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Using transportation accident databases to investigate ignition and explosion probabilities of flammable spills

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Abstract

Risk assessment of hazardous material spill scenarios, and quantitative risk assessment in particular, make use of event trees to account for the possible outcomes of hazardous releases. Using event trees entails the definition of probabilities of occurrence for events such as spill ignition and blast formation. This study comprises an extensive analysis of ignition and explosion probability data proposed in previous work. Subsequently, the results of the survey of two vast US federal spill databases (HMIRS, by the Department of Transportation, and MINMOD, by the US Coast Guard) are reported and commented on. Some tens of thousands of records of hydrocarbon spills were analysed. The general pattern of statistical ignition and explosion probabilities as a function of the amount and the substance spilled is discussed. Equations are proposed based on statistical data that predict the ignition probability of hydrocarbon spills as a function of the amount and the substance spilled. Explosion probabilities are put forth as well. Two sets of probability data are proposed: it is suggested that figures deduced from HMIRS be used in land transportation risk assessment, and MINMOD results with maritime scenarios assessment. Results are discussed and compared with previous technical literature.

Keywords: Ignition probability; Explosion probability; Event trees; Land transportation; Maritime transportation

1. Introduction

The Quantitative Risk Analysis (QRA) technique is a common way of determining individual and societal risk in or around an area characterised by certain activities to which accident scenarios can be associated. QRA is nowadays widely used in risk assessment of process plant sites and hazardous material transportation routes. Roughly speaking, it is made up of a more or less creative stage of risk identification, where the accident scenarios are proposed as representative for the area under observation, and by the calculation of their consequences [1]. The step of risk identification always involves the definition of the frequency of the accident scenarios, normally expressed by way of expected events per year (year^{-1}). Defining accident frequencies involves a decision as to the *frequency of an initiating event* and the *probability* of a certain outcome arising as a consequence of the initiating event. For the process industries, a typical initiating event is the spill of a hazardous material, whose ultimate outcomes can be a fire, explosion, or toxic gas cloud.

Normally, the chains of events initiated by a spill are represented by way of so-called event trees. The main advantages of event trees are their immediateness of representation and their potential for being described in a probabilistic way. Fig. 1 is a detailed event tree representing the possible aftermaths of an LPG spill. At each bifurcation of the tree, a probability P_i is assigned to the occurrence of an event, while the non-occurrence of this is associated with a probability $\bar{P}_i = 1 - P_i$. For example, if we refer to Fig. 1, the first bifurcation of the tree is the possibility of the pressurised LPG release being upward or downward-directed. The representation used in Fig. 1, which is commonly accepted, lists this condition in the upper part of the diagram ("Upward release"). The upper half of the tree is then associated with the positive response to this first condition, and therefore assigned a probability P_1, while the lower part is assigned a probability $\bar{P}_1$. The same applies to the subsequent bifurcations, associated with "Immediate ignition", "Delayed ignition" and "Flame front acceleration". Multiplying the probability of an event chain, from the root of the tree down to the

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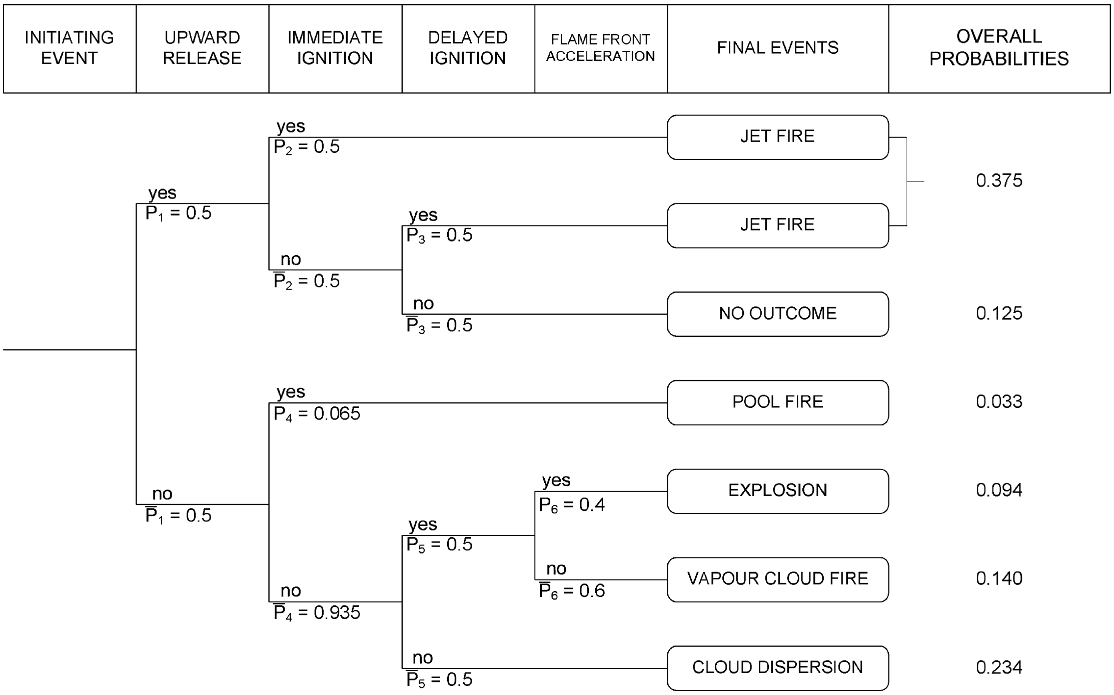

Fig. 1. Event tree for an LPG spill (data from Refs. [2,3]).

final outcomes, yields the overall probability of the outcome. For example, the overall probability of a flash fire, given the occurrence of an LPG spill (initiating event) is

$$P\ (\text{flashfire}) = \bar{P}_1 \times \bar{P}_4 \times P_5 \times \bar{P}_6 = 0.5 \times 0.935 \times 0.5 \times 0.6 = 0.14 \quad (1)$$

according to the tree represented in Fig. 1. In the context of QRA, overall probabilities are multiplied by the expected frequency of the initiating event. If at a given location, an LPG spill is expected to happen once every 100 years (frequency = 1×10^{-2} year^{-1}), then an LPG flash fire would be expected 1.4 times every 1000 years (1.4×10^{-3} year^{-1}).

For the performance of a consistent QRA, it is essential to define event probabilities as realistically as possible. Under- or over-estimation of these values can lead to errors of more than one order of magnitude in accident frequencies, and therefore in individual and societal risk. As often occurs with the frequencies of initiating events, probability data are generally assigned using expert judgement and historical-statistical criteria (or a combination thereof). In Fig. 1, P_1 has obviously been assigned by expert judgement. The risk analyst must have thought that, given random conditions of failure, the consequent spill would be equally likely to spread upwards or downwards.

Fires and explosions are a class of event to which probabilities are normally assigned by way of some historical and statistical analysis of past accidents. This is the case with the majority of events taken into account in the LPG spill tree of Fig. 1. Since no obvious conclusion can be drawn as to whether a flammable spill can encounter an ignition source, whether ignition takes place and how far (in space and time) ignition occurs from the spill location, historical data can be used to standardise ignition probabilities in QRA. The same applies to the formation of a blast wave, given the ignition of a flammable cloud.

Fig. 2 is a generalised event tree for the spill of a flammable material. The tree only contains three major bifurcations, to which the following check questions can be assigned: (1) is the spill immediately ignited?; (2) If not, is the subsequent vapour/gas cloud ignited (i.e. does delayed ignition occur)?; (3) If so, does the ignition cause a blast?

The difference between immediate and delayed ignition is more a spatial than a temporal one. Although there is no general agreement on this matter, recent literature (see for example [4,5,6]) refers to those fires that occur where the spill is produced as “immediately” ignited; conversely, vapour fires taking place at a certain distance from the spill are said to be initiated by a “delayed” ignition. If the spill undergoes immediate ignition, a jet fire or pool fire is produced. Delayed ignition causes a flammable cloud to undergo a flash fire. Flash fires are sometimes accompanied by a flame front acceleration that ultimately results in a vapour cloud explosion. The boundary between flash fire and low-velocity explosion (deflagration) is not clearly defined, but a value of 150 m/s for the flame front propagation speed can be assumed as critical, as above this speed, significant overpressure waves can be formed after the ignition [7, section 16.14.2].

The simplified tree is not dependent on the system analysed. In other words, it does not account for any special feature of the system under observation, whether due to the nature of the substance spilled, the technology used to store and process the substance, or the spill surroundings. For instance, it does not account for the direction of the spill (upwards, downwards), or whether or not the cloud reaches a particular known hot spot (e.g. a torch, welding sparks).

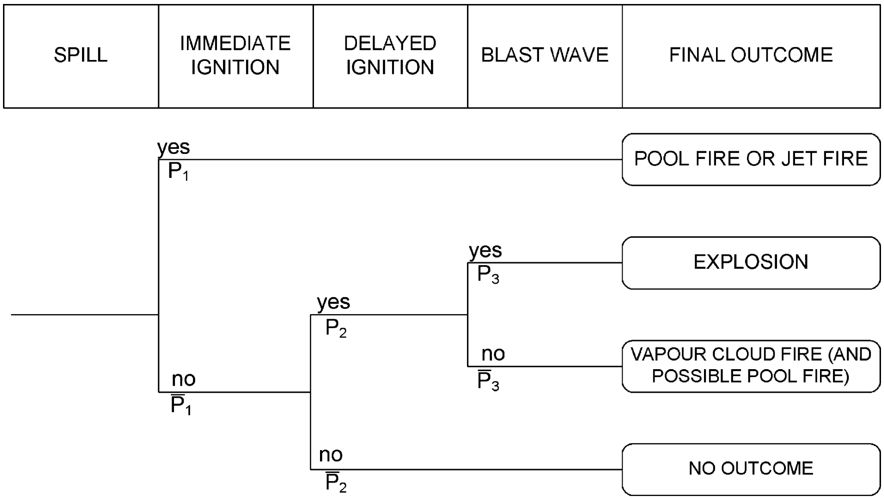

Fig. 2. General event tree for flammable material leaks.

For clarity and consistency, Fig. 2 is referred to throughout this paper, which is devoted firstly to reviewing ignition and explosion probability data proposed in the specialised literature on risk assessment, and secondly to designing new probability data from two sets of historical accident records. These data are finally validated through discussion and comparison with previous studies.

2. Review of literature data

2.1. Ignition probability

Table 1 is a comprehensive collection of ignition probability data found in specialised risk assessment literature. In total, nineteen studies were found that contain quantitative ignition probability data of flammable spills.

According to these studies, the factors that influence ignition probability are:

- flow rate or amount released: the greater the release, the larger the area covered by the ignitable cloud and the higher the probability of it finding an ignition source;
- the substance released: the more volatile and flammable the material, the more likely the ignition;
- the characteristics of the surroundings and the general conditions of the leak, on which the number and effectiveness of potential ignition sources depend.

How figures depend on the above factors is reported in the fourth column of Table 1, in which it is specified whether the data are function of: amount spilled (Q); material properties (MP); type of accident (ToA); density of ignition sources (DoIS); weather conditions, including wind speed and/or Pasquill stability class (W).

The amount spilled (Q) is expressed in quantitative or qualitative terms (“large”, “small”...). It can refer either to a sudden loss of containment or the flow rate of a continuous release. More often, the overall amount spilled is taken into account, regardless of whether the spill is continuous or instantaneous.

As regards material properties (MP), a probability can depend on the material spilled (e.g. LPG, petrol, and crude oil) or its respective flash temperature, which defines the flammability of the substance.

The latter three of the aforementioned variables (accident type, density of ignition sources, and weather conditions) account for the “characteristics of the surroundings and general conditions”, which represents a controversial issue to take into account when it comes to express the likelihood of ignition by way of numbers. In fact, it is an important aspect for the definition of ignition probabilities, but the fact that these variables depend on the spill setting, makes it difficult to standardise ignition probability data for their use in quantitative risk assessment.

For the “Comments” column of Table 1, in citing variables, an asterisk (*) has been attached to the variable any time this is implicit in the definition of the ignition probability. For example, the LNG ignition probability given in the first *Canvey Report* [11] is a function of the material properties, in that the probability applies to LNG clouds only, but this is obvious from the definition of the data itself. On the other hand, the data found in [8] explicitly depend on MP, since the author proposes three distinct figures, one each for LPG and two classes of flammable liquids.

Literature data can refer to immediate ignition, delayed ignition or to both at the same time. This is specified in the first column of Table 1, by way of the nomenclature introduced in Fig. 2: P_1 indicates the probability of immediate ignition, $\bar{P}_1 \times P_2$ the probability of delayed ignition and $P_1 + \bar{P}_1 \times P_2$ the overall probability of ignition.

A number of models use a more complex approach to defining ignition probabilities, allowing for the density of ignition sources and other surroundings-dependent parameters. The *Purple Book* [2] recommends a simplified model of this kind for delayed ignition of flammable gas clouds. Spencer and Rew [28], and Rew et al. [29] introduced a model for off-site, delayed vapour

Table 1
Review of ignition probability data

Scope	Probability data	Source	Comments
No obvious point of ignition In presence of explosion proof electrical equipment $= P_1 + \overline{P}_1 \times P_2$	Massive LPG release → 0.1 Flammable liquid ($T_{\text{flash}} < 110$ °F $= 43.3$ °C or $T > T_{\text{flash}}$) → 0.01 Flammable liquid (110 °F $< T_{\text{flash}} <$ 200 °F = 93.3 °C) → 0.001	[8]	*f*(Q, MP)
LNG and LPG $= P_1 + \overline{P}_1 \times P_2$	Area covered by cloud < 30 m^2 → 0.5223 … 1000 m^2 < area covered by cloud < 3000 m^2 → 0.8864 … 3 × 10^6 m^2 < area covered by cloud < 1 × 10^7 m^2 → 0.9992	[9]	*f*(Q, MP*) based on historical data
Fixed plants $= \overline{P}_1 \times P_2$	> 0.1 for losses of containment > 10 t (in the order of 0.5)	[10]	*f*(Q, ToA*)
LNG vapour clouds $= P_1 + \overline{P}_1 \times P_2$	Limited release → 0.1 Large release → 1	[11]	*f*(Q, MP*)
Lorry releases (mostly petrol) $= P_1 + \overline{P}_1 \times P_2$	0.24	[12]	*f*(ToA*) based on historical data
“On-site ignition”, is actually $= P_1 + \overline{P}_1 \times P_2$	“No” ignition source → 0.1 “Very few” ignition sources → 0.2 “Few” ignition sources → 0.5 “Many” ignition sources → 0.9	[13]	*f*(ToA, DoIS)
Ignition at jetty $= P_1$	Immediate ignition (< 30 s) → 0.6 after fire or explosion; 0.33 after collision		
Ignition at jetty $= \overline{P}_1 \times P_2$	Delayed ignition (0.5 ÷ several min) → 0.3 after fire or explosion; 0.33 after collision		
Ignition at jetty $= \overline{P}_1 \times P_2$	No ignition (in several minutes) → 0.1 after fire or explosion; 0.33 after collision		
Ignition with ship in transit $= \overline{P}_1 \times P_2$	Undeveloped site → 0 Industrial site → 0.9		
Ignition on built-up area $= P_2, \overline{P}_2$	Edge-edge ignition (ignition occurs when the cloud edge reaches the edge of a built-up area) → 0.7; Central ignition (ignition occurs when the entire cloud is above a built-up area) → 0.2; No ignition → 0.1		
LPG releases Ignition at source $= P_1$	Immediate ignition: Large instantaneous release → 0.25 1,000 t → 0.25 250 kg/s, 50 kg/s → 0.25 30 kg/s, 16 kg/s → 0.15	[14]	*f*(Q, W, MP*)
LPG releases Ignition at source $= \overline{P}_1 \times P_2$	Delayed ignition in presence of wind Large instantaneous release → 0.25 1,000 t → 0.25 250 kg/s, 50 kg/s → 0.25 30 kg/s, 16 kg/s → 0.15 Delayed ignition, no wind Large instantaneous release → 0.25 1000 t → 0.1 250 kg/s, 50 kg/s → 0.1 30 kg/s, 16 kg/s → 0.05		
LPG vehicle accidents $= P_1 + \overline{P}_1 \times P_2$	0.24	[15]	*f*(MP*, ToA*) based on historical data
Offshore blowouts (massive releases) $= P_1 + \overline{P}_1 \times P_2$	Crude oil → 0.08 Gas → 0.3	[16]	*f*(MP, Q*, ToA*) based on few historical data (≈ 100) on offshore blowouts

Table 1 (*Continued*)

<table>
<tr><td>LPG releases; road[(a)]
$= P_1, \bar{P}_1 \times P_2$</td><td>Broken pipe/hole in wall (hole diameter ≈ 3”)
$P_1 = 0.1$
$\bar{P}_1 \times P_2 = 0.05$
$(P_1 + \bar{P}_1 \times P_2 = 0.15)$
Instantaneous release of tank
$P_1 = 0.4$
$\bar{P}_1 \times P_2 = 0.5$
$(P_1 + \bar{P}_1 \times P_2 = 0.9)$</td><td>[3]</td><td>*f*(Q, MP*, ToA*, DoIS*)</td></tr>
<tr><td>LPG releases; railway[(a)]
$= P_1, \bar{P}_1 \times P_2$</td><td>Broken pipe/hole in wall (hole diameter ≈ 3”)
$P_1 = 0.1$
$\bar{P}_1 \times P_2 = 0.05$
$(P_1 + \bar{P}_1 \times P_2 = 0.15)$
Instantaneous release of tank
$P_1 = 0.8$
$\bar{P}_1 \times P_2 = 0.2$
$(P_1 + \bar{P}_1 \times P_2 = 1.0)$</td><td></td><td></td></tr>
<tr><td>LPG releases; waterway[(b)]
$= P_1, \bar{P}_1 \times P_2$</td><td>Spill rate = 30 - 50 kg/s
$P_1 = 0.5$
$\bar{P}_1 \times P_2 = 0.1$
$(P_1 + \bar{P}_1 \times P_2 = 0.6)$</td><td></td><td></td></tr>
<tr><td>Pipeline failures
$= P_1 + \bar{P}_1 \times P_2$</td><td>All sizes → 0.16
Ruptures → 0.26</td><td>[17]</td><td>*f*(Q, ToA*)</td></tr>
<tr><td>Pipeline failures
$= P_1 + \bar{P}_1 \times P_2$</td><td>Leaks → 0.1
Ruptures → 0.5</td><td>[18]</td><td>*f*(Q, ToA*)</td></tr>
<tr><td>LPG releases (200 t), industrial area Industrial setting (off-site)
$= P_1, \bar{P}_1 \times P_2$</td><td>
<table>
<tr><th></th><th>Immediate ignition (P_1)</th><th colspan="4">Delayed ignition ($\bar{P}_1 \times P_2$)</th></tr>
<tr><td>**Catastrophic (cold failure, 200 ton)**</td><td>0.05</td><td colspan="4">0.9 (F2 weather); 1.0 (D5)</td></tr>
<tr><td>**Vessel failure**</td><td>0.05</td><td>13 mm</td><td colspan="3">0.2</td></tr>
<tr><td></td><td></td><td>25 mm</td><td colspan="3">0.3</td></tr>
<tr><td></td><td></td><td>50 mm</td><td colspan="3">0.9</td></tr>
<tr><td></td><td></td><td></td><td colspan="3">**Density of sources**</td></tr>
<tr><td></td><td></td><td></td><td>Low</td><td>Medium</td><td>High</td></tr>
<tr><td>**Plant/ pipework failure**</td><td>0.5</td><td>13 mm</td><td>0.04</td><td>0.14</td><td>0.24</td></tr>
<tr><td></td><td></td><td>25 mm</td><td>0.05</td><td>0.25</td><td>0.45</td></tr>
<tr><td></td><td></td><td>50 mm</td><td>0.4</td><td>0.6</td><td>0.8</td></tr>
</table>
</td><td>[19]</td><td>*f*(ToA, DoIS, W, Q*, MP*)</td></tr>
<tr><td>Continuous releases
$= P_1 + \bar{P}_1 \times P_2$</td><td>
<table>
<tr><th></th><th>Gas</th><th>Liquid</th></tr>
<tr><td>**< 1 kg/s**</td><td>0.01</td><td>0.01</td></tr>
<tr><td>**1 ÷ 50 kg/s**</td><td>0.07</td><td>0.03</td></tr>
<tr><td>**> 50 kg/s**</td><td>0.3</td><td>0.08</td></tr>
</table>
</td><td>[20]</td><td>*f*(Q, MP)</td></tr>
<tr><td>Rail accidents
$= P_1, \bar{P}_1 \times P_2$</td><td>
<table>
<tr><th></th><th>Immediate ignition (P_1)</th><th>Delayed ignition ($\bar{P}_1 \times P_2$)</th></tr>
<tr><td>**Petrol**</td><td></td><td></td></tr>
<tr><td>**Small spills**</td><td>0.1</td><td>0</td></tr>
<tr><td>**Large spills**</td><td>0.2</td><td>0.1</td></tr>
<tr><td>**LPG**</td><td></td><td></td></tr>
<tr><td>**Small spills**</td><td>0.1</td><td>0</td></tr>
<tr><td>**Large spills**</td><td>0.2</td><td>0.5</td></tr>
</table>
</td><td>[21]</td><td>*f*(Q, MP, ToA*)
based on both historical data and expert judgement</td></tr>
<tr><td>Lorry accidents
$= P_1$</td><td>Petrol
Small spills → 0.15
Large spills → 0.50
LPG
Small spills → 0.25
Large spills → 0.75</td><td>[22]</td><td>*f*(Q, MP, ToA*)
based on expert judgement, after [12] and [15]</td></tr>
<tr><td>Rail accidents LPG
$= P_1$</td><td>LPG
Small spills → 0.30
Large spills → 0.90</td><td></td><td></td></tr>
<tr><td>Fixed installations
$= P_1$</td><td>
<table>
<tr><th colspan="2">Release source</th><th colspan="3">Product</th></tr>
<tr><th>Continuous</th><th>Instantaneous</th><th>K1 liquid[(c)]</th><th>Little reactive gas[(d)]</th><th>Reactive/very reactive gas[(e)]</th></tr>
<tr><td>< 10 kg/s</td><td>< 1,000 kg</td><td>0.065</td><td>0.02</td><td>0.2</td></tr>
<tr><td>10 ÷ 100 kg/s</td><td>1,000 ÷ 10,000 kg</td><td>0.065</td><td>0.04</td><td>0.5</td></tr>
<tr><td>> 100 kg/s</td><td>> 10,000 kg</td><td>0.065</td><td>0.09</td><td>0.7</td></tr>
</table>
</td><td>[2][(f)]</td><td>*f*(Q, MP)
based on the historical data of [24]</td></tr>
</table>

Table 1 (*Continued*)

Flammable releases (> 100 kg) in road transport $= P_1, \bar{P}_1 \times P_2$		**Product**			[26]	f(MP, Q*, ToA*)
		Flammable liquid, category LF2$^{(g)}$	**Flammable liquid, category LF1$^{(g)}$**	**Flammable gases$^{(g)}$**		
	Immediate ignition (P_1)	0.065	0.0043	0.8		
	Delayed ignition ($\bar{P}_1 \times P_2$)	0.065	0	0.2		
Flammable releases in inland waterways $= P_1, \bar{P}_1 \times P_2$		**Product**				f(MP, ToA*)
		Flammable liquid, category LF2$^{(g)}$	**Flammable liquid, category LF1$^{(g)}$**	**Flammable gases$^{(g)}$**		
	Immediate ignition (P_1)	0.065	0.01	0.5		
	Delayed ignition ($\bar{P}_1 \times P_2$)	0.065	0	0.1		
Flammable releases from pipelines $= P_1$		**Product**				f(Q, MP, ToA*)
		Flammable gases	**Liquefied flammable gases**			
	Leakage	0.04	0.14			
	Rupture	0.09	0.30			
Flammable releases from pipelines $= \bar{P}_1 \times P_2$	"At the most" $\bar{P}_1 \times P_2 = 1 - P_1$					f(ToA*)
Pipelines failures $= P_1 + \bar{P}_1 \times P_2$	Pinholes/cracks → 0.03 Holes → 0.02 Ruptures ≤ 16 in → 0.09 Ruptures > 16 in → 0.30 All sizes → 0.041				[27]	f(Q, ToA*) from historical data (1,123 spills over the period 1970-2004)

(a): Amount released > 100 kg

(b): Hull penetration ≥ 40 cm or hole cross section ≥ 100 cm^2

(c): A liquid belongs to K1 class if it is not a K0 liquid and $T_{\text{flash}} < 294$ K; a K0 is a liquid with $T_{\text{flash}} < 273$ K and boiling point < 308 K [23]. Examples of K1 liquids are light crude oils, petrol, petroleum naphtha and JP-4 jet fuel.

(d): Examples: ammonia, carbon monoxide, methane [23].

(e): Examples: 1-butene, 1,3-butadiene, acetaldehyde, butane, ethane, ethylene, propane, acetylene [23].

(f): In this first part of the *Purple Book*, probability data are also defined for direct ignition as a consequence of transport unit accidents in an establishment and delayed ignition in general. These figures do not depend on the substance, but instead on the release mode and the surroundings (type and number of ignition sources).

(g): Flammable gas as defined by the *IMDG Code* [25]; flammable liquid = a liquid with $T_{\text{flash}} < 334$ K; for LF1 liquids $T_{\text{flash}} > 296$ K (examples: heavy crude oils, diesel oil, kerosene, heavy naphtha) for LF2 liquids $T_{\text{flash}} < 296$ K (examples: light crude oils, JP-4 jet fuel, light naphtha, petrol).

[a] Amount released > 100 kg.

[b] Hull penetration ≥40 cm or hole cross section ≥100 cm^2.

[c] A liquid belongs to K1 class if it is not a K0 liquid and $T_{\text{flash}} < 294$ K; a K0 is a liquid with $T_{\text{flash}} < 273$ K and boiling point < 308 K [23]. Examples of K1 liquids are light crude oils, petrol, petroleum naphtha and JP-4 jet fuel.

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cloud ignition that takes into account the distribution of ignition sources in the surroundings of a potential spill location, as described by a grid where ignition sources follow a Poisson distribution. This methodology aims at defining the probability that, given the presence of a flammable cloud in a given location, sustained combustion be produced. The probability is thereby a function of the attributes of the location, which affects the density, strength and continuity of the ignition sources. Nevertheless, the probability of the cloud being present in the location, and its extension, must be known *a priori*. Daycock and Rew [30] extended the model proposed in [28] for on-site ignition scenarios, by introducing a new factor accounting for control of ignition sources.

These models are not discussed in the present paper. It should be noted, however, that they cannot be easily practical when it comes to use them in the context of a QRA, because they significantly add to the amount of computations required by that technique[1].

Instead, we focus here on those figures that directly define the ignition and explosion probabilities, such as those of Table 1. The following general observations can be made as to these probability data:

- The references cover a long time span, some dating as far back as the late 1960s. Hence, differences in numbers proposed could be attributed to technological progress, as safety conditions have improved in the last decades (e.g. ignition sources are now checked and limited more than before). Nevertheless, the particular criteria followed by the different authors generally appear to be more important than this "historical" aspect.
- The values proposed in the works of the late 1970s and early 1980s are relatively optimistic if compared to later figures. Overall values (i.e. $P_1 + \bar{P}_1 \times P_2$) never exceed 0.5, and are mostly of the order of 0.2–0.3. A key exception to this trend is the value of 0.9 presented in [13] for spills in the presence of "many" ignition sources. These studies do not account for the influence of the amount spilled on the ignition probability.
- An important step forward is represented by TNO's *LPG, a Study* [3]. This report was the result of a large QRA project for the LPG transport chain. Great importance was given to the probabilistic aspect of the study, and a variety of probability values were proposed. Due to the high level of detail of the study, the transport mode (i.e. road, rail, waterway, etc.) greatly affects the ignition probability. The values-again, referring to the overall ignition probability-range from 0.05 to certainty, in the case of the instantaneous release of a rail tank.
- Most recent studies have followed a "detailed" approach of this kind (i.e. a variety of probability data are proposed as a function of the aforementioned variables). An important example is the data recommended by the *Purple Book* on fixed installations [2] and on transportation accidents [26]. The *Purple Book* is probably the reference most commonly used in Europe when seeking probability data for QRA. The figures are lower than 0.1 in all cases except "reactive" gas spills, such as LPG – as opposed to liquefied methane, which is relatively non-reactive – which are assigned an ignition probability of up to 0.7.

The majority of data in Table 1 refer to LPG. LNG and methane are less represented. Sometimes LNG and LPG are grouped together or included within the generic classification of flammable gases. Otherwise, LNG is assigned a lower probability than LPG (e.g. in the *Purple Book*). Flammable liquids, such as crude oil, petrol, etc., are less represented in the literature, and are assigned values of the order of 0.1–0.2.

It is not always obvious whether figures are the result of expert judgement or historical analysis. Some references clearly state that they are derived from historical records (see last column of Table 1), but in most cases it must be induced that the authors used these in combination with expert judgement.

It is important to highlight that no specific probability data are proposed for the setting of sea transportation.

2.2. Explosion probability

In the present paper, the expression "explosion probability" refers to the likelihood of a flammable cloud forming a blast wave *once ignition has taken place*. In other words, this parameter is identified with the variable P_3 in Fig. 2. It must be stressed that the blast phenomena here accounted for are vapour cloud explosions (VCEs). Vapour cloud explosions can be either unconfined (UVCE) or partially confined, as is the case when the flame front finds some obstacle or obstruction on its way. It is important to recall that the greater the level of confinement, the higher the probability of blast wave formation. Vessel explosions will not be considered.

A list of explosion probability data found in literature is shown in Table 2. Studies on this topic are scarcer than in the case of ignition. In fact, defining the likelihood of a flammable cloud originating a blast involves a high degree of uncertainty.

All of the references cited, as shown in the column "Scope" of Table 2, are in agreement with the definition of explosion probability given above. The variables on which explosion probability depend, according to the authors cited in Table 2, are only material properties and quantity spilled. Incident surroundings and spill conditions have no influence.

Some reasons why explosion probability is affected by the properties of the substance are the following: (a) the mechanical yield of the explosion depends on the reactivity of the material, (b) molar combustion enthalpy, which is substance-dependent, also influences gas expansion. How these issues modify explosion probability will be explained later, based on the results of database analysis. Suffice it to say here that material properties are somehow accounted for by some authors: the *Canvey Reports* [11,13] propose a smaller figure for methane/LNG, while [22] assigns to "ethylene oxide-like" gases a higher probability than to LPG.

The size of the flammable gas cloud, i.e., the amount spilled, is important to the explosion probability mainly because (a) a certain lapse of time and (b) relatively high flammable concentrations are needed for the flame front to reach a high speed, and thus cause a significant overpressure. As a matter of fact, in risk assessment practice a threshold size is sometimes defined for flammable gas clouds under which it is assumed that explosion probability is negligible. In literature data (Table 2), small spills are consistently assigned smaller probabilities than large spills.

Two major considerations can be made as to the figures reported in Table 2:

- The majority of authors refer to gaseous materials or liquefied gases. Only Dahl et al. [16] explicitly reference a liquid (crude oil) assigning it a blast probability 0, based on historical data.
- Although values are diverse, the majority of authors propose figures in the range 0.3–0.4. This is especially true for large

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[1] This drawback can be overcome by using software which allows for several ignition sources, such as SAFETI by DNV.

Table 2
Review of explosion probability data

Scope	Probability data	Source	Comments
= P_3	> 0.1 for large clouds (> 10 t; $\overline{P_1} \times P_2 \times P_3 = 0.1$) 0.001 ÷ 0.01 for small clouds (≤ 1 t)	[10]	*f*(Q)
= P_3	**Large cloud (> 100 t)** / **Small cloud (< 100 t)** **LNG/methane**: 1 / 0.01 **Other gas**: 1 / 0.1	[11, 13]	*f*(Q, MP)
= P_3	0.13	[31]	based on 326 offshore accidents in the Gulf of Mexico
= P_3	Crude oil → 0 Gas → 0.34	[16]	*f*(MP) based on few historical data (≈ 100) on offshore blowouts
LPG = P_3	0.7 (or 2/3)	[3]	*f*(MP*)
Continuous releases = P_3	Small release (< 1 kg/s) → 0.04; Large release (1 ÷ 50 kg/s) → 0.12; Massive release (> 50 kg/s) → 0.3	[20]	*f*(Q)
= P_3	LPG → 0.33 "Ethylene oxide-like" gases → 0.50	[22]	*f*(MP) based on expert judgement
Transportation = P_3	0.4	[26]	based on the historical data of [24]

spills, variously identified as clouds of more than 10 t of gas [10], releases of more than 50 kg/s [20], etc. Outstanding exceptions are the *Canvey Reports* [11,13], which assign a blast probability of 1 to large clouds, and *LPG, a Study* [3], proposing the value of 0.7 for liquefied petroleum gas. Kletz [10], the *Canvey Reports* and Cox et al. [20] do not agree on the probability to be assigned to smaller spills, with numbers ranging from as little as 0.001 to as much as 0.1.

Again, none of the references specifically covers the topic of sea transportation.

3. The databases used for the analysis

Two databases were selected for the analysis of ignition and explosion probabilities:

- the Hazardous Materials Incident Reporting System (HMIRS).
- the Marine Investigations Module (MINMOD), also known as the Marine Casualty and Pollution Database.

Both are public and available online[2]. For a description of these databases see [32] and [33]. Reports [34] and [35] contain a detailed description of the data fields of HMIRS. See [36] and [37] for specific information on MINMOD.

The Hazardous Materials Incident Reporting System (HMIRS) is a part of the US Department of Transportation's HMIS (Hazardous Materials Information System). It contains data on the unintentional release of hazardous materials during the course of transportation in the USA. Here, the Federal Hazardous Materials Transportation Law requires carriers to notify the NRC (National Response Center) immediately via telephone of releases of hazardous materials occurring during the course of transportation that result in serious consequences. These telephonic notifications are received by the NRC and transmitted to the Department of Transportation. The Research and Special Programs Administration (RSPA) is the US DOT office ultimately responsible for maintaining the data. Regulations also require interstate carriers, and certain intrastate carriers, to submit written reports on all unintentional releases of hazardous materials occurring during the course of transportation. These written reports are entered into the HMIRS database. In the 12-year period, examined is this study, the US DOT entered information about over 180,000 incidents and spills. Details of each release are usually accurate. The majority of HMIRS information is validated, as fatality and injury information is verified through follow-up reports, increasing the accuracy of the data [34]. To attest to the completeness of the data, RSPA estimates that less than 0.1% of the records contain duplicates. Though the scope of HMIRS is HazMat transportation spills and accidents at large, there are almost no maritime/navigational accidents, and air/aircraft accidents are few. For this reason, in this study

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[2] HMIRS files can be downloaded from <http://hazmat.dot.gov/pubs/inc/hmisframe.htm>; for MINMOD refer to <http://transtats.bts.gov/>, a resource maintained by the US Bureau of Transportation Statistics containing several transportation databases.

HMIRS was investigated as essentially referring to accidents involving hazardous spills as a consequence of *land transport accidents* (either by rail or lorry; pipeline spills are not included in HMIRS).

MINMOD is a database maintained and operated by the US Coast Guard. It was started in 1992 to boost the marine pollution section of the Marine Safety Information System (MSIS), which had been implemented in the 1970s after the Federal Water Pollution Control Act. Under this and subsequent provisions, the Coast Guard was appointed to record any known discharge of oil or hazardous substance in a harmful quantity. Data are provided to the Coast Guard by responsible parties (a requirement of FWPCA), by other private parties, government agencies, or are recorded as discovered and reported by Coast Guard personnel. Included are all reported discharges into US navigable waters, including territorial waters (extending to 3 miles from the coastline), tributaries, the contiguous zone (extending from 3 to 12 miles from the coastline), onto shorelines, or into other waters that threaten the marine environment of the United States. MINMOD was replaced at the end of 2001 by a new system (MISLE), which preserves the previous data organisation. MINMOD's scope is therefore maritime spills in general, though the vast majority of them involve vessel accidents and incidents. Like HMIRS, MINMOD contains a very high amount of data: over 170,000 incidents were entered in the period examined (1992–2001). Around 45% of them involve hazardous materials spills.

The databases were searched for spills of the most important commercial energetic hydrocarbons transported either by sea or land:

- LNG;
- LPG;
- Light fractions, including petrol and naphtha;
- Crude oil;
- Kerosene and jet fuel;
- Diesel oil, gas oil and no. 1 and 2 fuel oil;
- No. 4, 5 and 6 fuel oil.

For HMIRS, we used data from 1993 to 2004, whereas for MINMOD, which was discontinued in 2001, we examined the entire database (1992–2001). Overall, 12,166 spills were considered for HMIRS, and 34,477 for MINMOD. Details on how data were retrieved and analysed can be found in Appendix A.

Besides identifying the substance spilled, we also sorted the events into five categories according to the amount spilled: $\leq$10 kg; >10 kg, $\leq$100 kg; >100 kg, $\leq$1000 kg; >1000 kg, $\leq$10,000 kg; >10,000 kg.

For the purpose of the present study, HMIRS data were considered representative of *land transportation* spills, and MINMOD data were regarded as a reference for *maritime transportation* spills. Accordingly, the figures and predictive equations proposed below (see in particular Section 5) and proceeding from HMIRS analysis are to be used in land transportation QRA; conversely, those obtained on the basis of MINMOD shall be applied in maritime transportation QRA.

It is important to note that HMIRS and MINMOD have significant advantages over other accident databases. First, they contain *huge amounts of data*, which is important for adding value to any statistical analysis.

More importantly, these US federal databases are free from the most common hindrance found in analysing accident databases – data bias – which normally occurs because those involved in gathering data have selective access to information. For example, the majority of accident databases present a general tendency to under-represent events which cause little or no damage, because they are either left unreported or information is not made available to the general public. A large spill is more likely to be reported than a small release, especially if considerable loss is involved in terms of human life or environmental damage. Fires and explosions cause more damage and are more visible than spills with no further consequences, and are therefore less likely to escape reporting. Nevertheless, this problem practically does not affect HMIRS and MINMOD, since it is *mandatory* by law to report any HazMat spill to the agencies that are responsible for the databases. Furthermore, the results of the investigations of the DOT and the USCG are entered in the databases as well, which partially compensates for those spills that are not reported by the carrier. While seeking ignition and explosion probabilities in other databases would lead to significant overestimation of results, HMIRS and MINMOD prove far more reliable.

Another bias commonly found in other data systems is *geographical*. Database managers tend to privilege events that happen in or near their own country, so databases comprising accidents from all over the world are inevitably biased and especially under-represent accidents occurred in developing countries. In contrast, the ambit of HMIRS and MINMOD is clearly defined (i.e. limited to the USA) and homogeneous. It would be unreasonable to think that some part of the country is over- or under-represented. This is an additional advantage, because results are not based on a variety of socioeconomic milieus but on a sole setting with homogeneous safety culture and technological conditions.

Last, but not least, these databases are *free* and publicly available online.

4. Patterns in probability data valuation as a function of the amount and substance spilled

The results presented and discussed in this section demonstrate the general trend of probability data as a function of amount and substance spilled. These two variables are considered separately, so the graphs and numbers presented cannot be used in a QRA scheme. Instead, in Section 5 equations and values are proposed that can be used in QRA, because they account for the influence of both variables on ignition and explosion probabilities.

Numerical results obtained from analysis of the two databases are included in Table 3. As seen in the table, the results regarding LNG and natural gas cannot be taken into account mainly because of the scarcity of database entries for spills of this substance: only 22 are recorded in HMIRS for the time span

Table 3
Numerical results of the analysis

Database	Criterion	Data group	No. of spills	No. of fires	No. of explosions	$P_1 + \bar{P}_1 \times P_2$	P'_3
HMIRS	Amount spilled	$\leq$10 kg	5,332	16	1	0.003	0.063
		]10 kg; 100 kg]	3,483	34	2	0.010	0.059
		]100 kg; 1000 kg]	1,888	36	8	0.019	0.222
		]1000 kg; 10,000 kg]	937	71	21	0.076	0.296
		>10,000 kg	526	187	74	0.356	0.396
	Substance involved (increasing T_{flash})	(Liquefied) Natural gas	22	0	0	*0.000*	–
		LPG	709	81	18	0.114	0.222
		Light fractions	5,738	203	70	0.035	0.345
		Crude oil	1,020	11	5	0.011	0.455
		Kerosene/jet fuel	844	9	4	0.011	0.444
		Diesel oil/gas oil	3,740	40	9	0.011	0.225
		No. 4–6 fuel oil	93	0	0	*0.000*	–
MINMOD	Amount spilled	$\leq$10 kg	15,745	47	12	0.003	0.255
		]10 kg; 100 kg]	10,408	77	18	0.007	0.234
		]100 kg; 1000 kg]	5,718	66	16	0.012	0.242
		]1000 kg; 10,000 kg]	1,929	29	8	0.015	0.276
		>10,000 kg	708	8	4	0.011	0.500
	Substance involved (increasing T_{flash})	(Liquefied) Natural gas	96	1	0	*0.010*	*0.000*
		LPG	37	0	0	*0.000*	–
		Light fractions	3,842	75	20	0.020	0.267
		Crude oil	7,963	10	3	0.001	0.300
		Kerosene/jet fuel	1,226	6	2	0.005	0.333
		Diesel oil/gas oil	19,821	137	20	0.007	0.146
		No. 4–6 fuel oil	1,492	2	2	0.001	*1.000*

The last two columns include the average ignition and explosion probability, respectively, as referred to the group of data defined in the column "Data group". Italics indicate average probability figures not to be taken into account because of low reliability of data (small number of accidents with respect to the number of events in the group).

considered, and only 96 in MINMOD. However, only one LNG fire (no explosion) was found in the databases. The shortage of LNG/NG accidents in HMIRS can be explained by the fact that this substance is seldom transported by road or rail as compared to LPG. Another reason not to consider LNG/NG in our analysis is the fact that (liquefied) gas technology has achieved a high level of safety not seen for other areas of the process industry.

For the other materials, the results were taken into consideration, and probabilities are included in the graphs presented in the sections below. There are some exceptions, however, also motivated by a lack of data. All the figures considered unreliable due to scarcity of information are shown in italics in Table 3.

Results are discussed below in two separate sections dedicated to ignition and explosion, respectively.

4.1. Ignition probability

As to ignition probability, it has to be stressed that it is not possible to attain the level of detail of Fig. 2 through historical data alone. In fact, estimating P_1 and P_2 as separate figures is unfeasible because it is impossible to tell whether a fire was the result of immediate or delayed ignition. Neither HMIRS nor MINMOD differentiate a pool/jet fire (immediate ignition) from a vapour cloud fire (delayed ignition). Thus, the figures obtained from the databases are overall ignition probabilities:

$$\text{estimated ignition probability} = \text{no. of fires/no. of spills} = P_1 + \bar{P}_1 \times P_2 \qquad (2)$$

Figs. 3 and 4 show how statistical probabilities vary as a function of the amount of substance spilled, regardless of the substance itself. Fig. 3 represents HMIRS data, and Fig. 4 represents MINMOD data.

The influence of the amount spilled is plain: the more material released, the more likely it will catch fire, which confirms what practically all the authors that are cited in Table 1 affirm. In the case of HMIRS, ignition probability increases at a slow rate with the amount spilled until it suddenly rises to as much as 0.35 for spills >10 t. MINMOD ignition probability is less influenced by the amount spilled: a constant value appears to be reached at around 0.014 for amount spilled >1000 kg (actually statistical ignition probability is even a little lower for spills >10,000 kg than for 1000–10,000 kg spills).

MINMOD probability values are far lower than those of HMIRS. Whereas the difference is not significant for amounts up to 1000 kg, it is one order of magnitude for larger spills.

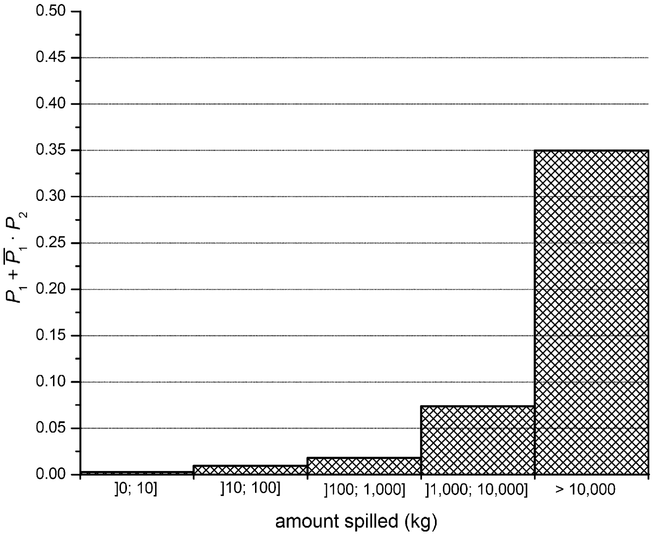

Fig. 3. Average HMIRS ignition probability data, as a function of the amount spilled. Data are representative of five ranges of amount spilled (]0 kg; 10 kg],]10 kg; 100 kg], . . .,]10,000 kg; +∞[).

We concluded that spills are more likely to be ignited during land transport than during maritime transport, because there are more ignition sources in the former. The fact that large maritime spills are not assigned significantly higher ignition probabilities than small spills is probably due to the fact that if the spill originates from a ship, the only ignition sources that the spill or the subsequent cloud can encounter are to be found on the vessel itself, and not in the surroundings (i.e. sea water). Hence, small, ignitable clouds, which cannot drift long distances, have nearly the same chance of finding an ignition source as larger spills.

Figs. 5 and 6 describe how the estimated probabilities vary as a function of the hydrocarbon blend. The different mixtures are represented using their average flash point, which was estimated taking into account the various blends and components belonging to each mixture (e.g. various types of naphtha and petrol are included in “light fractions”) and using data from the material safety data sheets found in the CHRIS database.

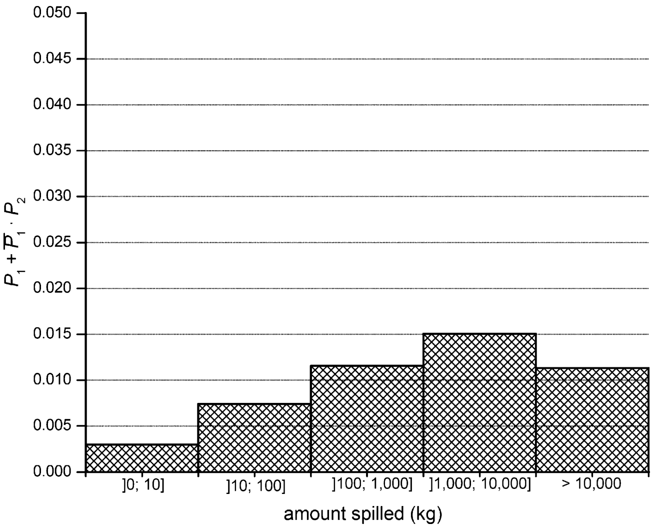

Fig. 4. Average MINMOD ignition probability data as a function of the amount spilled.

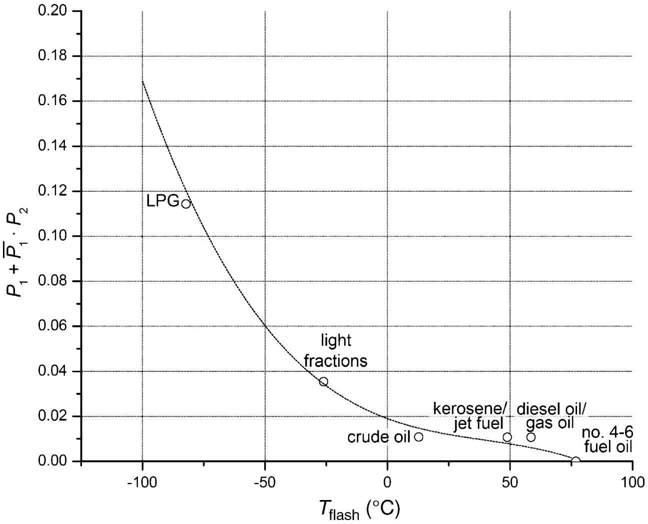

Fig. 5. Average HMIRS ignition probability data as a function of the average flash temperature of the hydrocarbon spilled. An interpolating curve (a cubic) has been added to demonstrate the decrease of $P_1 + \bar{P}_1 \times P_2$ with the flash temperature.

Both diagrams show how probabilities decrease with the flammability of the product. In the case of HMIRS, statistical values range from 0.11 (LPG) to 0.0 (no. 4–6 fuel oil); crude oil, kerosene/jet fuel and diesel all share values of ca. 0.011.

MINMOD data, apart from being lower (see above), vary from 0.020 (light fractions) to 0.001 (crude oil and no. 4–6 fuel oil). The decrease is not consistent in this case, as kerosene and diesel are assigned higher ignition probabilities than crude oil.

The figures obtained from the HMIRS database are comparable to those reported in Table 1, especially for large spills. The results of road accident studies [12] and [15] appear to be in good agreement with our own results. These studies pro-

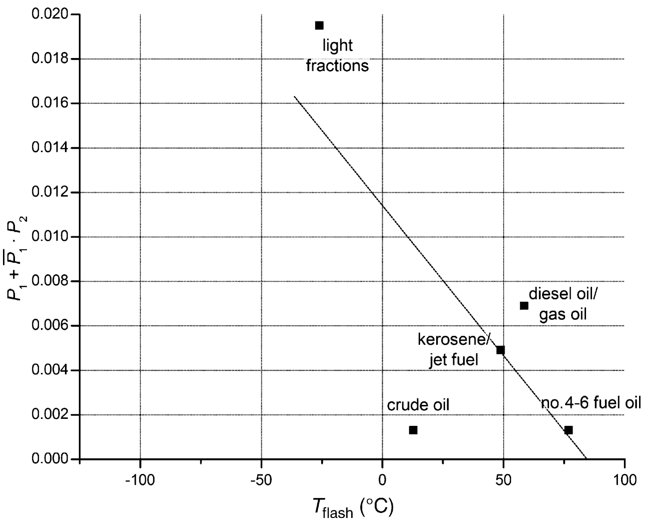

Fig. 6. Average MINMOD ignition probability data, as a function of the average flash temperature of the hydrocarbon spilled. An interpolating line has been added to demonstrate the decrease of $P_1 + \bar{P}_1 \times P_2$.

posed an overall ignition probability of 0.24 based on historical data.

Conversely, MINMOD values are lower than literature values. This can be explained by considering that there are no studies focusing specifically on maritime transport of flammable materials. The only exceptions are represented by the *Canvey Reports* [11,13], which deal with port operations. Nevertheless, these surveys were conducted on a highly industrialised port district, including land and loading operations apart from navigational spills. All the other works propose data either based on historical analysis of land/process plant accidents or conceived for that kind of setting.

4.2. Explosion probability

Regarding explosion probability, database analysis has yielded consistent results not only for LPG (in the case of HMIRS), but also for liquid hydrocarbons, which were overlooked in the studies cited in Table 2.

For the different sets of values defined by the amount spilled and the flash temperature, an "experimental" explosion probability P'_3 was calculated as

$$P'_3 = \text{no. of explosions/no. of fires} \tag{3}$$

The denominator of this ratio includes all accidents with ignition, because any vapour cloud explosion must actually involve a flash fire, given that all the materials considered are flammable. P_3 cannot be estimated directly, because, the two databases analysed do not differentiate between immediate or delayed ignition (see above). Referring again to Fig. 2, it can be seen that

$$P'_3 = \frac{\bar{P}_1 P_2 P_3}{P_1 + \bar{P}_1 P_2} \tag{4}$$

Thus, P'_3 should be lower than P_3. In particular, the higher the probability of immediate ignition, the lower the value of P'_3. Nevertheless, there is another aspect to be taken into account: neither database allows confined explosions to be excluded from the analysis. No specification is given beyond the fact that an accident involved a blast of some kind, so that it is impossible to determine whether an accident was primarily a vessel burst or a partially unconfined vapour cloud explosion.

Hopefully, the bias introduced by the impossibility of telling whether there is immediate or delayed ignition counteracts the effect of the presence of confined explosions in the data sets. It can be reasonably assumed that $P'_3 \approx P_3$. Comparisons between literature and database data are therefore legitimate.

In general, experimental explosion probability increases with the amount spilled, although this pattern is clearer for HMIRS data (see Figs. 7 and 8). In the case of HMIRS, the values rise from about 0.05 (0–100 kg spilled) to almost 0.4 (>10,000 kg spilled). The increase of MINMOD values with the amount spilled is less pronounced, if present at all, for spills <10,000 kg. For larger spills, the explosion probability rises up to 50%.

In spite of this, there is no evidence supporting the existence of a threshold cloud size under which explosion is impossible, since explosions have occurred even for spills of less than 10 kg. However, in these cases, the presence of confined explosions in the sample must definitely play an important role.

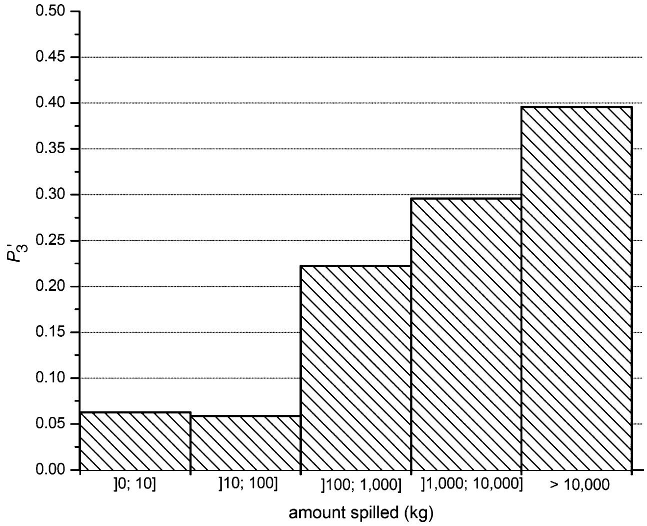

Fig. 7. Average HMIRS explosion probability data as a function of the amount spilled.

Fig. 9 represents the average explosion probabilities of the different hydrocarbon mixtures. Again, only significant figures are represented (i.e. data were excluded for cases in which the numerator of Eq. (3) was too low with respect to the denominator). Fig. 9 illustrates that an explosion is more likely to occur during land transport than during maritime transport, even if there is actually little difference. It is also interesting to note that:

- Contrary to [16] – the only study of Table 2 taking into account a liquid (crude oil) – our results show that explosion probability does not appear to be negligible for non-gaseous hydrocarbon mixtures.
- Moreover, the results from both databases show that explosion probability is even higher for light and medium fractions

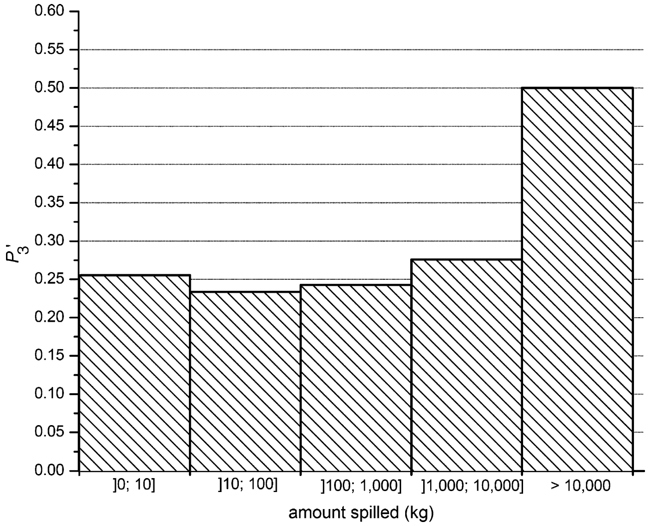

Fig. 8. Average MINMOD explosion probability data as a function of the amount spilled.

Table 4
Values of the parameters *a* and *b* of Eq. (5) and *c*, *d* and *f* of Eq. (6)

Substance	Land transportation		Maritime transportation		
	a	*b*	*c*	*d*	*f*
LPG	0.022	0.32	–		
Light fractions	0.00027	0.72	0.039	6.49	0.76
Crude oil, kerosene/jet fuel, diesel oil/gas oil	0.00055	0.53	0.013	40.75	1.00
No. 4–6 fuel oil	0.00	–	0.00	–	–

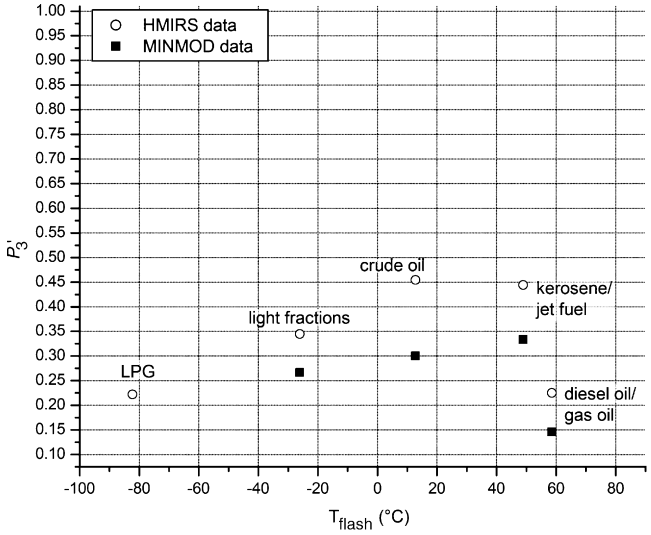

Fig. 9. Average HMIRS and MINMOD explosion probability data, as a function of the average flash temperature of the hydrocarbon spilled.

(from petrol to jet fuels) than for LPG. Actually, there seems to be a peak probability somewhere in the range of 10–50 °C flash temperatures, followed by a sudden decrease. The results for HMIRS are: P_3' is ca. 0.25 for LPG, 0.35 for light fractions, 0.45 for crude oil and kerosene/jet fuel, and 0.23 for gas oil.

The presence of a maximum in the “curves” of Fig. 9 can probably be explained by considering that hydrocarbon complexity has a decisive influence on the expansion of burning hydrocarbon mixtures. Hydrocarbons with high flash temperature are characterised by more complex carbon chains. This implies that, in case of combustion, the gas expansion induced by the sheer increase of gaseous molecules is higher for complex than for simple chains. Conversely, the molar heat of reaction decreases if the complexity and length of the chain increases, as does the thermal energy available for gas expansion. It can, therefore, be supposed that, for average chain complexity, the two effects overlap, determining a peak explosion probability.

5. Empirical approaches to predict ignition and explosion probabilities

The data presented in the previous section are important because they define the general pattern of the probability of ignition and explosion versus parameters such as the type and amount of substance spilled. Nevertheless, the results presented in Figs. 3–9 are essentially illustrative, as they describe the trend of probability data as a function of only one variable without taking into account the other. For example, Fig. 9 shows the influence of the substance type on the explosion probability, but does not consider the amount spilled. In this section, quantitative methods are proposed to predict ignition and explosion probabilities for their use in QRA, based on both the amount and substance spilled.

In order to obtain Eqs. (5) and (6) and the values collected in Tables 4 and 5 (see below), for each database, spills were organised according to both the substance and the amount spilled. For each resulting group (e.g. land transportation LPG spills between 100 and 1000 kg) average ignition and explosion probabilities were computed using Eqs. (2) and (3), respectively. These average probabilities were used as data points in order to infer empirical correlations predicting ignition and explosion probabilities as a function of the amount and substance spilled (where the amount spilled is the independent variable and the substance spilled a parameter).

In all cases, predictive curves were obtained by fitting series of five points, where each point represents the mean ignition or explosion probability of spills $\leq$10 kg; >10 kg and $\leq$100 kg; >100 kg and $\leq$1000kg; >1000 kg and $\leq$10,000 kg; and >10,000 kg, respectively. Data points were centred at the logarithmic mean of the corresponding amount range. In fact, the amount ranges that have been considered grow exponentially (10, 100, 1000, etc.).

5.1. Ignition probability

As for ignition probability, fitting curves are obtained using the least squares method. Figs. 10 and 11 represent the data points and resulting fitting curves for land and maritime transportation, respectively. Since points are representative of groups of data with different size (small spills are more numerous than large spills), for the regression each point has been assigned a weight equal to the number of spills corresponding to it. On the basis of Figs. 5 and 6, it is reasonable to assume that for both modes of transport, crude oil, kerosene/jet fuel and diesel/gas oil have practically the same ignition probability[3], so they were considered together in the frame of the present analysis. MINMOD

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[3] Although the data estimated on the basis of MINMOD prove a bit inconsistent here, since “experimental” ignition probability actually increases – though not to a great extent – passing from crude to kerosene to diesel oil (see Fig. 6).

Table 5
Explosion probability as a function of the substance and amount spilled and the mode of transportation

Mode of transportation	Amount spilled (kg)	Generic explosion probability	Specific explosion probability			
			LPG	Light fractions	Crude oil kerosene/jet fuel	Diesel oil/gas oil
Land	]0; 100]	0.06	0.043	0.067	0.088	0.044
	]100; 10,000]	0.30	0.22	0.34	0.44	0.22
	>10,000	0.40	0.29	0.45	0.58	0.29
Maritime	]100;10,000]	0.25	–	0.33	0.38	0.18
	>10,000	0.37	–	0.48	0.57	0.27

records few LPG spills, so spills of this material in maritime transportation were not analysed. Neither were no. 4–6 fuel oil spills, again due scarcity of data. However, a zero probability of ignition is assumed for this material, due to its very high flash temperature.

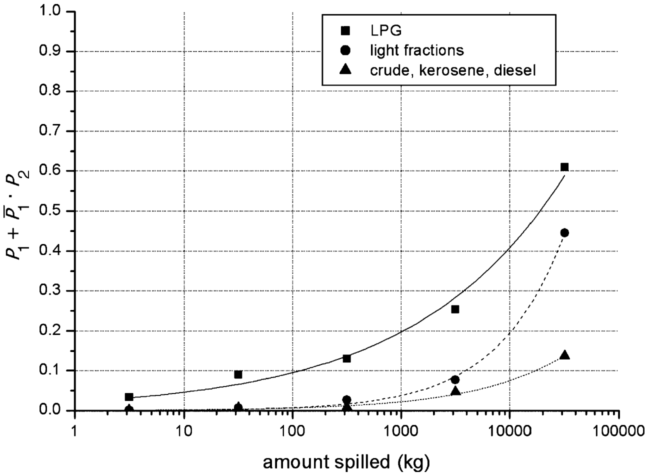

Fig. 10. HMIRS ignition probability data as a function of the hydrocarbon and the amount spilled. Data points are centred at the logarithmic mean value of each quantity range. Interpolating curves are based on Eq. (6) with coefficients from Table 4.

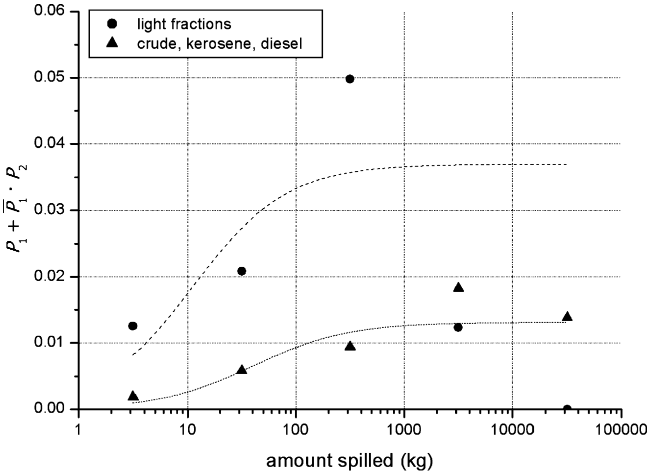

Fig. 11. MINMOD ignition probability data as a function of the hydrocarbon and the amount spilled. Interpolating curves are based on Eq. (5) with coefficients from Table 4.

For land transportation spills, a general trend in the form

$$P_1 + \bar{P}_1 \times P_2 = aQ^b \tag{5}$$

is proposed, in view of the fact that the increase of ignition probability in Fig. 3 is clearly exponential with respect to log Q: $P_1 + \bar{P}_1 \times P_2 \propto (\text{constant})^{\log Q} = Q^{\log(\text{constant})}$. Coefficients a and b resulting from the fitting operation are listed in Table 4. As it can be seen in Fig. 10, fitting curves match the data with good accuracy.

In the case of maritime transportation, as it can be seen in Fig. 4, ignition probability consistently increases with the amount released until 10,000 kg, after which a steady value is reached (probably due to the fact that no ignition sources are found outside the vessel or vessels involved in the accident). A good approximating function is therefore one that tends to a constant value for high amount spilled; furthermore, the value of the function must be 0 for $Q = 0$. A simple function fulfilling these requirements is the following[4]:

$$P_1 + \bar{P}_1 \times P_2 = \frac{c}{1 + dQ^{-f}} \tag{6}$$

Coefficients c, d and f are listed in Table 4. Fig. 11 shows that the fitting is good for crude oil, kerosene and diesel oil, whereas in the case of light fractions, the scarcity of data corresponding to high amounts spilled implies that the fitting curve obtained is mostly based on the data points associated with low amounts.

Eqs. (5) and (6) can be considered valid for any amount spilled, of course provided the probability value yielded does not exceed 1 (very high amounts spilled using Eq. (5)). In this case, for the purpose of performing QRA, it can be reasonably assumed that $P_1 + \bar{P}_1 \times P_2 = 1$.

5.2. *Explosion probability*

In this subsection, we propose explosion probability data for use in QRA. Data groups, in terms of number of accidents, are smaller than in the case of ignition probability, so that fitting P_3 as a function of the amount spilled is not viable (see Table 3). Therefore, another empirical method was used with the purpose of proposing probability data that account for both the amount and substance spilled.

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[4] The function in Eq. (6) is in fact a logistic curve whose independent variable is log Q.

First, in order to increase the significance of data, only three amount ranges (0 to 100 kg, 100 kg to 10,000 kg, and >10,000 kg) have been considered. Generic explosion probability data, for each of these amount ranges, were conservatively estimated on the basis of Figs. 7 and 8 (regardless of the substance spilled). In the case of MINMOD, spills of <100 kg were not taken into account, since experimental data (see Fig. 8) are certainly overstated in this range, probably due to a high incidence of confined explosions. Crude oil and kerosene/jet fuel were considered together in this scheme (again, in order to increase data significance), on account of the trend shown in Fig. 9, which makes it clear that their mean explosion probability is practically the same.

For each substance spilled, the generic probability was then multiplied by the ratio between the mean explosion probability of the substance and the mean explosion probability of *all* the accidents, to obtain specific probability data classified by both the substance and the amount spilled:

$$\begin{aligned} &P_3(\text{amount range } i,\ \text{substance } j)\\ &\quad = (\text{Generic expl. probability for amount range } i)\\ &\qquad \times \frac{\text{Mean expl. probability for substance } j}{\text{Mean expl. probability in database}} \end{aligned} \tag{7}$$

where the mean explosion probability of substance *j* is calculated on the basis of all the spills of substance *j* and the mean explosion probability of the database on the basis of all the accidents (both mean probabilities are obtained using Eq. (3)).

Eq. (7) “crosses” mean data referred solely to the amount spilled with ones that only account for the substance, thus, yielding explosion probability data as a function of both parameters.

All of the above operations were performed separately for the two databases, so two sets of explosion probability data were obtained. One is associated to land transportation and the other to maritime transportation. The results are shown in Table 5.

6. Discussion

We analysed two major accident databases to obtain ignition and explosion probability data. The probabilities proposed in the previous section are global, and unfortunately do not fit directly into the scheme of Fig. 2. In particular, ignition probability data are inclusive of both immediate and delayed ignition, whereas explosion probability figures suffer a distorting effect due to both the lack of clarity regarding immediate or delayed ignition, and the presence of confined explosions. These limitations are practically unavoidable when one is using accident databases. None of the existing databases makes a clear distinction between delayed and immediate ignition, or between confined and unconfined explosions. These can sometimes be distinguished in principle, but definitely not in practice. For example, the MHIDAS database, maintained by the UK Health and Safety Executive, has the potential to make such distinctions among accidents, as accident categories are defined with great detail. Nevertheless, most of the accident records fail to specify what kind of fire or explosion was produced. On the other hand, the MARS database, managed by the Major Accident Hazard Bureau, has complete descriptions of the accidents, but has a low number of entries (less than 1000 overall).

Although we consider the application of the explosion probability data to QRA to be legitimate (see Section 4.2), care must be taken in the case of ignition probability. In fact, if one wants to use these data in an event tree scheme such as that of Fig. 2, one must split values into a probability of immediate ignition (P_1) and one of delayed ignition ($\bar{P}_1 \times P_2$). Literature data can be useful for this task. Some of the studies cited in Table 2 [3,13,14,19,21,26] give data for both immediate and delayed ignition. If the ratio of delayed to immediate ignition probability is analysed, it can be seen that:

- Studies are seldom in agreement.
- According to the literature, the ratio depends on the substance spilled and sometimes on other factors (e.g. amount spilled, number of ignition sources).
- In the case of petrol and light fractions, the ratio varies from 0 to 2 according to [21] (small and large rail accident spills), whereas it is 1 according to the *Purple Book* [26].
- The only source explicitly referring to diesel oil and similar products is [26], in which a zero probability of delayed ignition was assigned.
- There is little agreement regarding LPG. The ratio of delayed to immediate ignition probabilities is 1 according to [14], and ranges from 0.2 to 1 (depending on spill mode) for [3], ca. 0.1 to as much as 20 according to [19], and 0.5–2.5 for [21]. Finally, it is about 0.2 in [26].

On the basis of these considerations, we can reasonably assume the following:

- For petrol and light fractions, a ratio of delayed to immediate ignition probabilities of 1:1 can be used.
- For LPG, a ratio of 1:1 can also be used, given the great variety of data available for this material class.
- For diesel/kerosene/crude oil, considering the only source found [26] and the low vapour pressure, the ratio will be very small. We suggest to use a value of 1:10, according to which delayed ignition is not deemed negligible, to take into account the possibility that the spill may happen above the ambient temperature.

The values and equations provided in Section 5 can also be useful for analysing process plants. Fixed establishments are generally characterised by a tight packing of equipment and activities, meaning that a certain number of ignition sources must be present. This aspect is taken into account in the design of the plant. Working procedures (e.g. hot work permits, wearing safety shoes) and use of ignition-proof equipment also help to limit both the amount and effectiveness of potential ignition sources. It is generally recognised that ignition in process plants is more difficult than in land transportation, a setting which, though less dense in terms of equipment, is less strictly controlled. For instance, if a road or rail accident occurs, the very vehicles that have crashed, or any other moving vehicle in the proximity of the accident, represent potential ignition sources

Table 6
Summary of probability data proposed

Event	Probability data		
	Land transportation	Maritime transportation	Fixed plants
Ignition			
Overall ignition probability ($P_1 + \bar{P}_1 \times P_2$)	Use Eq. (5) and parameters *a* and *b* from Table 4	Use Eq. (6) and parameters *c*, *d* and *f* from Table 4	Use a value intermediate between those for maritime and land transportation
Immediate/delayed ignition	Ratio of delayed to immediate ignition probability: 1:1 for light fractions (petrol, naphtha, etc.) and LPG 1:10 for diesel oil, kerosene and crude oil		
Explosion	Use specific explosion probability data for land transportation from Table 5	Use specific explosion probability data for maritime transportation from Table 5	Use specific explosion probability data for land transportation from Table 5

for HazMat spills. On the other hand, maritime operations offer less ignition sources than fixed establishments, as, apart from the vessel(s) involved in the accident, no other sources are usually present. Therefore, we suggest using values *intermediate* between those suggested for land and maritime transportation when one is seeking ignition probability data for use in QRA of process plant accidents.

As to *explosion* probabilities, it must be noted that the relatively small difference found between land and maritime transportation is not related to the density of ignition sources, but rather to some other attribute of the accident setting. In our opinion, the difference is due to the fact that land accidents involve partially confined or obstructed vapour clouds more often than do maritime spills. Since process plants probably offer confinement conditions at least equal to those entailed by land transportation, we propose the use of land transportation explosion probabilities for use in QRA of process plant accidents.

Table 6 summarises the probability data proposed in this study. In Appendix B a comparison is made between literature data and probabilities estimated using the scheme proposed.

7. Conclusions

In the first part of this paper, an extensive bibliographical analysis is presented of the ignition and explosion probability data used in quantitative risk analysis of hazardous materials spills. Figures put forth by a variety of authors during the last decades are seldom in agreement and depend on an array of variables such as material properties, amount spilled, and accident type. The probabilities collected have been put in their original context, which makes it possible to compare them. In particular, it has been specified whether ignition probabilities were referred to immediate rather than delayed ignition.

The spill databases HMIRS and MINMOD were investigated in order to propose alternative probability data for hazardous materials spills that occur during land and sea transport, respectively. A selection of significant commercial hydrocarbons were taken into account, which brought to examine more than 12,000 spills for HMIRS and more than 34,000 for MINMOD.

Database analysis has enabled us to explain how ignition and explosion probability vary as a function of the amount and the substance spilled. The analysis was surprisingly consistent and yielded coherent results (Figs. 3–9), due to the great amount of accident records provided by the two databases analysed. Ignition probability was found to increase with the amount spilled and to decrease with the flash temperature of the mixture spilled. Explosion probability grows with the amount spilled as well, whereas its trend as a function of flash temperature presents a peak corresponding to crude oil and kerosene. Significant differences were found between land and sea transport.

Accordingly, a quantitative scheme, which includes the possibility of extending the findings of the analysis to fixed plants (see Table 6), was proposed to predict ignition and explosion probability of hydrocarbon spills. Data estimated through this method were compared with literature data. Future work could involve further validation against reported data. The fact that specific ignition/explosion probabilities are put forth for sea transportation spills is particularly important, due to the near absence of such data for these scenarios in the literature.

The study has proved that the data systems analysed, apart from being broad, appear to be particularly reliable and unbiased. To date, there have been few studies carried out using these databases (see for example [39]). It would certainly be interesting to concentrate more efforts in the study of these and other US federal spill and accident databases, like ARIP, ERNS, HSEES [34,36]. Their use can be profitable above all to investigate probabilistic aspects and frequencies of accidental spills of hazardous materials in various industrial settings.

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Appendix A. Remarks on data retrieving and data treatment

HMIRS includes three tables. The most important is called HAZMAT and contains the information used to carry out the present analysis. The logic fields FIRE and EXPLO were brought into play to identify fire and explosion accidents. Three fields were analysed as to the substance involved in the event: CMCD, COMOD and TRADE. RQUAN was referred to in order to define the spilled quantity, together with RUNIT (unit of measure). Conversion from gallons and several other units to kilograms proved necessary at this stage.

Of the 19 tables that make up MINMOD, three were used in the analysis. CIRT (Marine Casualty and Pollution Master Table) provided a general reference, besides defining the primary nature (PRI_NATURE field) of the incident (whether this is a fire, explosion or something else—like capsize, flooding, etc.). Another field (TYPE), belonging to CEVT (Marine Casualty Event Table), was used to further define whether the incident involved a fire and/or explosion. It was considered that a record involves fire whenever its primary nature *or* type is "fire". The same applies to explosion. Finally, the CPDT (Marine Pollution Substance Table) was used to identify the substance involved in the accident and the amount spilled. As for HMIRS, a previous conversion in a consistent unit (kg) was required.

For both databases, accidents were considered only if the amount spilled was positively defined and greater than 0 kg. This means that: (a) non-spill accidents were excluded from MINMOD; (b) spills were excluded where the amount spilled was either zero or undefined.

The following points regarding data treatment must be emphasised:

- For the relatively few cases in which the databases identify an incident as an explosion but do not mention any fire, we nevertheless introduced a fire event. As the substances taken into account were all flammable or at least combustible, it is reasonable to think that explosions must be tied to combustion. The category "fire" here thus represents all events in which ignition is effective, including blasts with reduced or short-lasting flames.
- Regarding substances and mixtures, MINMOD is based on CHRIS, a hazardous materials database maintained by the US Coast Guard [38], whereas HMIRS basically makes use of UN numbers. Careful judgement was used to avoid misclassifying substances.
- Care was also taken to avoid accident repetition for both databases.

Appendix B. Comparison between some probabilities estimated using the scheme proposed with literature data

In order to validate Eqs. (5) and (6) and Table 5, let us consider two examples.

B.1. 5000 kg petrol spill

Ignition probability is 0.12 (land transportation, as per Eq. (5)) and 0.039 (sea transportation, as per Eq. (6)). Whereas it is not possible to compare the latter figure with those provided by the specialised literature, it is interesting to note that the former is close to what the Purple Book puts forth [26], i.e., an overall ignition probability equal to $0.065 + 0.065 = 0.13$. Note that the latter values are also in agreement with the assumption (see Table 6) that the ratio of immediate to delayed ignition probability is 1:1 in the case of light fractions. There is good agreement with [21] as well. Explosion probability (see Table 5) is 0.34 (land transportation) and 0.33 (sea transportation). Again, agreement with the Purple Book is good. In fact, the value proposed by [26] (regardless of the substance spilled) is 0.4.

B.2. 5000 kg LPG spill

No prediction can be made as to sea transportation spills. Ignition probability according to the scheme proposed is 0.34 for land transportation spills. This figure is not far from that recommended in [14], which proposes an overall probability of 0.35 or 0.40 (depending on the presence of wind). Studies that put forth slightly lower data are [15], which suggests using 0.24 and [3]. Other sources have instead overestimated this figure with respect to our proposal (see [22]; Wiekema and Janssen [26] even state that ignition would be certain in these conditions). On the other hand, explosion probability is 0.22, only slightly lower than predicted by [20,22,26].

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