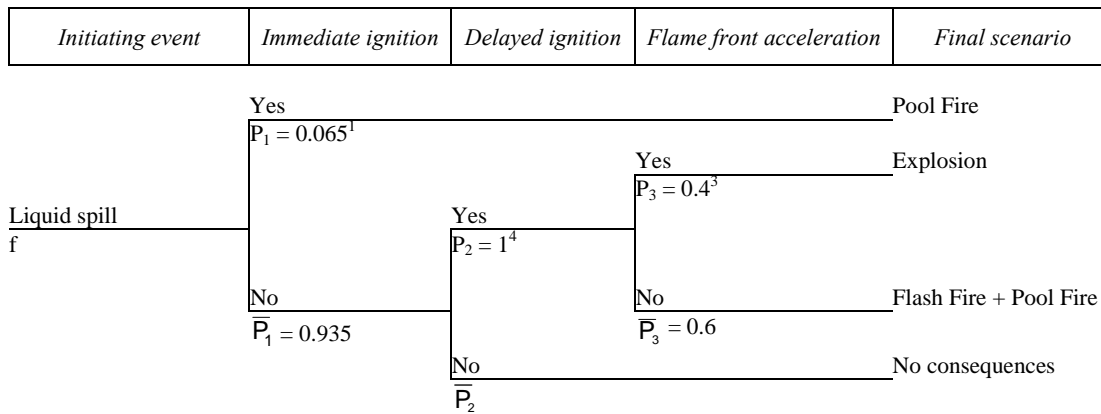
<i>Initiating event</i>	<i>Ignition</i>	<i>Final scenario</i>
Liquid spill F	Yes $P_1 = 0.01$	Pool fire
	No $\bar{P}_1 = 0.99$	Toxic dispersion

Flammability features and ignition probability: same values than for case 2.1.

2.3. Flammable and volatile liquid materials

For example, gasoline or naphtha or chemicals with $T_f \leq 21$ °C at room temperature, equivalent to *R11* flammable substances (according to EC labeling directives).

In the event of delayed ignition a flash fire or explosion can occur. In general, after the ignition, the flame will run back to the liquid pool and give rise to a pool fire. In some cases, due to congestion or to the large size of the flammable cloud, flame front acceleration can occur and the explosion scenario must be included.



1: Probability of immediate ignition taken from Bevi (2009) for highly flammable substances ($T_f < 21$ °C).

2: Default probability of delayed ignition (flammable vapor).

3: Probability of explosion in the event of flammable dispersion (Bevi, 2009), only if a minimum amount (usually 500 - 1000 kg) is between flammability limits in the cloud. If this criterion it is not fulfilled, use $P_3 = 0$

4: The criterion of 100% for the probability of delayed ignition is probably too conservative, as not always the release of these substances gives rise to a fire. The following values are therefore proposed:

Table 1

Probability	If LFL exceeds the establishment boundary*	Process releases**	Process releases in classified areas without any direct ignition sources	Storage releases***
P_2	1	0.7	0.1	0.07
\bar{P}_2	0	0.3	0.9	0.93

*From the Purple Book (2007).

**The highest value of Bevi (2009) as it is a zone with possible ignition sources.

***A low value is applied, being a zone without any direct ignition sources (Ronza et al, 2007).

Of course, a more accurate method can also be applied by considering the actual ignition sources and estimating the probability of delayed ignition as a function of the probability of ignition of each source and the probability that they be reached by the flammable cloud.

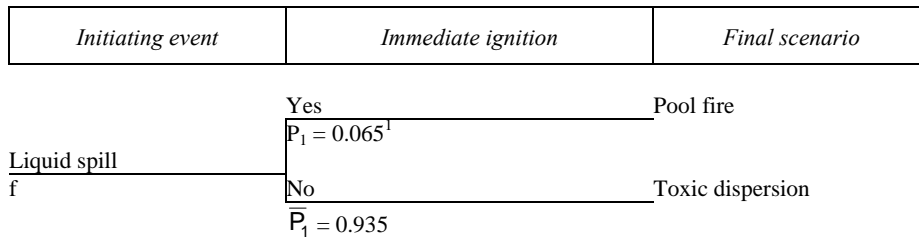
2.4. Toxic and flammable, volatile liquid materials

For example, benzene or acrylonitrile at room temperature. Event tree, flammability features and ignition probabilities: same values than in case 2.3. A significant difference: the “no ignition” branch must include the toxic dispersion outcome.

It should be noted that if the probability of delayed ignition is considered to be 100%, the toxic dispersion scenario is eliminated. In Bevi (2009), for toxic and flammable vapors the following criterion is proposed; the frequency of escape f is divided into two separate events:

- a purely flammable event (pool fire) when direct ignition occurs
- a purely toxic event (toxic dispersion) when there is not any direct ignition.

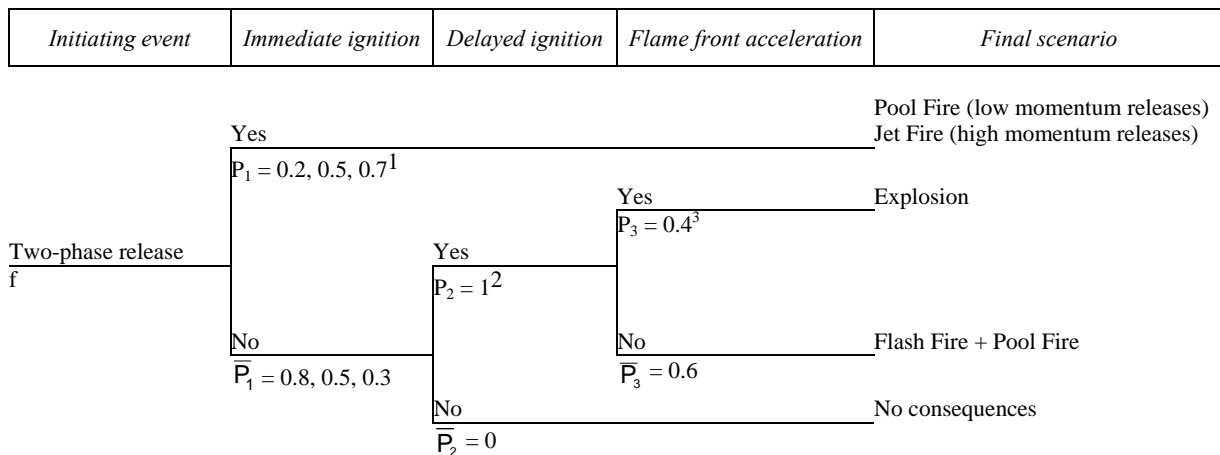
This criterion leads to the following practical event tree (not including vapor cloud explosion):



This implies that if there is no immediate ignition, toxic atmospheric dispersion should be always assumed. This is a very conservative approach. In fact a flash fire can occur if an ignition source is reached. The suggested approach considers only toxic dispersion because larger distances are expected. Toxic effects after ignition of the flammable cloud are not included. It is assumed that in this case the plume will rise and will not cause any further lethal toxic effects at ground level.

2.5. Continuous releases of extremely flammable pressurized liquefied gases

For example, liquefied propane or butane and chemicals with R12 phrase (“extremely flammable”) according to EC Directives (i.e. methyl chloride), at room temperature (see figure).

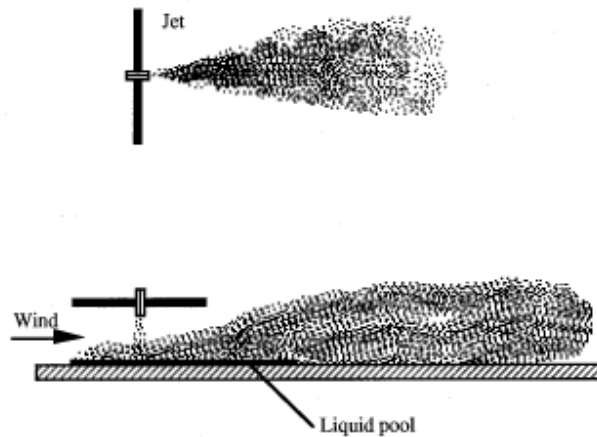


1: Probability of immediate ignition of flammable gases, depending on the released flow rate m (Bevi, 2009): 0.2 if $m < 10 \text{ kg s}^{-1}$; 0.5 if $10 < m < 100 \text{ kg s}^{-1}$; 0.7 if $m > 100 \text{ kg s}^{-1}$.

2: Default probability of delayed ignition (flammable vapour). For these substances $P_2 = 1$ because the possibilities of intervention in the event of a flammable cloud are very small. In some cases this assumption may be too conservative (Ronza et al, 2007). Probabilities given in 2.3 can also be used as alternative.

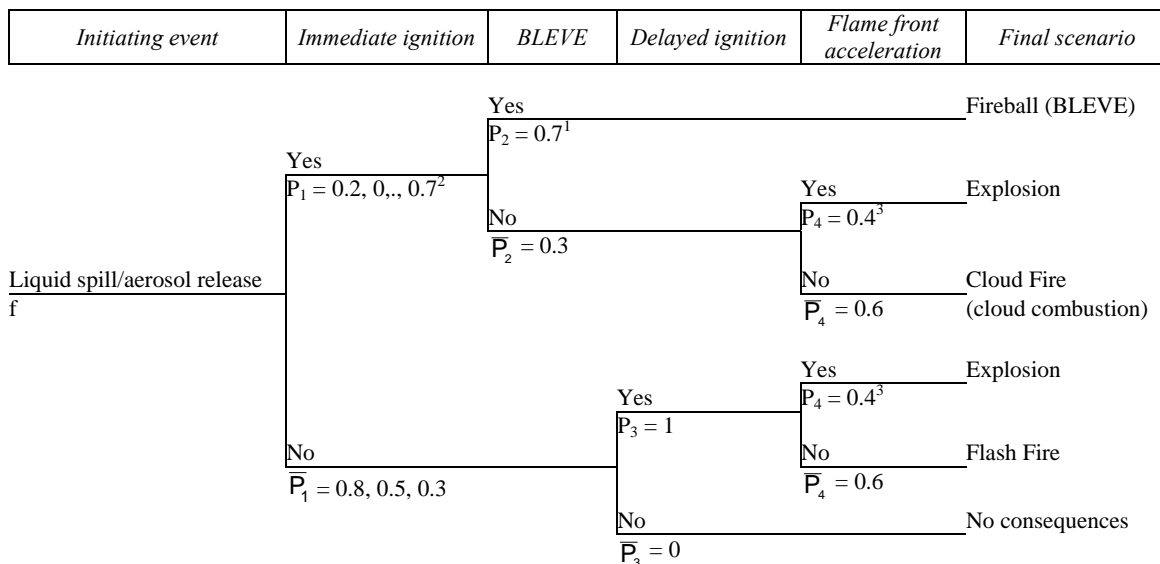
3: Probability of explosion in the event of flammable dispersion (Bevi, 2009), only if a minimum amount (usually 500 - 1000 kg) is between flammability limits in the cloud. If this criterion it is not fulfilled, use $P_3 = 0$.

The final scenario for immediate ignition will be usually a Jet Fire for high momentum free jet releases (horizontal or upwards). For an obstructed or downward two-phase release, a Pool Fire may be the most representative scenario.



2.6. Instantaneous releases of extremely flammable pressurized liquefied gases

For example, same as 2.5 case, but instantaneous.



1: Probability of immediate ignition depending on the released amount m (Bevi, 2009): 0.2 if $m < 1,000$ kg; 0.5 if $1,000 < m < 10,000$ kg; 0.7 if $m > 10,000$ kg.

2: Probability of occurrence of a BLEVE immediate ignition of an instantaneous spill (Bevi, 2009)

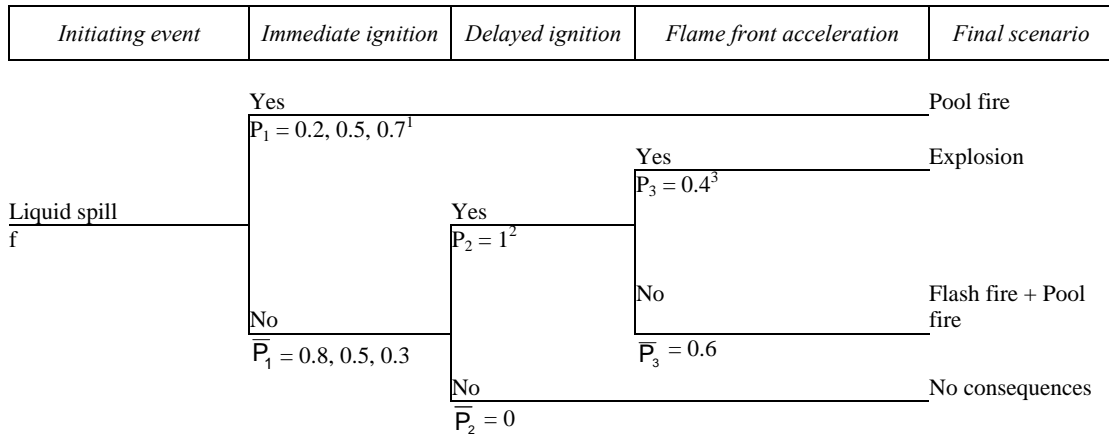
3: Default probability of delayed ignition (flammable vapour). For these substances $P_2 = 1$ because the possibilities of intervention in the event of a flammable cloud are very small. In some cases this assumption may be too conservative (Ronza et al, 2007). Probabilities given in 2.3 can also be used as an alternative.

4: Probability of explosion in the event of flammable dispersion (Bevi, 2009), only if a minimum amount (usually 500 - 1000 kg) is between flammability limits in the cloud. If this criterion it is not fulfilled, use $P_3 = 0$.

Cloud Fire (a flammable cloud burning with not previous dispersion) could be simulated, as a conservative case, using a fireball model.

2.7. Releases of cryogenic or fully refrigerated flammable liquids

For example liquefied ethylene, LNG stored close to normal boiling point or ethylene oxide fully refrigerated.

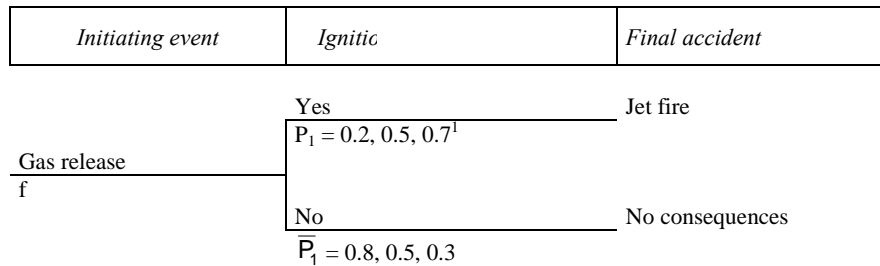


- 1: Probability of ignition of flammable gases, depending on the released amount/flow rate (Bevi, 2009).
- 2: Default probability of delayed ignition (flammable vapour). Probabilities given in 2.3 can also be used.
- 3: Probability of explosion in case of flammable atmospheric dispersion.

Some significant exceptions should be considered; for example, LNG in open terrain does not explode and $P_3 = 0$.

2.8. Flammable gases

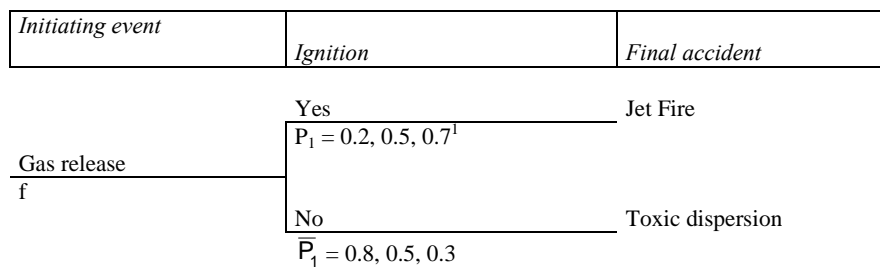
For example, hydrogen or compressed ethylene or natural gas (at room temperature).



- 1: Probability of ignition of flammable gases, depending on the released amount/flow rate (Bevi, 2009).
- The possibility of explosion is neglected, due to the quick dispersion in the case of high momentum jet releases.

2.9. Toxic and flammable gases

For example, hydrogen sulphide. Two possibilities:



- 1: Probability of ignition of flammable gases, depending on the released amount/flow rate (Bevi, 2009).

2.10. Toxic gases

As, for example chlorine (gas). Only one possibility:

<i>Initiating event</i>		<i>Final accident</i>
Gas release		Toxic dispersion
f		

2.11. Toxic liquids

For example, toluene di-isocyanate or dimethyl sulphate.

<i>Initiating event</i>		<i>Final accident</i>
Liquid spill		Toxic dispersion
f		

2.12. Continuous releases of toxic and extremely flammable pressurized liquefied gases

For example, ethylene oxide (stored as liquid close to room temperature).

Event tree, flammability features and ignition probabilities: same values than in case 2.5. There is only a significant difference: the “no ignition” branch must include the toxic dispersion outcome. Again, a problem arises due to the fact that if a probability of 1 is assumed for “delayed ignition”, the scenario of toxic dispersion is eliminated. The following event tree can be used as a conservative approach:

<i>Initiating event</i>	<i>Immediate ignition</i>	<i>Final scenario</i>
Liquid spill f	Yes $P_1 = 0.2, 0.5, 0.7^1$	Pool Fire (low momentum releases) Jet Fire (high momentum releases)
	No $\bar{P}_1 = 0.8, 0.5, 0.3$	Toxic dispersion

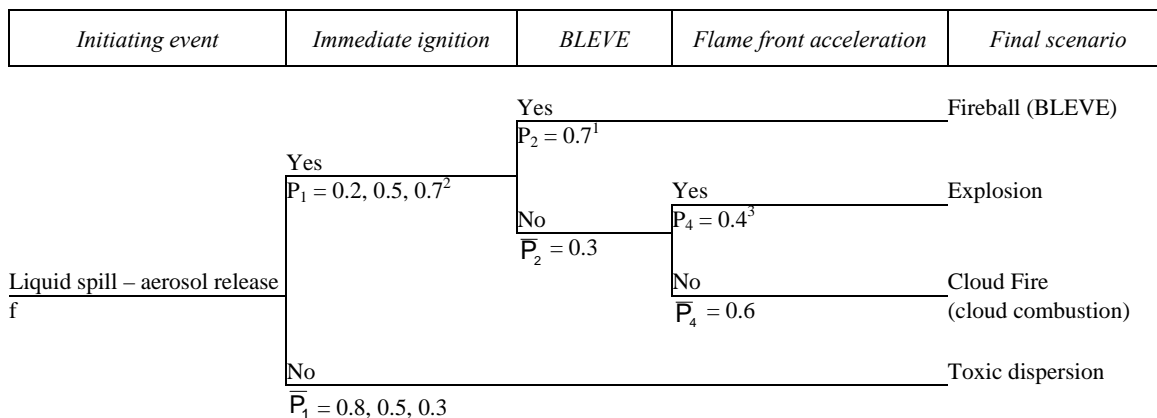
1: Probability of immediate ignition of flammable gases, depending on the released flow rate (Bevi, 2009).

2.13. Instantaneous releases of toxic and flammable liquefied substances

For example, ethylene oxide (stored as liquid close to room temperature).

Event tree, flammability features and ignition probabilities: same values than in case 2.6. There is only a significant difference: the “no ignition” branch must include the toxic dispersion outcome.

Again, if the probability of delayed ignition is taken as 1, the toxic dispersion scenario is eliminated. Thus, the Bevi (2009) event tree for continuous releases may be used.



3. DISCUSSION

The proposed set of event trees considering flammability, volatility and toxicity can be summarized in a table:

Flammability features	Volatility features	Acute toxicity?	Event tree n°	Hydrocarbon example/s	Chemical example/s
Flammable	Gas	yes	2.9	---	Hydrogen sulphide
		no	2.8	Compressed natural gas or ethylene	Hydrogen
	Cryogenic or fully refrigerated liquid	yes	(see Note)	---	---
		no	2.7	LNG, refrigerated liquid ethylene	Refrigerated ethylene oxide
	Pressurized liquefied gas	yes	2.12, 2.13	---	Ethylene oxide
		no	2.5, 2.6	Butane, propane	Methyl chloride
	Volatile liquid	yes	2.4	Benzene	Acrylonitrile
		no	2.3	Naphta, gasoline	R11 substance
	Low volatility liquid	yes	2.2	---	Allyl alcohol
		no	2.1	Kerosene, diesel	R10 substance
Non flammable or low reactivity flammable gas	Gas	yes	2.10	---	Ammonia (g)
	Liquid	yes	2.11	---	Toluene di-isocyanate, dimethyl sulfate

Note : Not considered in this study. Refrigerated ammonia can be a candidate for this case, but not using the standard ignition probabilities considered for hydrocarbon or regular flammable substances.

This set of event trees show the basic scheme for the evolution of the accident in the event of a loss of containment, as a function of the type of material released. For a given case, i.e. for the analysis of a given unit or plant, the eventual intermediate events –corresponding, for example, to the existence of mitigation systems, flow interruption, etc.– should be added.

All these event trees are proposed for materials at room temperature or refrigerated/cryogenic. If scenarios in process units are considered, hotter releases could occur. In each case the release condition should be evaluated in order to decide which event tree can be applied; for example, hot gasoline under pressure should be considered as LPG (when released, will undergo a flash vaporization).

REFERENCES

- Bevi, Reference Manual Bevi Risk Assessments, v. 3.1. National Institute of Public Health and the Environment (RIVM). Bilthoven (the Netherlands), 2009.
 Ronza, A., Vilchez, J. A., Casal, J. *Journal of Hazardous Materials* 146 (2007) 106-123.