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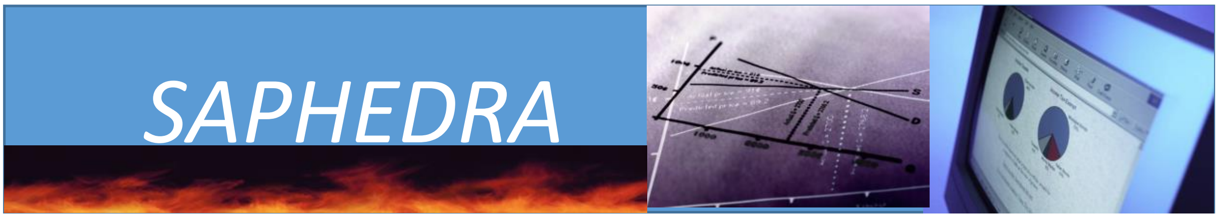
SAPHEDRA - Building a European Platform for evaluation of consequence models dedicated to emerging risk

Gap Analysis for Emerging Risk Issues

SAPHEDRA is a project funded in the framework of the ERA-NET SAF€RA "Coordination of European Research on Industrial Safety towards Smart and Sustainable Growth"



SAPHEDRA - Building a European Platform for evaluation of consequence models dedicated to emerging risks

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Report D2 "Gap Analysis for Emerging Risk Issues"

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Project:	SAPHEDRA - Building a European Platform for evaluation of consequence models dedicated to emerging risks					
Work Package:	2 – Gap Analysis for Emerging Risk Issues					
Abstract:	This report is the final deliverable of WP2. The report identifies a shortlist of the accident scenarios associated to new and emerging risks related to industrial technologies. The document also describes the results of the gap analysis between emerging risk scenarios and existing consequence models. A set of test cases for the comparison of the available models is also identified. The results of the gap analysis between emerging risk scenarios and existing consequence models are also reported. A set of test cases for the comparison of the available models is also identified.					
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TABLE OF CONTENTS

1. Definition of the scope and limits of the study

Task D2.1 of the SAPHEDRA Project is aimed at the identification of a selected shortlist of emerging risk issues with specific reference to the context of EU Member States. These will be later considered for a Gap Analysis (Task D2.2 and D2.3) in order to identify the potential deficiencies in the current consequence modeling methods.

A definition of emerging risks can be derived from EU-OSHA (EU-OSHA 2005):

An emerging risk is a risks that is both new and increasing.

By new, it means that:

- *The risk was previously unknown and is caused by new processes, new technologies, new types of workplaces, or social or organisational change; or,*
- *A long standing issue is newly considered to be a risk due to changes in social or public perceptions; or,*
- *New scientific knowledge allows a long standing issue to be identified as a risk.*

The risk is increasing if:

- *The number of hazards leading to the risk is growing; or,*
- *The likelihood of exposure to the hazard leading to the risk is increasing, (exposure level and/or the number of people exposed); or,*
- *The effect of the hazard on the worker's health is getting worse (seriousness of health effects and/or the number of people affected).*

The main focus of the SAPHEDRA Project is on models for consequence assessment. Therefore, the scope of the activity is restricted only to those emerging risks that require a step of consequence assessment modelling in their analysis and management. Hence only processes and technologies where the release of hazardous material and/or the release of energy due to the presence of hazardous materials is possible, will be considered in the following.

Furthermore, only the consequence modeling necessary to the definition of impact on human targets will be considered as a selection criteria for emerging risk identification, neglecting consequence models uniquely aimed at the evaluation of environment and asset damage.

It should be further remarked that consequence modeling is not considered to include the step of impact assessment (i.e. quantification of damage to targets), which lies beyond the goals of the current study.

2. Data sources and search method

The electronic resources in the current globalized world provide wide access to resources that could help the identification of what is currently perceived as emerging risk.

A query in a common web search engine (e.g. www.google.com) would however return a number of results difficult to handle within the limits of current research project (Table 1).

The use of databases specialized in scientific literature (e.g. Scopus or Web of Science) would anyway provide hundreds of results (Table 1).

Table 1 - Summary of the search of on-line databases

Source	Query	Number of results
www.google.com	"emerging risk"	390.000
	"emerging risk"+"EU"	86.100
	"emerging risk"+"hazardous materials"	6.170
www.scopus.com	"emerging risk"	920
apps.webofknowledge.com	"emerging risk"	687

In order to limit the search to a small number of authoritative data sources, EU level initiatives and EU funded research project were considered as a source of data. In particular the following documents were selected, on the basis of the relevance to the scope of current study and the access to the data available to the partners of the SAPHEDRA Project:

- Deliverables of the FP7 iNTeg-Risk Project (Early Recognition, Monitoring and Integrated Management of Emerging, New Technology related Risks)
- Key Enabling Technologies considered in Horizon 2020 Program

A brief summary of the content of both resources is provided in the following.

These sources will be screened for emerging risk processes and technologies that meet the criteria described in section 1 and summarized in the following:

- be of interest in the EU context;
- involve an hazardous material and/or the potential release of energy due to the presence of hazardous materials;
- be able to cause damage to human targets by a mechanism that require a step of consequence modeling.

2.1 Summary of the INTeg-Risk Project

The iNTeg-Risk Project (Early Recognition, Monitoring, and Integrated Management of Emerging, New Technology related Risks) was funded under the EC FP7 Programme (European Commission Seventh Framework Programme for Research and Technological Development) in the area of “Nano-sciences, Nano-technologies, Materials and new Production Technologies”. The main goal of iNTeg-Risk Project was to establish a holistic approach for facing the challenges of emerging risks, coming from to new materials and technologies applied in the next 15 years.

The iNTeg-Risk solution was based on the analysis of 17 individual applications of new technologies, the so-called iNTeg-Risk ERRAs - Emerging Risk Representative Applications in EU Industry, involving nanotechnologies, H_2 technologies, underground storage of CO_2, new materials, intense use of LNG, etc. The solutions from these single applications were generalized and have been used for the definition of the iNTeg-Risk framework. The solutions identified are available to the users in the form of the iNTeg-Risk "one-stop shop". The solutions include issues of early recognition and monitoring of emerging risks, communication, governance, pre-standardization, education & training, dissemination, as well as new tools such as Safetypedia, Atlas of Emerging Risks, Reference Library, etc.

In iNTeg-Risk, the Emerging Risks Representative (industrial) Applications (ERRAs) are significant examples of applications related to industrial safety (emerging risks). Solutions for the these single, specific problems related to emerging risks should allow to capitalize upon and, by generalizing the solutions, build the common European approach to emerging risk. Some of the most significant ERRAs of interest for the current project are briefly presented in the following:

- ERRA A1 of the iNTeg-Risk project was devoted to CO_2 capture, transport and injection of CO_2, considering both technical risks and governance risk. Different areas of interest in the CCS chain were studied: i) potential release of large quantities/ flow rates of CO_2 from surface CCS installations including capture plant, pipelines, intermediate storage (if any) and injection; ii) potential release of large quantities of CO_2 from underground storage; iii) climate change and global warming occurring from the failure to establish the new emerging technology of CCS.
- ERRA A4 focused on Liquid Natural Gas (LNG) regasification in sensitive areas on-shore and off-shore. The aim of this ERRA was to produce reference solution containing documents, methods and tools, for the assessment and management of emerging risks related to new and intensified technologies available for LNG regasification terminals.
- ERRA B1 explored health and safety issues related to monitoring of emerging risks in production, storage and transport of nanomaterials on industrial scale in small and medium enterprises (SMEs). This ERRA focused on the improvement of the risk management for SMEs dealing with Nanotechnologies with respect to public health and medical aspects. The specific goal was to develop reference methods and documents for self-assessment carried out by those companies who are producing or working with Nanomaterials (with special focus on SMEs).

- ERRA B2 (Emerging risks related to advanced storage technologies for hazardous materials) studied, among the other, the hazard and risk issues related to hydrogen. This ERRA was focused on the delivering of a common and integrated reference solutions for emerging risks that are related to different aspects of storage above ground, including cryogenic storage of liquid hydrogen and storage of pressurized hydrogen.
- ERRA C4 (Atypical, one-of-the-kind major hazards/scenarios and their inclusion in the normal HSSE practice) was devoted to issues coming from major incidents which occurred in Europe in recent years (e.g. Buncefield, Toulouse) but were not considered by their site Seveso II Safety Case. The objective of this sub-ERRA was to improve hazard identification and was the incubator of the DyPASI method.

2.2 Summary of the Key Enabling Technologies (Horizon 2020 Program)

The European Commission has identified KETs as a key priority within its Europe 2020 strategy. Key Enabling Technologies (KETs) are a group of six technologies that have a wide range of product applications such as developing low carbon energy technologies, improving energy and resource efficiency, and creating new medical products. They have huge potential to fuel economic growth and provide jobs.

KETs are seen by the European Commission as essential to flagship initiatives such as Innovation Union and Digital Agenda for Europe. Their importance to Europe's industrial future is also remarked in the EU industrial policy. KETs are instrumental in modernising Europe's industrial base and in driving the development of entirely new industries.

The group of six KETs was identified on the basis of current global research and market trends, given their economic potential, contribution to solving societal challenges and knowledge intensity:

- **Nanotechnology** holds the promise of leading to the development of smart nano and micro devices and systems and to radical breakthroughs in vital fields such as healthcare, energy, environment and manufacturing;
- **Micro- and nanoelectronics**, including semiconductors , are essential for all goods and services which need intelligent control in sectors as diverse as automotive and transportation, aeronautics and space. Smart industrial control systems permit more efficient management of electricity generation, storage, transport and consumption through intelligent electrical grids and devices;
- **Photonics** is a multidisciplinary domain dealing with light, encompassing its generation, detection and management. Among other things it provides the technological basis for the economic conversion of sunlight to electricity which is important for the production of renewable energy, and a variety of electronic components and equipment such as photodiodes, LEDs and lasers.

- **Advanced materials** offer major improvements in a wide variety of different fields, e.g. in aerospace, transport, building and health care. They facilitate recycling, lowering the carbon footprint and energy demand as well as limiting the need for raw materials that are scarce in Europe;
- **Biotechnology** brings cleaner and sustainable process alternatives for industrial and agro-food operations. It will for example allow the progressive replacement of non-renewable materials currently used in various industries with renewable resources, however the scope of applications is just at the beginning;

The potential of these technologies is largely untapped. Increasingly systemic solutions will need to evolve in order to address major societal challenges, such as ensuring high-speed communication, ensuring food supply, the environment, finding appropriate transport solutions, ensuring high levels of health care for an ageing population, unlocking the potential of services, ensuring internal and external security and addressing the energy question. Low carbon technologies and applications will play a vital role in reaching European energy and climate change targets. For instance, CCS and CO_2-related transport grids will be needed to reduce CO_2 emission in countries that will continue to rely heavily on fossil energy sources. KETs, such as new materials for energy production, transportation and storage play an essential role. They could lead to better resource and energy efficiency and their environmental impact needs to be assessed in a life-cycle perspective, taking advantage of the related initiatives promoted at EU level in this context.

A detailed description of these technologies including their estimated current market potential is presented in the SEC (2009) 1257.

3. Identified emerging risk issues

3.1. Emerging Risk 1 – LNG Regasification

Natural Gas is an important part of the European energy market, both for power generation, heating, domestic use. More than 50% of the Natural Gas used in Europe is imported (almost all from three only countries: Russia, Norway and Algeria). The Natural Gas import is expected to increase up to 70% in 2020. Security of the supply, where the diversification of the sources plays an important role, is an important issue for the energy future of Europe and a specific European Directive (2004/67/CE) is dedicated to this issue. Import of Liquefied Natural Gas allows increasing the supply of gas and the flexibility of the system, not requiring a rigid pipeline link to a specific producing country. The number of regasification plants in Europe is going to increase, and new technologies to install these plants offshore begin to be applied. New and emerging risks related to floating or off-shore installations are not fully explored to date and the hazards associated to these installations in general is highly perceived by the population.

Within the IntegRisk Project, a specific ERRA had the objective of exploring the emerging risk related to the safety and security of new and alternative technologies for LNG regasification and propose solutions based on a qualified and standardized approaches for risk assessment and management.

In spite of apparently being a long-standing technology and a relatively simple process, LNG regasification terminals are classified by the IntegRisk Project as an emerging risk for Europe. In facts, the envisaged LNG regasification facilities meet all the relevant criteria of EU-OSHA 2005 (EU-OSHA 2005): the risk related to LNG technologies is both new (due to new process/technologies or due to a change in perception or to new scientific knowledge) and increasing (due to growing number of hazards or increased number of people exposed). More in particular the following issues are identified:

- New technology: offshore terminals (floating or gravity-based) implement the known process into a new technology, of which only a few plant exist. Risk issues for these technologies need to be assessed to understand if any new, unforeseen risk exists;
- Change in public perception: a search in Internet with keywords “LNG Safety” or “LNG Risk” gives back hundreds of entries related to concerns that local populations have with respect to any type of these plants (either onshore or offshore). Groups against installation of new terminals or upgrading of existing ones are active in practically all sites where these projects are proposed, while up to ten years ago no specific concerns was posed by population with respect to risk issues in LNG regasification.
- Increased exposure: the number of proposed terminals is increasing, and frequently they are proposed in industrial areas or nearby residential areas, thus increasing both the number of hazards and the number of people exposed.

The emerging risk posed by LNG regasification terminals has been included in the shortlist considered in current task since:

- It involves an hazardous substance, the LNG, which is able to trigger hazardous phenomena due to its intrinsic properties and its handling conditions (it can release flammable vapors, it is a cryogenic liquid capable of low temperature heat exchange, it can undergo explosive vaporization in particular conditions, etc.)
- The description of the hazardous phenomena above occur through the unfolding of different phenomena that fall indeed in the domain of consequence models (material release models after loss of containment, liquid pool spreading and vaporization models, jet release and dispersion models, explosive evaporation models for BLEVE[1] and RPT[2], etc.)

3.2 Emerging Risk 2 – Biogas production

The worldwide demand for energy from renewable sources is strongly increasing in recent years and the forecast indicates a further increase up to 2035, as a result of the support strategies for the reduction of air pollution and sustainable development implemented by several governments around the world. In this panorama, the role of biogas is becoming crucial.
Europe is the most important producer of biogas in the world. The latest EurObserv'ER Biogas Barometer report (EurObserv'ER Biogas Barometer, 2013) estimates about 13 million tonnes oil equivalent of biogas primary energy were produced during 2013 (1.2 m toe more than in 2012 representing more than 10% of increase). In 2013, there were over 14500 biogas plants in Europe with an installed capacity of 7.8 GW.
The leading country in biogas production are Germany, UK and Italy. For instance, in Italy the number of biogas production sites more than doubled in 2013, growing from 521 to 1264, thanks to the incentives for small-scale facilities allocated by the Ministry of Economic Development. In 2013, in Central Europe (Hungary, the Czech Republic, Slovakia and Poland) an increase of 18% in the number of biogas plants was recorded (European Biogas Association (EBA), 2015).
Despite the widespread installation of biogas plants, the safety of such energy supply was not specifically addressed to date and there is a lack of dedicated safety standards aiming at the control of hazards and risks associated to biogas production and upgrading. Most of the biogas production plants are of small or medium scale, therefore falling below the thresholds for the application of legislation aimed at the control of major accident hazard, as the Seveso Directive.
A recent survey of accidents (Casson Moreno et al., 2015) resulted in the identification of 169 accidents related to biogas supply chain occurred in the last 20 years, from 1995 to 2014 (Figure 1). The time distribution of collected events seems important. Focusing on the five years period 2007-

[1] BLEVE: Boiling Liquid Expanding Vapor Explosion
[2] RPT: Rapid Phase Transition

2011, the number of accidents in the biogas sector has increased more than five times, a growth that is higher than the one experienced by the number of biogas installations. The reduction in the number of accident files collected in the following three years (period 2012-2014) is likely a consequence of deficiencies and delays in reporting rather than the consequence of an improvement in process safety in biogas facilities.

In the same plot, major accidents (according to Annex VI of the Seveso III Directive) are shown: these are 20 events over 169, representing almost 12% of the events in the database.

Considering the geographical distribution of events, 96% of the accidents retained for the analysis took place in Europe (163 over 169). Most of them happened in Germany (76%), while a lower amount were documented in France (11%), Italy (6%), and UK (2%). This fact can be explained considering that Germany is leading the European biogas market and is, in fact, the country where the highest number of plants is operating. For the same reason, awareness about risks related to biogas production is deeper in Germany than in the rest of Europe.

Analysing the number of accidents with respect to time compared to the biogas production in Europe (Figure 2), it is possible to notice that both the number of documented accidents and the production of energy from biogas are increasing in recent years. However, it is evident that the number of accidents is growing faster than biogas production.

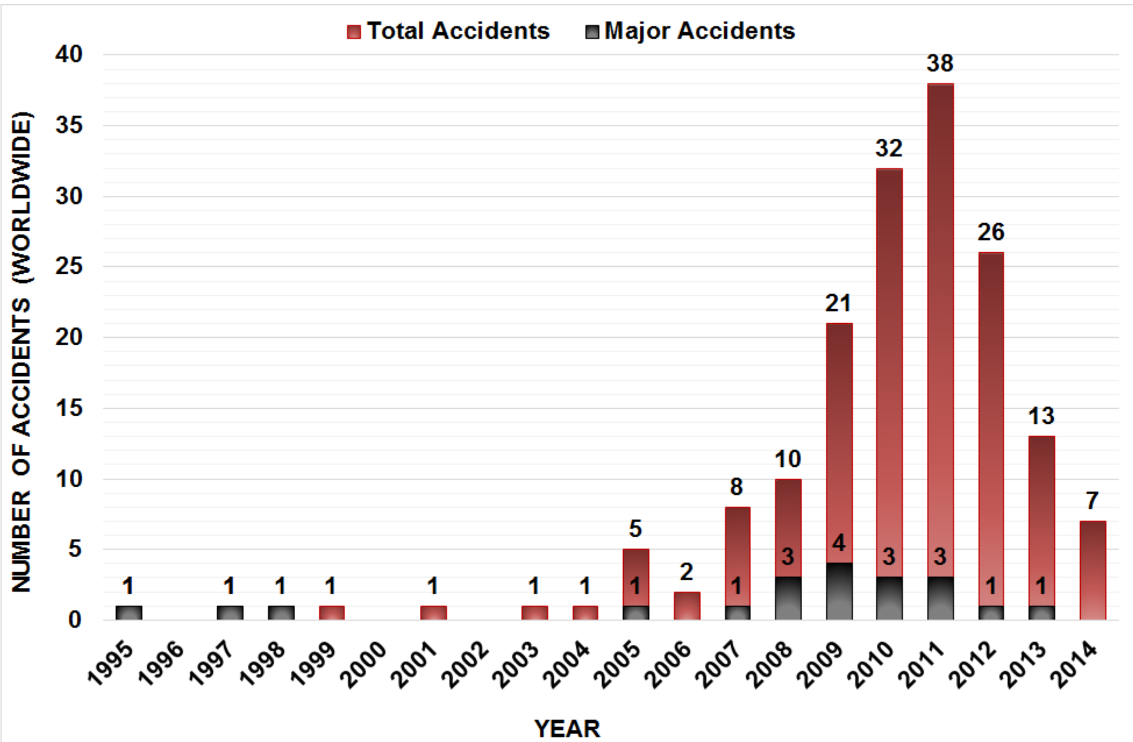


Figure 1 - Distribution with respect to time of the accidents in biogas industry. In red: total number of accidents; in black: major accidents (according to the definition provided in Annex VI of the Seveso III Directive).

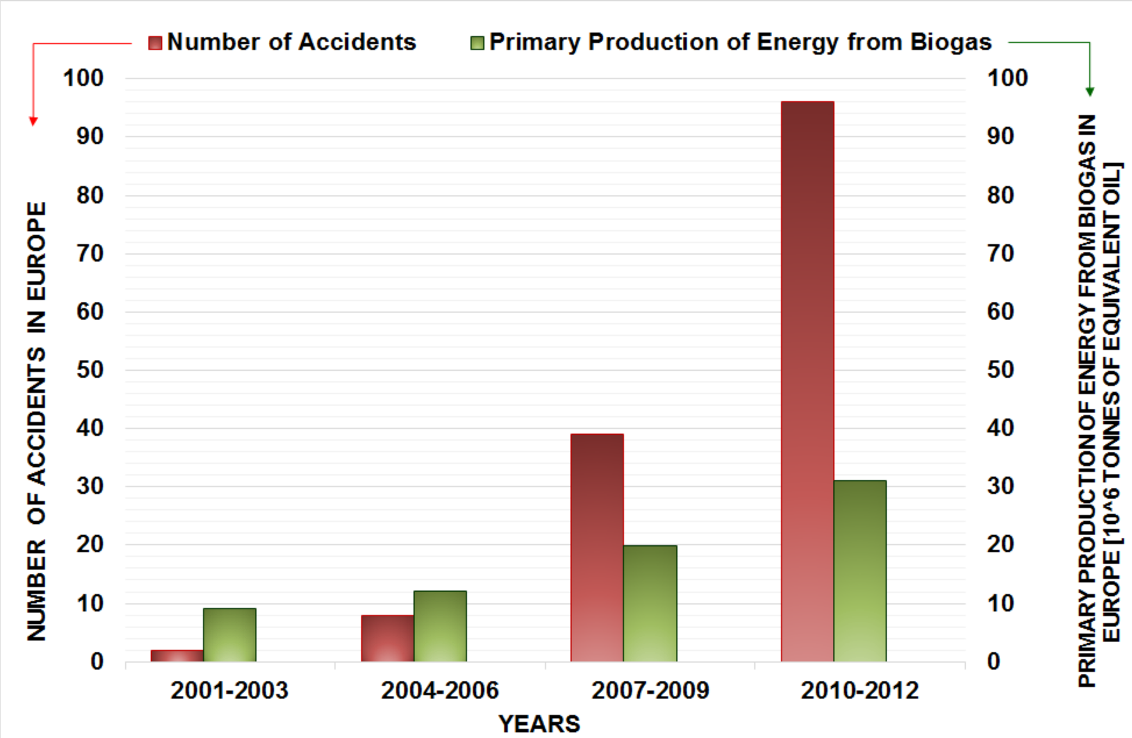


Figure 2 - Trend of accidents in biogas production and upgrading collected in the present study compared to primary production of energy from biogas in Europe.

The activities related to biogas production present a non-negligible risk profile with respect to major accident hazards when the frequency and severity of past accidents is considered. Such result should be considered as an early warning, and rise concern about the need of improving the safety culture and risk awareness in the biogas production sector. Other recent studies in the literature aimed at the exploration of biogas safety issues suggest the need for specific and harmonized international standards for biogas production and upgrading (Casson Moreno & Cozzani, 2015b; Heezen et al., 2013; Scarponi et al., 2015). Several authors remarked the progress that process safety in the biogas sector could achieve thanks to the sharing of experience, feedback and results of accident investigations (Rivière & Marlair, 2010; Salvi et al., 2011). This may also contribute to improve the safety culture in the biogas field that is presently limited as pointed out in different studies.
Altogether, biogas production can be identified as an emerging risk for Europe since it involves risks that are both new (due to new process/technologies or due to a change in perception or to new scientific knowledge) and increasing (due to growing number of accidents and early warnings in the sector or to the increased number of people exposed). More in particular the following issues are identified:

- New technology: digesters and upgrading processes use new technologies for which a limited experience exist (new digester design, innovative CO_2 separation systems).
- Increased exposure: the number and size of proposed plants is increasing, thus increasing both the number of hazards and the number of people exposed.

- Poor safety culture: as evidenced above, operators and nearby population, may have poor understanding of operational and safety procedure involved both in accident prevention and mitigation.
- Adverse in public perception: a search in the news articles of the last few years evidences a number of protest events opposing biogas plants and, more in general, “green energy” installations.

The emerging risk posed by biogas production facilities has been included in the shortlist considered in current task since:

- It involves hazardous materials (methane, hydrogen sulfide, ammonia, etc.), which are able to trigger hazardous phenomena due to its intrinsic properties and handling conditions;
- It can cause damage to human targets by a mechanisms that falls indeed in the domain of consequence modelling (material release models after loss of containment, vapor cloud dispersion, etc.).

3.3 Emerging Risk 3 – Carbon capture transportation and storage

In the next decade the development of advanced clean energy technologies is expected to accelerate in order to address the global challenges of energy security, climate change and sustainable development. There is now a general consensus of scientific opinion that unless greenhouse gases in the atmosphere are controlled, the result will be global warming, with associated climate change, gradual melting of polar ice, and rise in sea levels. The analysis in the IEA publication Energy Technology Perspectives 2008 (ETP) projects that energy sector CO_2 emissions will increase by 130% above 2005 levels by 2050 in the absence of new policies or from supply constraints resulting from increased fossil fuel usage. Addressing this increase will require an energy technology revolution involving a portfolio of solutions: greater energy efficiency, increased renewable energies and nuclear power, and the near-decarbonisation of fossil fuel-based power generation. At European level this is recognized by several initiatives, as for example the strategy EUROPE 2020 and the 2050 Energy Strategy. The IEA CCS Technology Roadmap (IEA, 2009) states that carbon capture and storage (CCS) is the only technology available to mitigate greenhouse gas (GHG) emissions from large-scale fossil fuel usage in fuel transformation, industry and power generation. The Roadmap sets out an ambitious programme of development of CCS, including investment of US$ 2.5-3 $x10^{12}$ between 2010 and 2050 to achieve a 50% reduction in CO_2 emissions by 2050. It follows that the next 40 years will see a massive development and implementation of this new technology, which currently has only a small (but increasing) number of small-scale demonstration projects worldwide.

The CCS chain involves:

- Capture of CO_2 from a potential emission source such as a power station, steelworks, cement works, etc;
- Transport to the injection site. This may involve intermediate storage;
- Injection of the CO_2 into the long-term storage;
- Storage in an underground saline aquifer, depleted oil/gas reservoir or coal bed.

Per se, CO_2 is not a new material in industrial scale applications. CO_2 has been handled extensively in many industrial sectors such as brewing, gas reforming and gas processing. It has a host of small-scale applications and is used as an inerting gas and fire extinguishant. It is also routinely manufactured and transported by industrial gas companies. Its properties are well understood in these industrial settings for the quantities and under the conditions involved. Moreover, there is a considerable history of incidents involving CO_2.

The hazard profile of the CCS system depends instead on the innovative details of the technology employed and the design and layout of the plant. While, on principle, there is existing experience of many of the technologies envisaged for CCS (e.g. natural gas sweetening involves CO_2 removal, CO_2 transportation in the US for enhanced oil recovery EOR was practiced in the last few decades), the scale of use of these technologies will increase dramatically with the uptake of CCS. Moreover, new and improved technology will be developed for economic reasons. Also, there will be a use of these technologies in industries (e.g. power generation, steelmaking, cement works) that do not currently apply them and that may have significant gaps in their safety culture related to CO_2 specific hazards.

Lack of substantial operational experience in a novel process or technology generally leads to significant difficulties in identifying accurately the associated hazards associated. There are very few risk-based reference points in handling high pressure CO_2 in large (600 tons) quantities against which estimated risks to persons can be compared to establish if a robust case for safety has been made. Consequently, poorly defined major hazard implications require to fully define reliable models for the release behavior of supercritical CO_2.

For underground installations (the underground storage), a number of factors affect possible releases from underground storage and introduce considerable uncertainty. Firstly, in depleted oil fields, many ancient wells are unknown, and many are poorly plugged (completed). Secondly, within or along a well many different pathways are possible (through the cement, after its lixiviation, along the interface casing/cement or cement/rock, within the excavation damaged zone of the rock (EDZ)) and it is difficult to know, in the longer term, if a well will be safe even if it was well understood/characterized and well-completed (plugged). There is also a lack of knowledge of the impurities (nature, rate), which will be injected into the sink along with the CO_2. Impurities can have important effects on the hazards.

From the social point of view, the whole CCS chain is at stake. This emerging technology has to demonstrate its safety and its low impact on the environment. It will be necessary to ensure feedback to various stakeholders including regulators, non-governmental organizations (NGOs), public/local associations etc. Inadequate risk communication could affect the uptake of CCS and hence impact on risks arising from global warming. A few of studies were carried out on the social perception of the phenomena (e.g. The Public Perceptions of Carbon Capture and Storage (Tyndall, 2004) and the EU 6thFW ACCSEPT project (ACCSEPT, 2007)): it appears that support to CCS mainly depend upon concern about human-caused climate change, CO_2 emission reductions and transition to zero-emission economy; however also the aspects related to potential risks to humans from potential major accidents has been evidenced as a concern.

CCS is therefore an emerging risk because it is:

- introducing new technologies;
- massively increasing the uptake of these technologies, so that the frequency of hazardous events will increase;
- increasing the exposure to the hazards;
- causing an increase of perceived risk due to ongoing changes in social or public perception of the problem.

Out of the possible hazards posed by CCS technologies, some have been ruled out of the scope of the current project. Potential harmful effects on the environment caused by the long-term storage of CO_2 (e.g. potential alteration of the underground structure, long term leakage form storage sites, etc.) do not present acute or short-term hazard for human targets and are therefore beyond the scope of the Saphedra project. On the other hand, the conventional hazards related to auxiliary materials used in the capture plants (ammine solutions, oxygen separation and storage, etc.) are not specific of the sole CCS technology and were excluded from the analysis. Hence, the scope was limited only to the scenarios involving large-scale release of CO_2 from process, transportation equipment and injection facilities (surface CCS installations). Massive releases from underground storage (e.g. well blowout) are also possible scenarios.

The emerging risk posed by CCS surface facilities has been included in the shortlist considered in current task since:

- It involves a material (carbon dioxide), which is able to trigger hazardous phenomena due to its intrinsic properties and handling conditions (high pressure, low temperatures upon release, asphyxiating dense gas).
- The description of the possible hazardous phenomena falls in the domain of consequence models (material release models after loss of containment, vapor cloud dispersion, etc.).

3.4 Emerging Risk 4 – Hydrogen

Introduction

Elementary hydrogen (H) is abundantly present in nature. Hydrogen may occur in its molecular form (H_2) or in compound molecules such as water (H_2O), ammonia (NH_3) and organic hydrocarbons. Because of its reactivity and its fundamental role in organic chemistry, it has been used in the process industry for more than a century. Typical applications of hydrogen are the cracking, modification and recombination of hydrocarbons (e.g. h, hydrocracking, hydrogenation and reforming) and the production of ammonia, methanol and hydrogen chloride. In aviation industry, hydrogen has been used for many years as a rocket fuel.

Hydrogen is expected to come to play a role in the transition towards a low-carbon industry that is induced by (fear of) climate change. To mitigate the effects of climate change, a reduction of emissions of greenhouse gasses (GHG) is required. A portfolio of alternative energy and technology options is needed to achieve the desired reduction of GHG emissions. Hydrogen technology is one of these alternatives and has been recognised as such in the EU strategy for the development of low-carbon technologies (EC, 2009) and in the EU strategy for the deployment of an alternative fuels infrastructure (Directive 2014/94/EU).

Hydrogen is one of the few fuels that does not produce greenhouse gasses in combustion. Water and energy (heat) are the only reaction products of the reaction of oxygen with hydrogen. However, as no natural reserves of hydrogen exist, hydrogen must be produced by physical or chemical processes. It is therefore not an energy source, but an (intermediate) energy carrier. The real carbon footprint of hydrogen technology depends on the way in which the hydrogen is produced and transported.

An advantage of hydrogen as an intermediate energy carrier is that the conversion of electrical energy into hydrogen ('power to gas') and the conversion of hydrogen into electrical energy ('gas to power') are both relatively easy. As such, it can play a role to integrate two energy systems – the electricity grid and the fuel distribution system – and increase the reliability of both. "Hydrogen can link different energy sectors and energy transmission and distribution networks and thus increase the operational flexibility of future low carbon systems" (IEA, 2015). Conversion of electricity into hydrogen is also an option to make more use of solar and wind energy in times of overproduction of electricity, and thereby increasing the efficiency of sustainable energy production. Lastly, hydrogen can play a role in reducing the dependence on fossil fuels and increasing energy security for nations with no or little national reserves of fossil fuels.

In the light of these advantages, several initiatives were undertaken to coordinate research and development for hydrogen technologies and to stimulate their use. These initiatives have resulted in abundant information on economic and technological perspectives of hydrogen economy including information on the state of art of current technology and white papers on knowledge gaps. At global level, the International Energy Information Hydrogen Implementing Agreement (www.ieahia.org) has produced a number of useful documents. Within Europe, the public private partnership Fuel Cell and Hydrogen Joint Undertaking (www.fch.europa.eu) provides an umbrella for many European research activities.

In the paragraphs below, hydrogen technology is described in more detail with distinction between hydrogen production, hydrogen distribution, hydrogen storage and hydrogen application/use. The following sources were used to determine the current state of art and future perspectives of various technologies:

- Multi-Annual Work Plan 2014-2020 of the **Fuel Cells and Hydrogen Joint Undertaking** (FCH-JU, 2014).
- The Energy Technology Perspectives 2012 of the **International Energy Agency** (IEA, 2012), the Technology Roadmap Hydrogen and Fuel Cells of the IEA (IEA, 2015), the Strategic Plan 2015-2020 of the IEA Hydrogen Implementing Agreement (IEAHIA, 2014) programme and the Final report of Task 28 of IEAHIA considering infrastructure (Weeda and Elgowainy, 2015).
- The website of the Fuel Cell Technologies Office of the US **Office of Energy Efficiency & Renewable Energy**: http://energy.gov/eere/fuelcells/fuel-cell-technologies-office.
- The website of the **H2Trust** project: http:/h2trust.eu, and the H2Trust dissemination handbook Hydrogen: application and safety considerations (Ruiz et al., 2015).

Hydrogen production

Hydrogen can be produced in various ways. The website of the Fuel Cell Technologies Office of the US Office of Energy Efficiency & Renewable Energy is a good starting point for further information and gives an overview of the main technological challenges today.

- Steam **reforming**. Currently, nearly half of the hydrogen is produced by steam reforming of natural gas (IEA, 2015). Steam reforming of methane requires two steps: (i) $CH_4 + ½\ O_2 \rightarrow 2H_2 + CO$ and (ii) $CO + H_2O \rightarrow H_2 + CO_2$. Other options for chemical production of hydrogen are steam reforming of methanol, ammonia reforming and steam reforming of diesel and coal. Steam reforming of diesel and coal requires gasification of the liquid/solid material prior to the reforming. In steam reforming, the greenhouse gas CO_2 is produced. If reductions of emissions of carbon dioxide (CO_2) are desired, steam reforming needs to be combined with carbon capture and storage (CCS). Alternatively, biomass can be used as a feedstock for reforming (e.g. biogas or biodiesel).
- **Electrolysis** can be used to split water into hydrogen and oxygen ($H_2O \rightarrow H_2 + ½O_2$) using electricity as input. The process is as 'clean' as the electricity that was used for electrolysis. Using sustainable electricity (e.g. solar, wind or hydro) provides a good opportunity to achieve reductions of greenhouse gas emissions. Compared to steam reforming, electrolysis is more expensive.
- **Photo-electric water splitting**. Sunlight can be used to split water into hydrogen and oxygen in an electrolyte. At first glance, the process is somewhat similar to electrolysis. The components required are quite different however and the technology is not as far developed.

- **Thermo-chemical water splitting**. This involves a process cycle to split water into hydrogen and oxygen at high temperature (500-2000°C). The required temperature can be acquired from sunlight or from waste heat in (nuclear) reactors.
- **Microbiological** hydrogen production. Microorganisms such as algae and bacteria can produce hydrogen from organic material. The technology seems to compete with the production of biogas (biomethane, bioethane) or bioliquid (biomethanol, bioethanol) by microorganisms and is not (yet) as advanced.

The above technologies each have specific advantages and disadvantages and it is expected that they will play different roles in the transition towards a low-carbon economy. Gas reforming is an existing technology that can be applied immediately (today) to start-up the hydrogen economy. In order to reduce carbon dioxide emissions, either renewable biofuels must be used as feedstock or emitted carbon dioxide must be captured and stored. Carbon capture and storage (CCS) is not regarded as a sustainable option for the long-term, but could play a role in the transition period, e.g. between 2020 and 2050. The use of biofuels for hydrogen production competes with direct use of biofuels, and might therefore only play a limited role in the future energy system. Electrolysis is beyond demonstration phase and ready for market, but competes with direct use of electricity. It is however a very good buffer option to produce hydrogen as an intermediate energy carrier in times of overproduction of electricity. Electrolysis benefits from the wide availability of electricity. All other production alternatives are still in the experimental and/or demonstration stages.

Figure 3 shows how hydrogen production could evolve according to the International Energy Agency (IEAHIA, 2006). It is anticipated that until 2050 hydrogen will mainly be produced from fossil fuels, in particular natural gas (dark blue and light blue) and coal (purple). CCS (light blue and purple) will effectively come into play from 2030 onwards, according to IEAHIA.

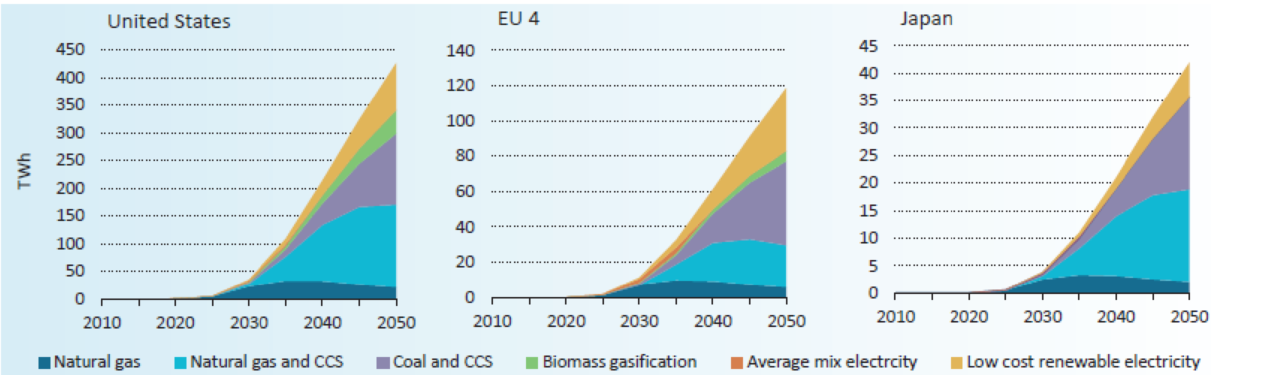


Figure 3 - Main hydrogen pathways. Reproduced from (IEAHIA, 2006)

Another question is whether future hydrogen production will be centralised (at large scale production sites) or distributed (at local small scale production facilities). In order to make optimal use of resources, the future energy system should diversify and provide tailored solutions for specific local conditions. The same applies to hydrogen. Large central production could be beneficial in some cases, and local production more advantageous for other cases. It is therefore expected that the future hydrogen supply system will be a combination of central and local production.

Hydrogen distribution

For some applications, hydrogen can produced on-site, e.g. using electrolysis or natural gas reforming. For other applications, hydrogen will be produced at a distance and needs to be distributed/transported to the end-user. The following options exist for transporting hydrogen.

- Transportation of compressed gaseous hydrogen (CGH2) through dedicated hydrogen pipelines. Some pipeline networks are already in place to transport compressed gaseous hydrogen between industries through dedicated pipelines. Further extension of these networks requires considerable investments (which are not likely to be made during the start-up phase of hydrogen economy). Transportation of liquid hydrogen through pipelines is not feasible for long distance, due to the large boil-off of hydrogen.
- Transportation of compressed gaseous hydrogen through mixed hydrogen and natural gas pipelines, using the existing natural gas pipeline infrastructure. Up to 15 Vol% of hydrogen can be blended into natural gas pipelines without compromising system safety, system reliability and public safety (Melaina et al., 2013). If the hydrogen is produced in a sustainable way, the carbon dioxide emissions related to gas consumption reduce. Separating pure hydrogen from a mixed natural gas and hydrogen pipeline for the use of pure hydrogen is possible, but requires a separation step that reduces the energy efficiency of this option.
- Transportation of compressed gaseous hydrogen by road, rail or ship. Compressed gaseous hydrogen can be transported in high pressure gas cylinders (tubes). Road transportation using tube trailers is existing technology. The focus lies currently in increasing the pressure from 180 bar to 500 bar (Weeda and Elgowainy, 2015). Transportation of hydrogen tubes by rail or ship is possible, but demand appears to be limited. The storage capacity of compressed gaseous hydrogen is limited when compared to liquid hydrogen. Therefore, liquid hydrogen transportation will replace gaseous hydrogen transportation once hydrogen economy starts to mature.
- Transportation of liquid hydrogen (LH2) by road, rail or ship. Transporting liquid hydrogen has the advantage that larger quantities can be transported. Boil-off can be considerable and could/should be used to fuel the truck. Liquid hydrogen can also be transported by ship. Rail transportation is feasible but the demand appears to be limited.

Hydrogen transport by pipeline is most efficient, but requires substantial investments. Existing networks can be used, but new pipelines will only be constructed after hydrogen economy has further matured. Tube trailers are fit to distribute hydrogen to local consumers if the daily demand is not too large. Liquid hydrogen trucks are needed for larger demands. For remote areas, where delivery of liquid hydrogen from a central location is expensive, local production of hydrogen is likely to be the most economic option.

Table 2 - Overview of hydrogen distribution options. Reproduced from (Weeda and Elgowainy, 2015)

Type of transport	Capacities	Transport distance	Energy loss	Fixed costs	Variable costs	Deployment phase
CGH2 tube trailers	Low	Low	Low	Low	High	Near term
LH2 truck trailers	Medium	High	High	Medium	Medium	Mid to long term
CGH2 pipelines	High	High	Low	High	Low	Mid to long term

Hydrogen storage

Most hydrogen applications require some form of hydrogen storage, for example buffer storage. The following options exist for storing hydrogen.

- Storage of compressed gaseous hydrogen (CGH2 or simply GH2). CGH2 can be stored in steel tanks (currently up to 400 bar) or composite tanks (up to 1000 bar) (Weeda and Elgowainy, 2015). Composite tanks are more expensive but have larger capacities due to the larger pressure that can be achieved. The density of compressed hydrogen can also be increased by lowering the temperature. At temperature below 120 K, the storage is usually referred to as 'crycompressed' gaseous hydrogen (CCGH2).
- Storage of liquid hydrogen (LH2). LH2 can be stored in steel tanks at temperatures below 20K. Storage pressure is usually below 5 bar. Current capacities are in the order of 800 to 4000 kg (Weeda and Elgowainy, 2015). For liquid hydrogen storage, boil-off rates can be high even if the tank is double-walled and well-isolated.
- Storage in porous materials. Hydrogen can be stored in porous materials and nano-structures in higher volumetric densities than in open containers. The downside of these systems is that they have low charging/uncharging capacities and that charging/uncharging goes hand in hand with energy losses.
- Hydrogen bonding. Hydrogen can be bonded to metals and other elements to form hydrides. These hydrides can act as a hydrogen carrier. Hydrogen can be 'stored' by chemical hydrogenation and released by dehydrogenation. As for porous materials, volumetric density for storage is increased. Long charging/uncharging times and energy losses are disadvantages. As hydrogen is substituted by less hazardous hydrides, and operating conditions are more moderate than for pure hydrogen, storage in hydrides is inherently safer than storage of pure hydrogen (Landucci et al., 2008).
- Underground storage. Larger storage capacities may be required once the hydrogen consumption has further matured. Options for underground storage in salt caverns, depleted oil and gas fields and aquifers are being investigated.

For the storage of CGH2, CCGH2 and LH2, existing technology is in place. The focus of R&D lies in increasing the achievable capacities and reducing the costs. The other storage options are still in the experimental and small-scale demonstration stage.

Hydrogen use/application

Traditionally, hydrogen is used as a chemical feedstock for process industries and as a fuel for aviation (rockets). New application modes for hydrogen are listed below.

- For industry (e.g. steel and cement industries), hydrogen can be a green energy source and/or a feed stock that may (partly) replace the current use of fossil fuels.
- Hydrogen as an intermediate energy carrier. Hydrogen can be generated from electricity and converted into electricity relatively easily. It is therefore a good candidate for temporary storage of energy (buffer capacity) in times of overproduction of electricity.
- Combined heat and power (CHP) generation from hydrogen is efficient because heat losses in electricity production that are normally wasted, are now effectively used for heating. It is anticipated that CHP can (economically) compete with electrical heating and (therefore) that is will partly replace electrical heating. Micro-CHP units can provide electricity and heating to individual houses, mini-CHP are intended for apartment buildings. CHP-units for hospitals and other care institutions, large education centres and office buildings are referred to as 'CHP-commercial'.
- For the automotive industry, hydrogen can replace fossil fuels. Two different technologies exist: fuel cells (FC) and internal combustion (IC) engines. In both cases hydrogen reacts with oxygen to produce water. The difference between the two is that internal combustion creates thermomechanical energy, while fuel cells produce electric power. In addition to the reduction of emissions of greenhouse gasses, the use of fuel cell vehicles is also beneficial for air quality (clean exhaust gasses) and noise (very limited noise production). Therefore, hydrogen fuel cell electric vehicles (HFCVs) and buses (HFCBs) are attractive options for urban environments. The technologies that are developed for vehicles and buses can also be applied to ships.
- The use of hydrogen by the (auto)motive industry, requires a network of Hydrogen Refuelling stations (HRSs) that is sufficiently dense.
- Forklift trucks using fuel cells share advantages such as clean exhaust gases and low noise production with electrical forklifts, and (potentially) have a larger action range than electric forklifts.

Level of maturity

Since some ten years, it is predicted that the development of a self-sustained hydrogen economy is near (e.g. ESFRI, 2006) and that many applications are at a point where commercial application is readily foreseeable. Such claims have been made for all parts of the hydrogen economy chain (production, distribution, storage and end use).

Current estimations for the moment when technologies will become widespread vary between different information sources. Most stakeholders state that implementation of hydrogen application is starting now, and that the transformation into a mature hydrogen economy will take place between 2015 and 2030/2050. As an illustration, different stages for hydrogen production identified by the International Energy Agency (IEA) are shown in Table 3, and stages for commercialisation identified by the Japanese New Energy and Industrial Technology Development

Organization (NEDO) are depicted in Table 4. A more specific forecast made in the context of the Fuel Cell and Hydrogen – Joint Undertaking is reproduced in Table 5.

Table 3 - Stages in hydrogen production according to the IEA. Source: (IEA, 2006).

Time period	Stage	Activities
2003-2015	Building market	Decentralised production by electrolysis, small scale steam methane reforming
2015-2030^{+}	Building infrastructure	Increased production, in particular by carbon based reforming
2030^{+}-	Hydrogen economy	Use of renewable energy and waste heat from nuclear power plants for the production of hydrogen by electrolysis

Table 4 - Stages in the transition towards a hydrogen economy according to the Japanese NEDO. Source (FCCJ, 2010).

Time period	Stage	Activities
2000-2010	Technology demonstration	Solving technical issues and identifying needs for (modifying) legislation, codes and standards
2011-2015	Market demonstration	Demonstration that hydrogen has added benefits for society
2016-2025	Early commercialisation	Lowering costs and expanding production and sales. At the end of the term, approximately 2 million hydrogen HFCVs running 1000 hydrogen refuelling stations (HRSs) operating.
2026-	Full commercialisation	Profitable business and self-sustaining market

Table 5 - Expected start of commercialisation for different types of technology. Source of information: (FCH-JU-2013)

Application	Technology	Expected start of commercialisation
Transport	Cars	2015
	Buses	2016
	Material handling vehicles (e.g. forklifts)	2014
	Refuelling stations	2015
Energy	Domestic CHP	2017
	Industrial CHP	2017
	Backup power	2013
Production	Electrolyser	2015
	From biofuels	2016
	From conventional fuels	2016
Storage	Mass storage	2018

Jedicke and Inge-Dahl (Jedicke and Inge-Dahl, 2013) have noted that progress until now has been slower than anticipated and that a substantial number of technical and scientific challenges still need to be overcome. Market is only partially ready for hydrogen and positive perception of hydrogen economy among society has not yet been sufficiently demonstrated. Given these observations from Jedicke and Inge-Dahl, and the knowledge gaps identified in the H2FC infrastructure project (H2FC, 2015), the transition towards a self-sustained hydrogen economy is more likely to occur somewhere between 2030 and 2050.

For combined heating and power (CHP) production, mini-CHP is already available for the market. In Japan, more than 120,000 subsidised small CHP stations for domestic purposes (‘ENE-farms’) have been sold between 2009 and 2015 (Fuel Cell Works, 2015). The strategic aim of the Japanese government is to have more than 1.4 million ENE-farms sold by 2020. A self-sustained market should establish somewhere between 2020 and 2030. Mini-CHP and CHP-commercial are in the demonstration phase.

While recently only a few hundred hydrogen fuel cell vehicles were operating world-wide, production volumes rapidly increase. Currently Hyundai ix35 FCEV and Toyota Mirai are produced in numbers around 1000 per year and increasing towards 10,000 per year. These cars have a driving range that is comparable with conventional fuel cars. Honda, Nissan, Daimler and Ford are expected to introduce mass production of HFCVs within years (Weeda et al., 2014). A volume of 100,000 HFCVs worldwide should be reached within years (see Table 6). According to Ball and Wietschel (Ball and Wietschel, 2009), hydrogen vehicles could eventually reach shares of 30-70% of the global vehicle stock by 2050, under the most favourable circumstances.

Table 6 - Existing and planned number of hydrogen fuel cell electric vehicles on the road. Reproduced from (IEA, 2015).

Country or region	Running HFCVs	Planned HFCVs on the road - 2015	Planned HFCVs on the road – 2020
Europe	192	5000	~350,000
Japan	102	1000	100,000
Korea	100	5000	50,000
United States	146	~300	~20,000

As the number of HFCVs is increasing, development of dense networks of hydrogen refuelling stations is also starting to come off the ground. Within Europe, as a result of the Directive 2014/94/EU on the deployment of alternative fuels infrastructure, several nations have developed National Implementation Plans (NIPs) for the construction of HRS networks. These initiatives are further stimulated by the Hydrogen Infrastructure for Transport (HIT) project (www.hit-tent.eu) and the Hydrogen Mobility Europe (H2ME) project (www.h2me.eu). One of the initiatives is to roll out a 1000 km corridor of refuelling stations between Rotterdam (the Netherlands) and Gothenburg (Sweden). Table 7 provides an overview of existing and announced hydrogen refuelling stations, based on various national and international stimulation programmes, reproduced from (IEA, 2015).

Table 7 - Existing and planned number of hydrogen refuelling stations. Reproduced from (IEA, 2015).

Country or region	No of existing HRSs	Planned HRSs – 2015	Planned HRSs – 2020
Europe	36	~80	~430
Japan	21	100	>100
Korea	13	43	200
United States	9	>50	>100

Regarding distribution, mixed natural gas and hydrogen pipelines and dedicated hydrogen pipelines were very common in the 19th and early 20th centuries, when "town gas" was produced from coal and petroleum products11. Dedicated hydrogen pipelines have been in use for various decades and currently around 16,000 km is used worldwide (Ball and Wietschel, 2009). Hydrogen trucks have been in use in small numbers for several decades.

In Table 8, the various components of hydrogen economy are listed, and a summary of their 'level of maturity' is provided. Appendix F of (Weeda and Elgowainy, 2015) is a good reference for specific details about the current technological status of various components.

Table 8 - Level of maturity of various hydrogen technologies and applications

Application	Type of technology	Level of maturity
Production	Steam reforming	Existing technology.
	Electrolysis	Technology available and used for small scale applications. Focus on increasing performance, capacity and lifetime and reducing costs.
	Photo-electric water splitting	
	Development phase.	
	Thermo-chemical water splitting	Development phase.
	Microbiological hydrogen production	Development phase.
Distribution	Dedicated CGH2 pipelines	Existing technology.
	Mixed CGH2 and CNG pipelines	Existing technology, focus on increasing the H2 content in the gas mixture.
	CGH2 tube trailers	Technology available and used in demonstration projects. Focus on increasing performance, capacity and lifetime and reducing costs.
	LH2 tankers	Technology available and used in demonstration projects. Focus on increasing performance, capacity and lifetime and reducing costs.

Storage	Storage of CGH2, cCGH2 and LH2	Technology available and used in demonstration projects. Focus on increasing performance, capacity and lifetime and reducing costs.
	Storage in porous materials	Development phase.
	Storage in metal and chemical hydrides	Development phase.
	Underground storage	Future development.
Use	Combined heat and power (CHP)	Micro-CHP available for the market. mini-CHP and CHP-commercial in demonstration phase.
	Fuel cells for automotive industry (vehicles, busses, scooters, forklifts)	Technology available. Emerging introduction into the market. Focus on increasing performance and lifetime and reducing costs.
	Internal combustion engines for automotive industry	?
	Internal combustion engines for industrial application	?

Hydrogen properties

Hydrogen (H_2) is the smallest and lightest molecule in the universe and has some physical and chemical properties that deviate from other (heavier) common molecules. The most relevant deviating physical properties are:

- the low melting point and boiling point;
- the small molecular weight and corresponding small gas and liquid densities;
- the large gas diffusion coefficient;
- the large viscosity;
- the low Joule-Thomson inversion temperature (-80°C).

In addition, some of the flammable properties of hydrogen also deviate from other flammable gases:

- hydrogen has a low ignition energy
- hydrogen has a wide ignition range and high stoichiometric concentration
- hydrogen has a high laminar burning velocity
- hydrogen has a high combustion energy per kg and a low combustion energy per mole;
- hydrogen has a low flame emissivity.

Table 9 - Physical and chemical properties of hydrogen (H_2), methane (CH_4) and propane (C_3H_8)

Property	**Hydrogen**	**Methane**	**Propane**
Molecular weight (kg/kmol) [a]	2.02	16.04	44.10
Melting point (°C) [a]	-259 (14 K)	-182 (91K)	-188 (85 K)
Boiling point at atmospheric pressure (°C) [a]	-253 (20 K)	-161 (112 K)	-42 (231 K)
Critical temperature (°C) [a]	-240	-83	97
Critical pressure (N/m^2) [a]	13	46	42
Gas density at T=15°C and p = 1 atm. (kg/m^3) [a]	0.085	0.680	1.899

Liquid density at normal boiling point (kg/m^3) [a]	71	422	581
Latent heat of vaporisation (J/kg) [a]	449	511	426
Diffusion coefficient in air at T=20°C (m^2/s) [b]	6.1×10^{-5}	1.6×10^{-5}	1.2×10^{-5}
Gas viscosity T=20°C and p=1 atm (g/cm s) [b]	8.3×10^{-7}	6.5×10^{-6}	8.2×10^{-6}
Ignition energy in air (J) [c]	1.7×10^{-5}	2.8×10^{-4}	2.5×10^{-4}
Stochiometric concentration in air (Vol%) [d]	29.5%	9.5%	4.0%
Flammability range in air (Vol%) [c]	4.0 – 75	5.3 - 15.0	2.2 - 9.6
Auto ignition temperature (°C) [c]	510	537	470
Laminar burning velocity (m/s) [d]	3.1	0.4	0.45
Fraction of energy radiated from flame [b,e]	0.05 – 0.15	0.1 – 0.33	0.1 – 0.5
Lower heating value (J/kg) [d]	1.2×10^8	5.0×10^7	4.6×10^7
Lower heating value (J/kmole)	2.4×10^8	8.0×10^8	2.0×10^9

[a] http://encyclopedia.airliquide.com
[b] HSL Hazards of liquid hydrogen (Pritchard and Rattigan, 2010)
[c] HyFacts training material - hydrogen fundamental properties (HyFacts, 2013b)
[d] A comparison of hydrogen and propane fuels (US DoE, 2009)
[e] Safety issues of the liquefaction, storage and transportation of liquid hydrogen (Lowesmith et al., 2013).

Liquid hydrogen has a volumetric energy density that is about 40% of the volumetric energy density of LPG, and about 30% of the volumetric energy density of gasoline (Thomas, 2000).

Labelling and classification

For compressed hydrogen, some official classifications, labels and risk and hazard phrases, are listed in Table 10.

Table 10 - Classification and labelling of compressed hydrogen

Type	Value
CLP Classification (according to EC 1272/2008)	Flammable, category 1 Compressed gases
CLP Hazard phrases (according to EC 1272/2008)	H220 – Extremely flammable gas H280 – Contains gas under pressure; may explode if heated
UN number	1049 (hydrogen, compressed)
ADR classification	Class 2.1f (compressed flammable gas)
R- phrases (no longer in use) (according to EC 67/548)	R12 – Extremely flammable

Identified hazards for hydrogen

Many documents are publicly available that list hazardous properties of hydrogen. The HyFacts training material (HyFacts, 2013a) and the HSL report on hazards of liquid hydrogen (Pritchard and

Rattigan, 2010) provide good overviews. The following hazardous properties of hydrogen have been referred to in literature:

- Hydrogen gas is colourless and odourless and difficult to detect.
- Hydrogen gas has a low viscosity, leading to larger emissions from gaskets, welds and fittings, when compared to other materials.
- Hydrogen gas can diffuse in materials relatively easily. Steel and other materials can become brittle and vulnerable to material failure. Hydrogen can diffuse through porous materials.
- Gaseous hydrogen is stored, transported and used at pressures up to 1000 bar, which is uncommonly high for process and energy industries, and poses safety issues on the materials used.
- Liquid hydrogen is stored, transported and used at low temperature (20 K), which is uncommonly low for process and energy industries, and poses safety issues on the materials used.
- Hydrogen gas at atmospheric pressure and temperature is buoyant and can accumulate under ceilings. This induces added explosion risk.
- At low temperatures, hydrogen can be heavier than ambient air and may spread as a dense gas.
- At very low temperatures, impurities in the hydrogen such as nitrogen and oxygen, or nitrogen purge gas, can solidify in installations and plug/block the flow. Solidification of oxygen can create oxygen-enriched mixtures when re-evaporated. Solidification of impurities in closed volumes can lead to under-pressure and may cause air ingress (Pritchard and Rattigan, 2010).
- Liquid hydrogen expands much quicker with increasing temperature than common liquids such as water.
- Liquid hydrogen has relatively high volumetric evaporation (boil-off) for heat exchange with the environment.
- Spills of liquid hydrogen can lead to condensation of oxygen. Re-evaporation of oxygen can create oxygen-enriched flammable atmospheres (Pritchard and Rattigan, 2010).
- Hydrogen has a very low ignition energy and a higher likelihood of ignition than other fuels. Releases of hydrogen from high pressure systems can ignite spontaneously (Dryer et al., 2007), (Yamada et al., 2011).
- Hydrogen combustion produces neither CO_2 nor soot. Hydrogen flames are therefore more transparent than common flames and difficult to observe and detect.
- Hydrogen has a high laminar burning velocity and a relatively high propensity to detonate if ignited (Pritchard et al., 2009), (Moonis et al., 2010). As for other flammable substances, the propensity to explode is highest in enclosures and in oxygen-rich environments.
- Hydrogen can react spontaneously and violently at room temperature with chlorine and fluorine (EC-IPSC, 2012).

Other properties of hydrogen are safer than those of other materials:

- Hydrogen is neither toxic nor corrosive.

- Hydrogen has a high diffusion coefficient and dilutes easily.
- Hydrogen flames have low radiation emissivity.

If these differences are adequately taken into account into design, construction and operation, hydrogen can be used as safely as other flammable gases (e.g. natural gas and LPG).

Physical effects of hydrogen releases

Releases of hydrogen can result in the following events:

- Thermal effects: cold burns;
- Heat radiation from fire: jet fire, flash fire and fireball;
- Overpressure: release from pressurised equipment, BLEVE (Lowesmith et al., 2013), confined vapour explosion, DDT in obstructed environment, rapid phase transition (Pritchard and Rattigan, 2010).

Emerging risk issues

According to EU-OSHA (EU-OSHA 2005), an emerging risk is a risk that is new and/or increasing. By new, it means that:

1. The risk was previously unknown and is caused by new processes, new technologies, new types of workplaces, or social or organisational change; or,
2. A long standing issue is newly considered to be a risk due to changes in social or public perceptions; or,
3. New scientific knowledge allows a long standing issue to be identified as a risk.

The risk is increasing if:

4. The number of hazards leading to the risk is growing; or,
5. The likelihood of exposure to the hazard leading to the risk is increasing, (exposure level and/or the number of people exposed); or,
6. The effect of the hazard on the worker's health is getting worse (seriousness of health effects and/or the number of people affected).

For the use of hydrogen as a new energy source, which use is primarily promoted in order to reduce the emission of greenhouse gases, the following conditions apply:

1. Several new technologies have recently been developed. Examples of new technologies are Combined Heat and Power (CHP) units for hydrogen, hydrogen Fuel cell electric vehicles (FCEVs) and buses (FCEBs) and high-pressure storage (700 – 1000 bar) in composite materials. The risk can therefore be considered as new.
2. Public perception of hydrogen applications depends on many factors, including the level of knowledge about hydrogen, trust in science and technology and environmental concerns. Yetano Roche et al. (Yetano Roche, 2010) have analysed various studies on public perception of hydrogen. Most studies showed that the level of knowledge among the general public was low. Attitudes towards hydrogen technology varied between generally positive and mixed positive and negative. Achterberg (Achterberg, 2014)

observed positive support for hydrogen applications among the Dutch population in 2008, and reduced support in 2013, which may have been caused by a more general decline in faith in science and technology.

3. Hydrogen has been studied extensively in the 20th century, and hazards of hydrogen such as fire and explosion risks, have been known since long time. Other potentially dangerous properties, such as its permeability (causing embrittlement of materials and transport through materials), its low viscosity (e.g. making releases from gaskets more hazardous) and its buoyancy (propensity to accumulate under ceilings) have also been identified long ago. Pritchard and Rattigan (Pritchard and Rattigan, 2010) identified that releases of hydrogen on water may induce Rapid Phase Transition (RPT). This possibility is not (yet) commonly recognised in literature on hydrogen safety.
4. The 'number of hazards leading to a risk', involves the intrinsic and external causal factors for hazardous events. New intrinsic causal factors could be the increased pressure and capacity of components, though there is no clear indication that high pressure high capacity systems indeed have a larger probability of failure than low pressure low capacity systems. Regarding external factors, a relevant development is that current hydrogen refuelling stations are usually hydrogen only, while combined fuel stations are more likely for the future (Nakayama et al., 2015). As such there might be an increased risk of domino-events in the future (Sakamoto et al., 2016). Another possible cause for increased risk is the shifting context of application. Whereas safety has received considerable attention in the demonstration projects so far, applying hydrogen more broadly in society might lead to a lesser degree of risk awareness, and increased risk of not using the technology in a safe manner.
5. The number of hydrogen applications will increase substantially and will also be integrated more and more into the built-up environment, including urban environments. Hydrogen refuelling stations are likely to be integrated in existing refuelling stations, whether remote or in populated areas (Markert et al., 2015). In addition, as the volumetric energy density of hydrogen is lower than for carbon-based fuels (even in liquefied form), the number of transport movements will increase substantially. Regarding exposure, the risk is certainly increasing.
6. Apart from increased likelihood of exposure, the health effects themselves are not changing.

Considering the above, the use of hydrogen as a new energy source can be regarded as an emerging risk, because the technology is partly new, the context of application is changing and the exposure is increasing.

Relevance for the Saphedra project

The main risk attributed to hydrogen applications involves the possibility of accidental releases of hydrogen. Apart from the immediate release of energy, there is also a risk of associated fire and/or explosion. These risks must be evaluated with appropriate physical consequence models, thus making the case relevant for Saph€dra.

Case selection for further studies

Hydrogen has physical properties that deviate from more common materials used in process and energy industries, and therefore potentially all hydrogen applications can be used as a case to study the validity of consequence models used. Hydrogen refuelling stations (HRSs) have been selected as the case for further study because the risk assessment for HRSs includes a large variety of scenarios (e.g. releases from pipes, transport units and storage systems). In addition, future HRSs will be public areas located in urban environments, and thus impose a risk to the general public. This makes the risk assessment for HRSs more relevant than risk assessment for industrial and private areas.

4. Scenario identification method and selection criteria

The scenarios were identified for each emerging risk using both conventional techniques, innovative tools and expert consultation. In particular, the following techniques were considered, using the most appropriate for each case studied:

- Past accident survey
- Hazard Identification (HAZ-ID)
- Hazard and Operability Analysis (HazOp)
- Methodology for the Identification of Major Accident Hazards (MIMAH)
- Dynamic Procedure of Atypical Scenarios Identification methodology (DyPASI methodology)

Only the scenarios directly related to the emerging risk issue were considered. Accident scenarios typical of generic industrial activities or related to hazardous material present in utilities and auxiliary components of the main system are beyond the scope of current analysis.

For the data source, the main focus was on scientific literature and available accident data.

Starting from the generic scenario list, a limited number of plausible scenarios were selected to be screened for gap analysis.

The results are discussed in detail separately for each emerging risk identified, in sections from 7 to 10. Though several possible accident scenarios were identified, consequence assessment involves modeling a limited number of consequence phenomena common to all the scenarios. A short summary of the consequence phenomena identified for each emerging risk is provided below.

In the case of the emerging risk related to LNG Regasification terminals, the accident scenarios selected in section 7.1 evidenced the need to model the following consequence phenomena:

- Liquid release through rupture/breach
- Liquid pool spreading and evaporation
- Jet dispersion
- Vapor cloud dispersion
- Pool fire
- Vapor Cloud Explosion
- Flash fire
- Rapid phase Transition
- Burst/BLEVE of the unit
- Fireball from ignited aerosol release

In the case of the emerging risk related to Biogas production, the accident scenarios selected in section 8.1 evidenced the need to model the following consequence phenomena:

- Gas release (rupture/breach or quasi-instantaneous)
- Vapor cloud dispersion
- Vapor cloud explosion
- Flash fire
- Confined explosion of a digester

In the case of the emerging risk related to Carbon capture transportation and storage, the accident scenarios selected in section 9.1 evidenced the need to model the following consequence phenomena:

- High pressure CO_2 release from rupture/breach
- Vapor/aerosol cloud dispersion

In the case of the emerging risk related to hydrogen refueling stations, the accident scenarios selected in section 10.1 evidenced the need to model the following consequence phenomena:

- Internal tank or pipe explosion
- Explosion in an open pipe or vent
- Release of gaseous hydrogen from an installation under high-pressure, due to rupture, breach or leak
- Release of liquid hydrogen at low pressure due to rupture, breach or leak
- Jet dispersion
- Vapor cloud dispersion
- Liquid pool spreading and evaporation
- Jet fire
- Flash fire and Vapor Cloud Explosion
- BLEVE (burst) and fireball following rupture of a cryogenic vessel or tanker
- Fireball following rupture of a pressurised gas vessel or tanker
- Pool fire

Available model identification and gap analysis will be discussed in the next section.

5. Procedure used for gap analysis and selection of test cases

The scenarios identified in section 4 (Task 2.2) were screened to identify gaps between emerging risk scenarios and existing models.

Gaps between scenarios and available models are described in a qualitative way. For example, typical gaps can be:

- The model was developed/validated for a substance different than the one of interest for the accident scenario;
- The model was developed/validated for a different release path or surrounding environment.
- The model was developed/validated for different conditions (temperature/pressure/flow rate range) than the one of interest for the accident scenario;

In the summary of the results for each emerging risk, the color code defined in Table 11 has been adopted in order to improve visual communication of the results.

Table 11 - Colour code used for presentation of gap analysis results.

Rank	Model Availability Rank	Model Validation Rank
Green	Sufficiently detailed models are available to simulate the phenomena involved in the scenario	Model has been validated for the scenario and substance of interest
Orange	Only low detail models / simplified models are available to simulate the phenomena involved in the scenario	Limited validation of the of models is available for the analyzed scenario and substance or validation is available only for reasonably comparable substance
Red	No model / incomplete models are available to simulate the phenomena involved in the scenario	No validation of models for the analyzed scenario

The gap analysis will also identify the needs for future model development.

A set of test cases for the comparison of the available models will be identified for further activities in Task 5. Selection will be based on the entity of gaps identified for the scenario and on the availability of applicable models for the comparison. The test cases will be further screened in order to select a sub-set whose assessment will be compatible with resources available to the project.

The gap analysis, and more in general this report, will be later reviewed by experts for each emerging risk identified within the Saphedra Project, in order to validate the content and provide integrations, if needed.

6. Shortlist of selected test cases

The following tables summarize the results of the gap analysis carried out in Section 7 to 10.

The results of the gap analysis evidenced the lack of a complete portfolio of validated consequence models for all the analyzed emerging risks.

Table 12 - Results of the scenario gap analysis for LNG terminals.

Scenario	Model Availability	Model Validation
Liquid release through rupture/breach *Into air:*	**GREEN** Alternative models available: • Quasi-one-phase models • Homogeneous equilibrium models (HEM) • Non-homogeneous models • 'Frozen' models	**ORANGE** Validated for different substances Validated in different conditions (T, P)
Into water:	**RED** Only theoretical studies available	**RED** No conclusive validation available
Jet dispersion	**GREEN** Models available for: • Flash or the breakage of the liquid phase • Droplet size, evaporation and the rain-out • Concentration and size of a two-phase jet	**ORANGE** Few validation tests available, incomplete analysis of all the conditions
Liquid pool spreading and evaporation *Pool on land/still water:*	**GREEN** Several models for spreading and evaporation	**ORANGE/GREEN** Some validation experiments carried out and validated some models (more confirmation tests are needed)

Pool on non-still water:	**RED** No model available to account the effect of waves, wind, etc.	**RED** No validation available
Vapor cloud dispersion	**GREEN** Alternative models available: • Distributed parameter models (CFD models) • Shallow Layer Models • Lumped parameter models (Integral Models) • Point source models (Gaussian)	**ORANGE/GREEN** Good predictions in certain ranges of parameters (e.g averaging time, weather conditions). More uncertainty beyond the range (further validation needed: e.g. large scale tests with obstacles)
Pool fire	**GREEN** Alternative models available: • Semi-empirical models • Field models	**ORANGE/GREEN** Some validation tests available, more tests/data needed for complete validation Field modes require more work validation (complexity in describing phenomena involved)
Flash fire	**ORANGE** Alternative models available: • Dispersion based models (low detail) • Diffusive flame models (low detail/limited data for applicability) • CFD models (high complexity/high need of reliable input data)	**ORANGE** Limited validation (few cases). Further tests/validation trials needed
Vapor Cloud Explosion	**GREEN** Alternative models available: • Empirical models • Lumped parameter models • Distributed parameter models	**RED** No VCE observed in a large scale test.
Rapid phase Transition	**RED** Few theoretical approaches; incomplete modeling of phenomena involved (e.g. ice formation, interaction with waves)	**RED** Few occurrences in field tests. No validation trial available.

Above water release: *Under water release:*	**RED** No model (theoretical speculations only)	**RED** No test
Burst/BLEVE	**ORANGE** Burst and BLEVE models developed for other materials (simplified assumptions present in original models)	**ORANGE** No test for LNG (Validation of models based on other substances/conditions)
Fireball	**ORANGE** Fireball models developed for other materials (simplified assumptions present in original models)	**ORANGE** No test for LNG (Validation of models based on other substances/conditions)

Table 13 - Results of the scenario gap analysis for Biogas production.

Scenario	**Model Availability**	**Model Validation**
Gas release through rupture/breach or quasi-instantaneous *From pressurized equipment:*	**GREEN** Models available for: • Continuous release of a compressible gas through a hole • Continuous release of a compressible gas through a pipe • Instantaneous release/expansion of a compressed gas	**GREEN/ORANGE** Validated for different substances (no relevant difference is expected for biogas mixtures)
From quasi-atmospheric equipment:	**RED** No models available. CFD may be applicable.	**RED** No validation
Vapor cloud dispersion	**ORANGE** Models available for pure gases: • Free jet models • Plume rise/rounding models	**ORANGE** Models validated for pure gases on many substances

	• Passive dispersion models (positively buoyant and neutral gas) • Passive dispersion models (negatively buoyant gas) • Short distance / complex terrain dispersion models (CFD) Models non applicable to gas mixtures if component separation occurs (except CFD)	No validation available for dispersion of gas mixtures
Flash fire	**ORANGE** Alternative models (non-specific for biogas) available: • Dispersion based models (low detail) • Diffusive flame models (low detail/limited data for applicability) • CFD models (high complexity)	**ORANGE** Limited validation. Validation available only for other materials.
Vapor Cloud Explosion	**ORANGE/GREEN** Alternative models (non-specific for biogas) available: • Empirical models • Lumped parameter models • Distributed parameter models	**ORANGE** Limited validation. Validation available only for other materials.
Confined explosion in digester	**ORANGE/GREEN** Models for venting confined explosion may be applicable CFD may be applied to model near-field effects	**ORANGE** No validation for biogas digesters is available.

Table 14 - Results of the scenario gap analysis for Carbon Capture, Transposition and Storage.

Scenario	Model Availability	Model Validation
High pressure (supercritical) CO_2 release	**ORANGE** Liquid outflow models are applicable	**ORANGE**

from rupture/breach _Surface equipment failure:_	No specific model is available (e.g. role of dry ice formation)	Models validated for other materials/release conditions
Well blow-out:	**ORANGE** Models for well blowout in the oil&gas sector (e.g. OLGA)	**ORANGE** No validation for CO2/water mixtures
Vapor cloud dispersion	**RED/ORANGE** Models for pure gases are applicable if thermodynamics of dry ice formation is accounted No model available for dry ice rain-out and deposit sublimation.	**RED/ORANGE** Few field tests (still ongoing) No complete validation trial available.

Table 15 - Results of the scenario gap analysis for Hydrogen.

Phenomenon	Model Availability	Model Validation
Gas releases: discharge and dispersion – instantaneous release	**RED** No models available for hydrogen. Generic models not accurate.	**RED** No validation available.
Gas releases: discharge and dispersion – continuous release	**GREEN** Models available.	**GREEN/ORANGE** Validation available for free jets. Limited data available for attached jets and impinging jets.
Pressurised gas tanks: vessel burst	**ORANGE** No models available for hydrogen. Validity of generic models	**RED** Two test carried out. Data quality might be limited.

	needs to be demonstrated.	
Pressurised gas tanks: fireball	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**RED** Two test carried out. Data quality might be limited.
Vented pipe explosion	**GREEN** Phenomenon assumed to be well-known and well-understood.	GREEN Models assumed to be sufficiently validated for hydrogen.
Liquid releases: discharge, pool vaporisation and dispersion	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**ORANGE** Validation data available but too limited given the complexity of the topic.
Instantaneous superheated liquid releases: BLEVE and fireball	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**RED** No validation available.
Ignited gas releases from orifices (gaseous hydrogen jet fires)	**GREEN** Both generic and specific models exist	**GREEN/ORANGE** Many experiments carried out. More validation desired for the effects of wind, surfaces and obstacles.
Ignited liquid releases from orifices	**ORANGE** No specific models were found and just few generic models for liquid jet fires.	**RED** The two sets of experiments do not provide enough detail for validating models.

Pool fire	**RED** No models available for hydrogen. Generic models not accurate.	**RED** No validation available.
Vapour cloud explosion (deflagration and detonation)	**ORANGE** Generic models available but validity not demonstrated. Specific CFD models can capture specific aspects of explosion behaviour, but integrated models that capture all relevant aspects are still lacking.	**ORANGE** Quite a few tests have been carried out, but given the complexity, more tests are required to fully understand vapour cloud explosions of hydrogen-air mixtures and to validate models.

The selection of a set of scenarios for consequence simulation in the test cases of Task 5 should therefore be based on the identification of the emerging risk for which a larger number of alternative applicable model and some validation tests are available.

The comparison of the results in Table 12 to Table 15 suggests that the following starting set of test cases may be defined on the basis of the unavailability of models and of unavailability of data:

1) LNG

- liquid release through rupture/breach into water
- liquid pool spreading and evaporation on non-still water
- rapid phase transition (both above and under water)

2) Biogas

- instantaneous/continuos gas release from quasi-atmospheric equipment

3) Carbon capture, transportation and storage (CCS)

- dispersion of carbon dioxide vapor clouds

4) Hydrogen

- instantaneous gas release: discharge and dispersion
- liquefied hydrogen pool fire

7. Emerging Risk 1 – LNG Regasification

7.1. Scenario identification

The liquefied natural gas chain is composed by 5 main phases (namely Exploration and Production, Liquefaction, LNG transportation, Storing LNG, and Regasification). The last 2 phases of the LNG chain take place in regasification terminals, which are usually the final destination of LNG carriers. Storage occurs in double wall tanks specially designed for their purpose and are well insulated to keep the natural gas at -160°C (in its liquid form). The regasification process is a purely physical process, where the liquefied natural gas is pumped out of the tanks and warmed so that it returns to its natural gas state. The natural gas is then delivered into the country natural gas transmission system with the quality specifications required before the distribution.

The basic features of the regasification process are essentially the same, independently of the specific technologies and lay-outs adopted. At the regassification terminal LNG is offloaded from the carrier and transferred to storage tanks. In some configurations (e.g. TRV regasification terminals) the storage function is not present and LNG is vaporised onboard and offloaded as compressed natural gas by a sealine. In the other cases, LNG is transferred via the unloading arms from the carrier at berth or at the floating unit (FSRU) to the LNG storage tanks by cryogenic pipelines. Once moored, pumps onboard a LNG carrier delivers LNG through unloading arms and transfer pipelines to the LNG storage tanks. Cool-down of the unloading arms is started by introducing a small LNG flow. Two or three of the arms is generally dedicated for unloading LNG to the transfer pipelines, one is for vapour return to the LNG carrier, and one can also be a hybrid arm used for unloading but also capable of returning vapour as a backup. Each unloading arm is fitted with powered emergency release coupling valves to isolate the arm and the carrier in the event of a non-scheduled separation and to minimize LNG spillage.

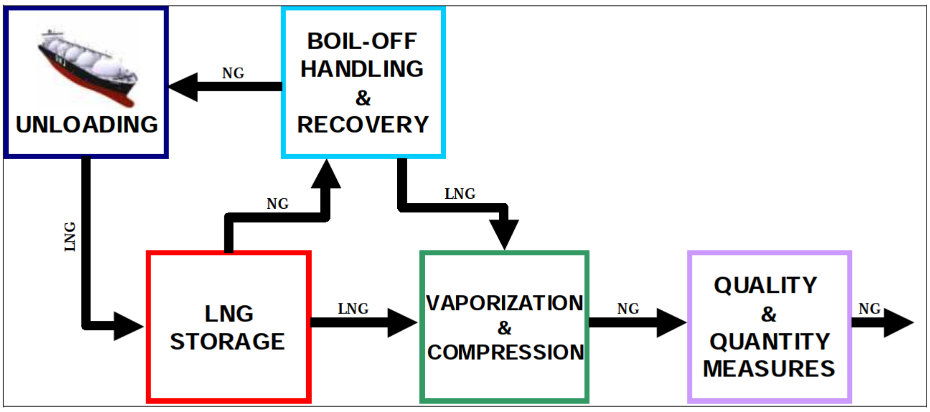


Figure 4- The LNG regasification process.

The pressure in the LNG carrier during unloading is maintained through a system that allows vapour to flow back from the storage tanks to the carrier. In the vaporization stage, LNG is compressed to the desired final delivery pressure and vaporized by dedicated heat exchangers (i.e. vaporizers). Alternative configurations use different heat sources (hot combustion gases, seawater, ambient air, waste heat, etc.) and heating media (propane, water, water/glycol mixtures, air, etc.). In the correction and measurement sections of the process, the quality of the gas is brought to the specification of the national grid. The correction usually consists in introducing dosed quantities of air or nitrogen-enriched air in the natural gas. In this section, the quantity of gas delivered to the national grid is also measured. This operation is usually located onshore, but installation in floating units is technically possible.

Nowadays LNG regasification terminals may be grouped in 4 main categories, which basically mirror the available regasification terminal lay-outs:

- On-shore terminal: the most common and developed technology. The plant is built nearby the sea, usually within a seaport area; it consists of a docking area, storage tanks and a process area.
- Off-shore gravity based structure (GBS): an off shore fixed structure (usually concrete) which houses modular self-supporting prismatic storage tanks and, on the upper decks, all process (i.e. vaporization and compression) equipment.

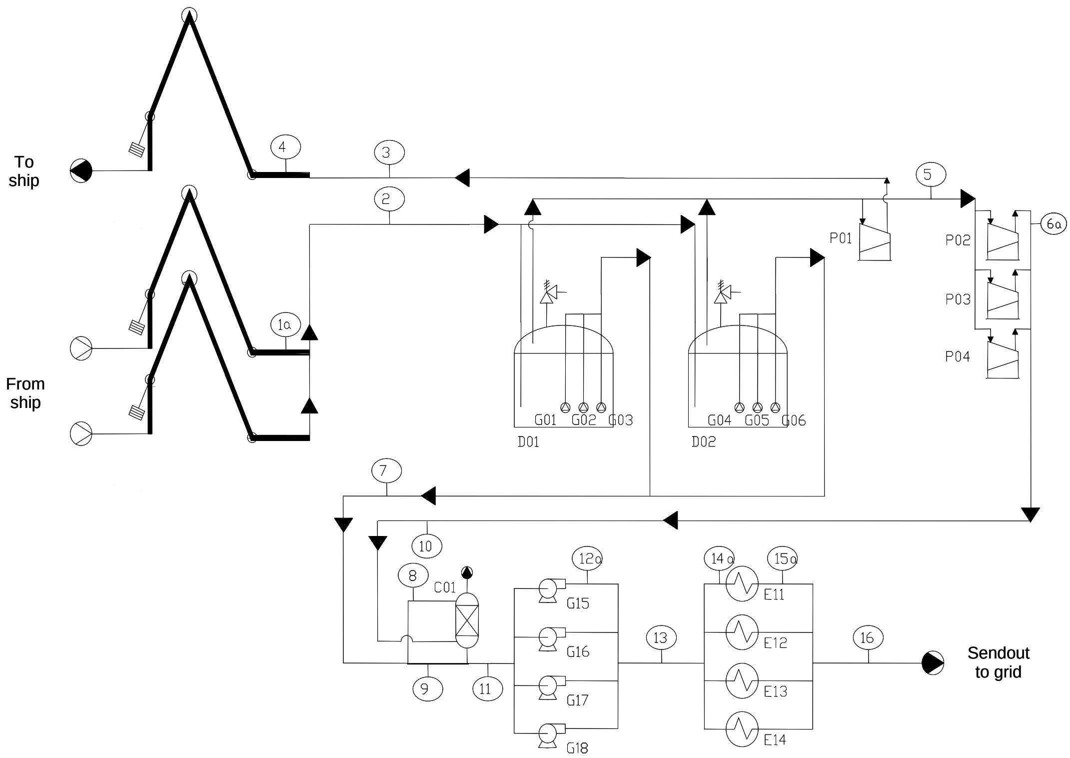


Figure 5- Reference process flow diagram for onshore facility.

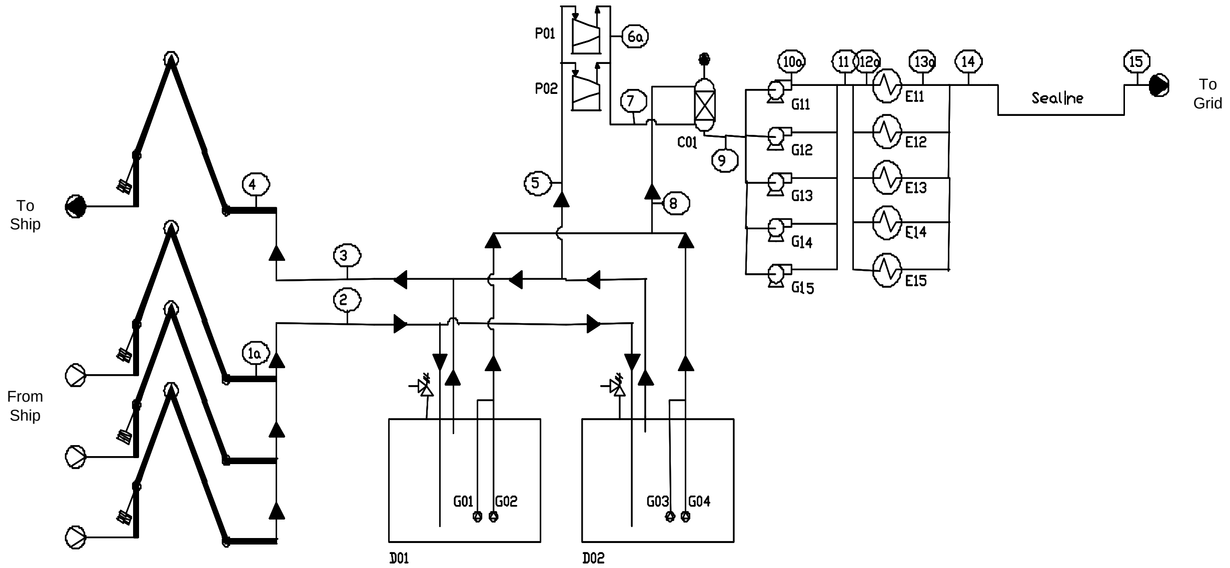


Figure 6 - Reference process flow diagram for Gravity Based Structure (GBS) facility.

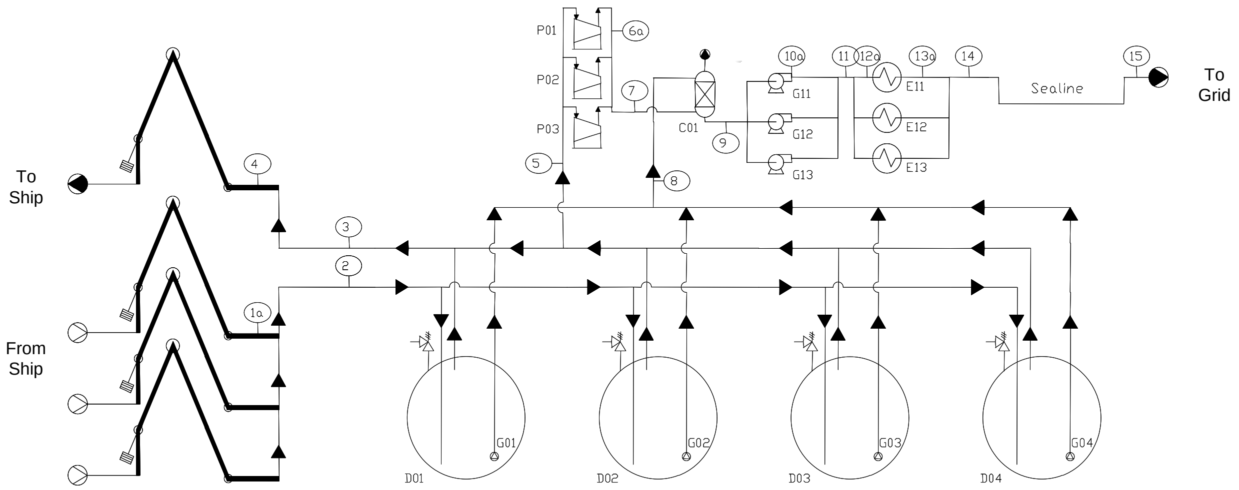


Figure 7 - Reference process flow diagram for Floating Storage and Regasification Unit (FSRU) facility.

- Off-shore floating storage and regasification unit (FSRU): it is a floating vessel (usually a converted LNG carrier) permanently moored off-shore, which receives LNG carriers in a side-by-side configuration. One of the advantages is the independence from the sea bed, which provides a more operational flexibility.
- Off-shore transport and regasification vessel (TRV): similar to the FSRU terminal but not permanently moored, therefore maintaining its function of LNG transport. Once reached an outfitted deepwater port, it can deliver CNG by means of a Submerged Turret Loading (STL) buoy providing the mooring and the connection with natural gas pipelines.

The current trend toward offshore layouts is justified by some advantages: in particular, off-shore installations keep considerable safety distances between the process and the populated.

An extensive hazard identification study for LNG terminals was carried out within the activities of the iNTegRisk Project (IntegRisk, 2010). A set of reference process and equipment schemes was defined (Figure 5 - Figure 7) considering all the three possibilities for layout of the terminal described above (TRV was not explicitly considered since similar to some sections of a FSRU layout). The following hazard identification techniques were applied:

- **Survey of accidents occurred in LNG Transport and Regasification (past accident analysis)**: data on past accidents were obtained from different accident databases with the purpose of identifying the critical issues related to this technology and the new possible threats. The analysis of these data has shown that accidents involving LNG are mostly devoted to collisions during transport operation; loading and unloading operations are also identified as a critical source of accidents. In the case of technological accidents, accidental leaks resulted the more frequent type of accident. In the case of an effective loss of containment, the more likely scenario is the LNG spillage with formation of a pool (on land or on sea) and consequent evaporation and dispersion (18%). In some cases, natural gas is released in the vapor phase with no consequences (6%). In a few cases, the RPT (rapid phase transition), a peculiar phenomenon associated to cryogenic spills which consists in a violent evaporation connected with overpressure effects, was observed (5%). The remaining part of the accidents for which the effects were documented (25%) was associated to generic fires or explosions events (Figure 8).

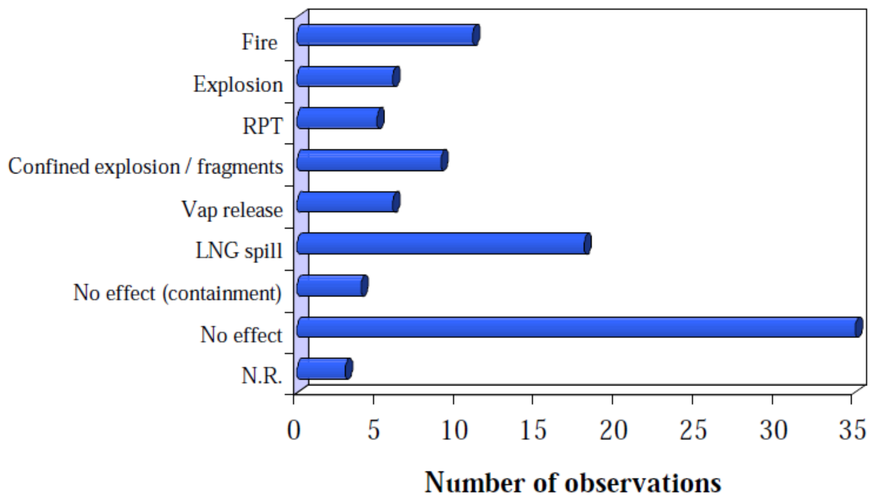


Figure 8 - Main consequence scenarios for the past NG accidents. Total records: 102. (Adapted from Integrisk, 2010).

- **MIMAH methodology (Methodology for the Identification of Major Accident Hazards)**: The MIMAH methodology was originally developed within the EC FP6 ARAMIS project (Delvosalle et al., 2006). It somehow represent an advanced synthesis of the state-of-the-art in hazard identification, providing a guided reference method for the construction of bowtie diagrams. Reference fault and event trees are proposed within the method, effectively constituting an extensive checklist of causes and final scenarios to be associated to equipment units. This method can be considered as a reference for structured hazard assessment methods as checklists, event tree analysis, fault tree analysis, risk ranking, etc.

The application of MIMAH to the LNG reference diagrams evidenced as equipment units of concern in an LNG plant are qualitatively the same for all the considered process layouts (on-shore, GBS, FSRU). In facts, the unit operations, and, thus, the equipment units are essentially linked to the storage and regasification process that is the same, no matter the layout. Hence the critical events, the fault tree and the event tree straightforwardly associated to these units will be the same, no matter the layout or set-up of the installation. The main critical events (Loss Of Containment (LOC) events for LNG and compressed natural gas) are breaches of various size on the in vapor or in liquid phase for equipment units, leak of various size from gas or liquid pipes, catastrophic rupture of equipment units, collapse (vacuum implosion) and collapse of the roof of the storage tanks. The comparison of the event trees obtained for the alternative technologies evidences again great similarity among the results. For each unit of the alternative layouts, a gaseous release may potentially lead to VCE, flash-fire or jet-fire, while a liquid release is generally leading to a pool formation followed by pool fire, flash fire, or vapour coud explosion, depending on the delay and conditions at the moment of ignition. This confirms one more time that, except for configuration specific scenarios (e.g. presence of water, enclosures, etc.), the similitude in the material properties and operative conditions (essentially the same for every technology and set up) inherently influence the hazardous scenario that may be originated. This influence is *de facto* stronger than the effect of actual technological options.

- **Hazard and Operability Study (HazOp)**: The Hazard and Operability Analysis (HazOp) technique was developed to identify and evaluate safety hazards in a process plant, and to identify operability problems which, although not hazardous, could compromise the plant's ability to achieve design productivity (CCPS, 2008). The application to LNG terminals identified the top-events that should be considered in the definition of reference accident scenarios and the failure chains leading to the top-events from various clusters of causes. The analysis substantially confirmed the top-events identified by the MIMAH study stressing the possible chain of causes leasing to such events.
- **Checklists from Standards**: a review of the available technical Standards (CEN standards, NFPA standards, etc.), safety report (for operative and proposed LNG terminals) and technical literature concerning Hazard Identification in LNG regassification plants outlined the state of the art in the definition of accident scenarios.

  The hazards typically considered are both LNG related as well as related to other process conditions. Though consolidated lists of reference hazards exist in technical standards, the practice in analyzing the hazards may considerably differ from case to case.

  As regard the accident scenarios typically identified for LNG, they are related to loss of containment from ruptures and disconnections in equipment units and pipework. The subsequent consequences are usually assessed for the typical flammability-related scenarios of volatile materials (e.g. pool fire, flash-fire, etc.). Other final scenarios (e.g. RPT), though recognized, are usually considered of second order in effects and, frequently, not further investigated.

- **Hazard Identification (HazId) for external threats**: HazId is a structured review technique based on brainstorming sessions. Although its guidewords are in part standardized (e.g. in ISO 17776) HazId relies mainly on the HazId leader and team experience to ensure a complete identification of threats during the brainstorming meetings. HazId overcomes the inherent limitation of other hazard identification studies (e.g. HazOp Analysis) which focus only on causes of internal origin.
  The HazId analysis dentified the external threats that can lead to accident scenarios. The analysis for offshore terminals evidenced that the more relevant hazards are related to:
  - natural events (extreme weather conditions and flooding), which may lead to the potential loss of the terminal, respectively due to loss of mooring and entrance of water;
  - man made events (external direct attack, by collision or by shooting the LNG tanks). The first case (collision) may produce a loss of containment on board (the characteristics of the release need to be investigated, focusing on the expected leak size, flow rate and possibility of immediate ignition, also taking into account catastrophic scenarios); in the second case (shooting), the heat transfer between the projectile explosion and the stored LNG need further investigation, since it may cause a massive LNG evaporation in the tanks, able to increase the pressure and furthermore to lead to a loss of containment.

  In the case of Onshore terminals, the major hazardous natural events are related to flooding/tsunami waves, which may impact on structures, process piping and equipment. However such events are likely to lead only to minor losses of LNG. No major losses from storage tanks are expected due to resistance of the concrete secondary containment. For the same reason, external man-made events may result in a major impact only on the LNG carrier, moored on the jetty, rather than on the terminal itself. Hazards connected to the LNG carrier are therefore similar to the ones already discussed for offshore terminals.
  The possible influence of the primary cause (threat) on the type of final scenarios following the loss of containment is manly related to the increase in the probability of ignition caused by some threats (e.g. attack by shooting/explosives).
- **DyPASI methodology (Dynamic Procedure of Atypical Scenarios Identification)**: DyPASI is a product of the IntegRisk Project. It consists in a self-learning method for the systematization of information from past accidents and near-misses and the generation of bow-tie branches consistently.
  DyPASI was applied to the analysis of storage tanks in a Floating Storage Regasification Unit (FSRU). The analysis produced a set of comprehensive bow-tie diagrams concerning various typologies of Loss Of Containment (LOC) for the unit. The methodology was able to include in the bowties lessons learned from past events/near misses, such as the RPT, and to translate inherent studies showing specific hazards in handling LNG, into elements of the bow-tie diagrams (BLEVE, cryogenic damage, asphyxiation, etc.).

The results, in terms of critical event (top-event or loss of containment event) obtained from the hazard identification techniques listed above were integrated and homogenized in a single set of reference results for typical LNG terminals.

It should be noted that these results refers to generic installations, missing the specific issues and hazards that may characterize actual plants. Specific assessment by relevant hazard identification methods is complemented, but not substituted by the list. Moreover, the results presented in the following refer to potential hazards, irrespectively of their actual possibility and/or credibility for a given plant. As such it ignores protection and prevention measures (even inherent and passive) that may exclude the occurrence of scenarios or causes in actual plants.

Table 17 lists and compare the critical events identified for the three alternative layouts considered for regasification terminals. It should be noted as all the critical events are related to a loss of containment of LNG or NG. Depending on the equipment and causes, the release can be continuous or quasi-instantaneous. It should be otherwise noted as, with a few exceptions (vessel collapse, collapse of the roof), the release events are qualitatively similar among all the units considered.

Table 16 - ID codes of the critical event of Table 17.

Code	Critical Event
CE6	Breach on the shell in vapour phase
CE7	Breach on the shell in liquid phase
CE8	Leak from liquid pipe
CE9	Leak from gas pipe
CE10	Catastrophic rupture
CE11	Vessel collapse
CE12	Collapse of the roof

Table 17 - Critical events identified for reference layouts for LNG terminal (see Table 16 for codes of the critical event) (Adapted from Integrisk, 2010).

Unit class	On-Shore	GBS	FSRU
LNG Storage	CE6, CE7, CE8, CE9, CE10, CE11, CE12	CE6, CE7, CE8, CE9, CE10, CE11	CE6, CE7, CE8, CE9, CE10, CE11
Pressure change equipment on gas streams	CE6, CE9, CE10	CE6, CE9, CE10	CE6, CE9, CE10
Pressure change equipment on LNG streams	CE7, CE8, CE10	CE7, CE8, CE10	CE7, CE8, CE10
Recondenser (column)	CE6, CE7, CE8, CE9, CE10	CE6, CE7, CE8, CE9, CE10	CE6, CE7, CE8, CE9, CE10
Vaporizer	CE6, CE7, CE8, CE9, CE10	CE6, CE7, CE8, CE9, CE10	CE6, CE7, CE8, CE9, CE10
Pipework containing LNG	CE8	CE8	CE8
Pipework containing Gas (Cold)	CE9	CE9	CE9
Pipework containing Gas (Not Cold)	CE9	CE9	CE9
Loading arm (LNG)	CE8	CE8	CE8
Loading arm (balance gas)	CE9	CE9	CE9

Figures from Figure 9 to Figure 11 show the set of event tree associated to the critical events identified above. As evident from the figures a number of different accident scenarios is possible depending on the condition of the material before release, of the releasing equipment, of the location, of the type of release.

Among the possible scenarios, the ones that are originated form the release of the LNG liquid phase (Figure 9) were selected for model gap analysis (Task 2.3), excluding gas-phase and two-phase releases. As a matter of facts, scenarios involving release of natural gas or compressed natural gas (Figure 10) are well known accident scenarios in the Oil&Gas and energy sector, for which consolidated models are available. On the other hand, loss of containment of a two phase streams (Figure 11) involves only a limited number of equipment units in the plant (mainly vaporizers) and, except maybe for the source term, it results in dangerous phenomena that can be described with models similar to the ones applicable to LNG or CNG releases.

From the point of view of consequence modeling, the analysis of the scenarios in Figure 9 identified the following phenomena to be screened for gap analysis (Task 2.3):

- Liquid release through rupture/breach
- Liquid pool spreading and evaporation
- Jet dispersion
- Vapor cloud dispersion
- Pool fire
- Vapor Cloud Explosion
- Flash fire
- Rapid phase Transition
- Burst/BLEVE of the unit
- Fireball from ignited aerosol release

Note*: the hazard identification techniques also identified, as a specific hazardous phenomenon occurring in LNG storage tanks, the roll-over (massive vaporization of cryogenic liquid from a rapid spontaneous mixing of LNG layers in a tank, following situations in which layers or cells of different density were created by inadequate mixing of fresh LNG input). However roll-over is a phenomenon of interest as accident initiator (pre-release phenomena) rather than in the post-release consequence modeling and, therefore, it is not considered in the following being beyond the scope of current analysis.*

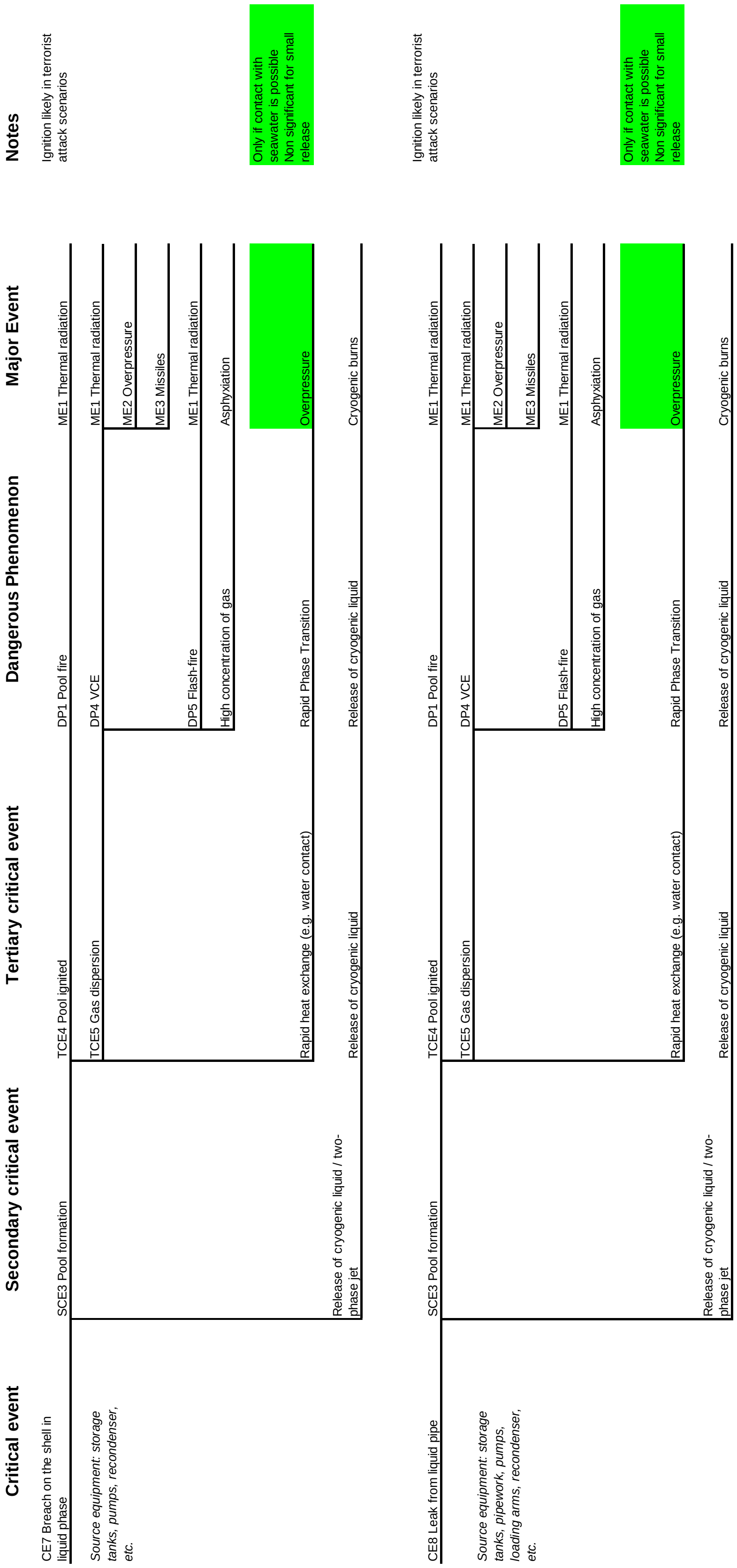


Figure 9 a – Integrated event tree for LOC of Liquefied Natural Gas (LNG).

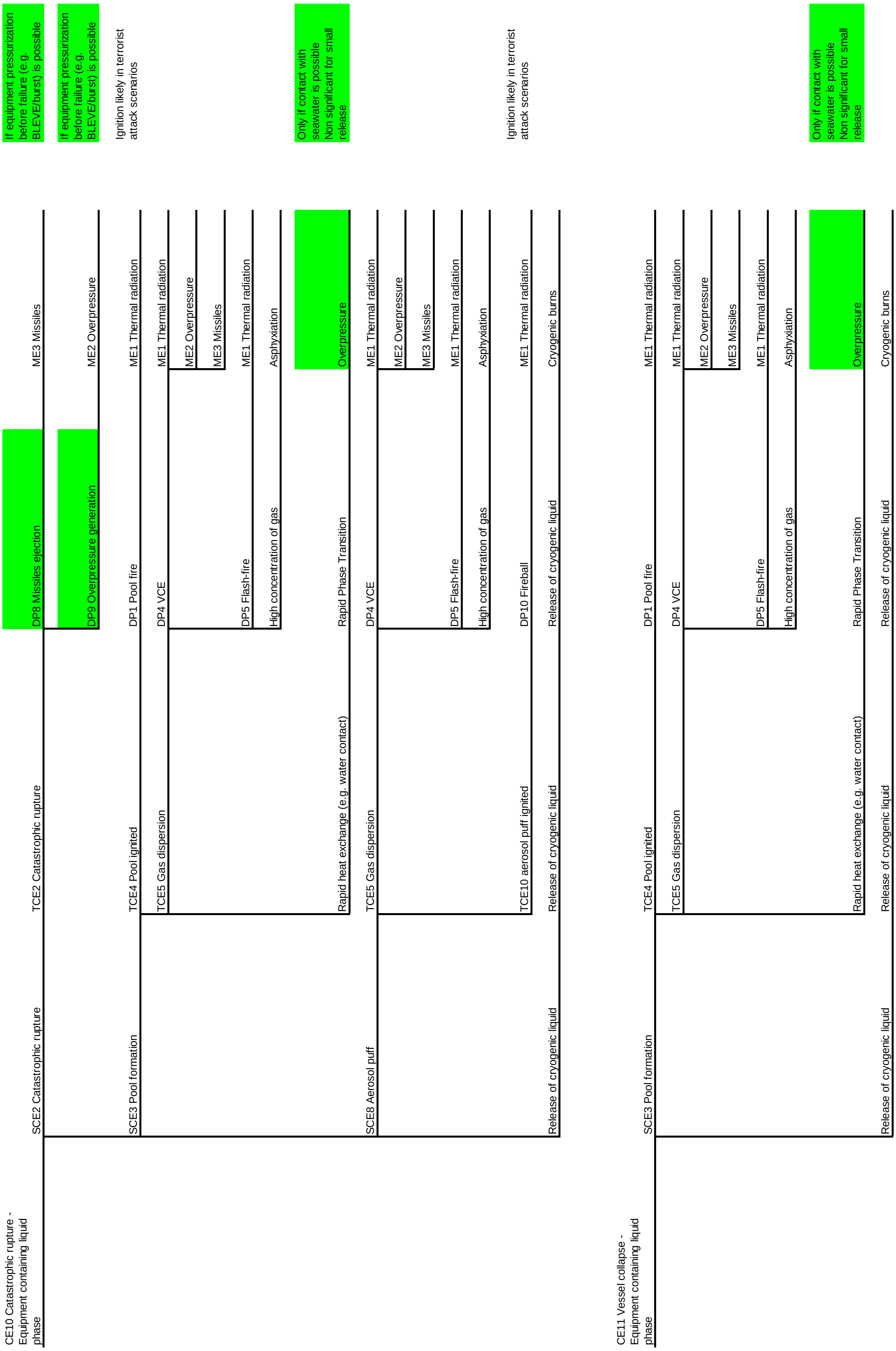


Figure 10b – Integrated event tree for LOC of Liquefied Natural Gas (LNG).

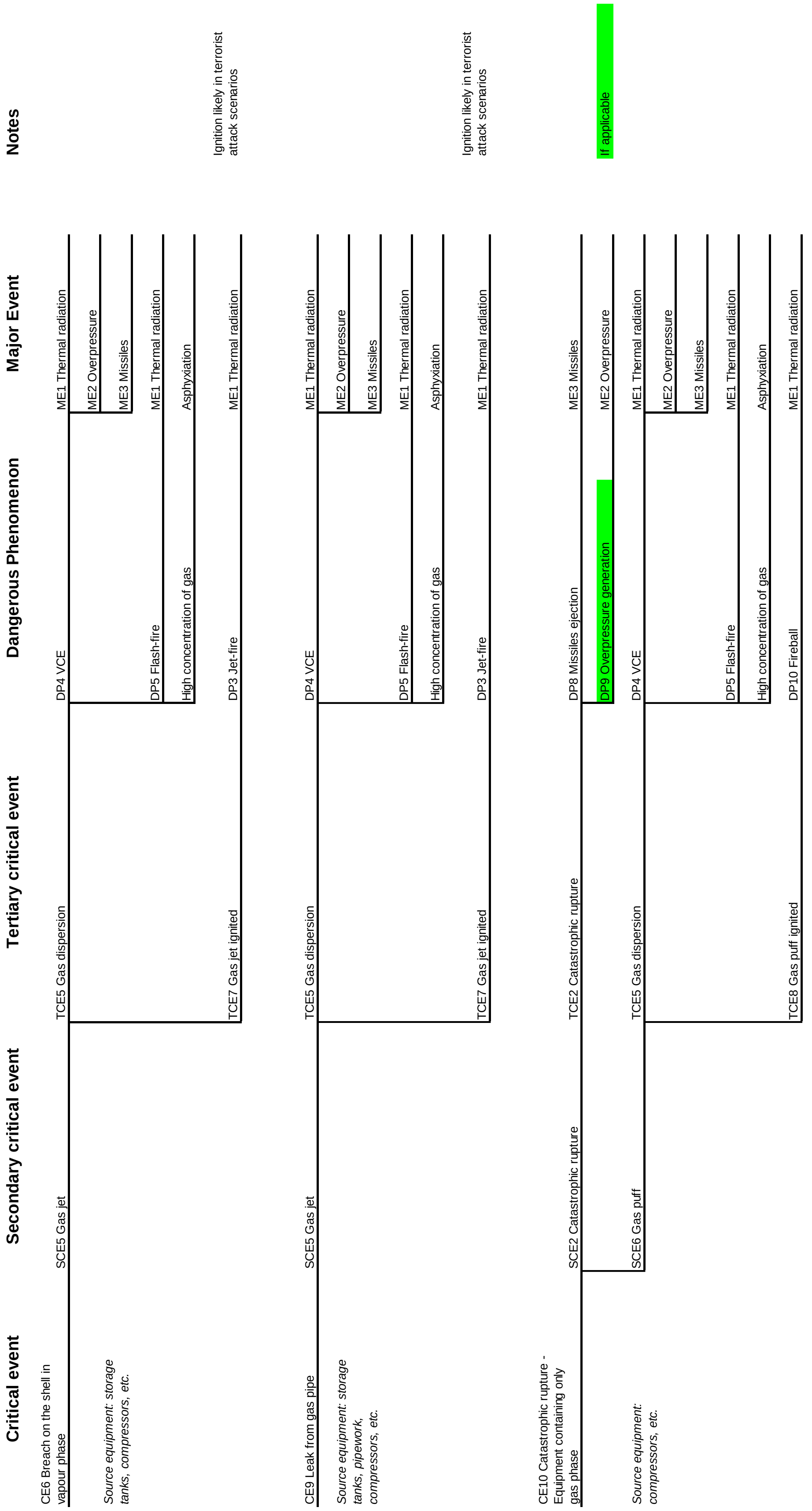


Figure 10 - Integrated event tree for LOC of Natural Gas (CNG).

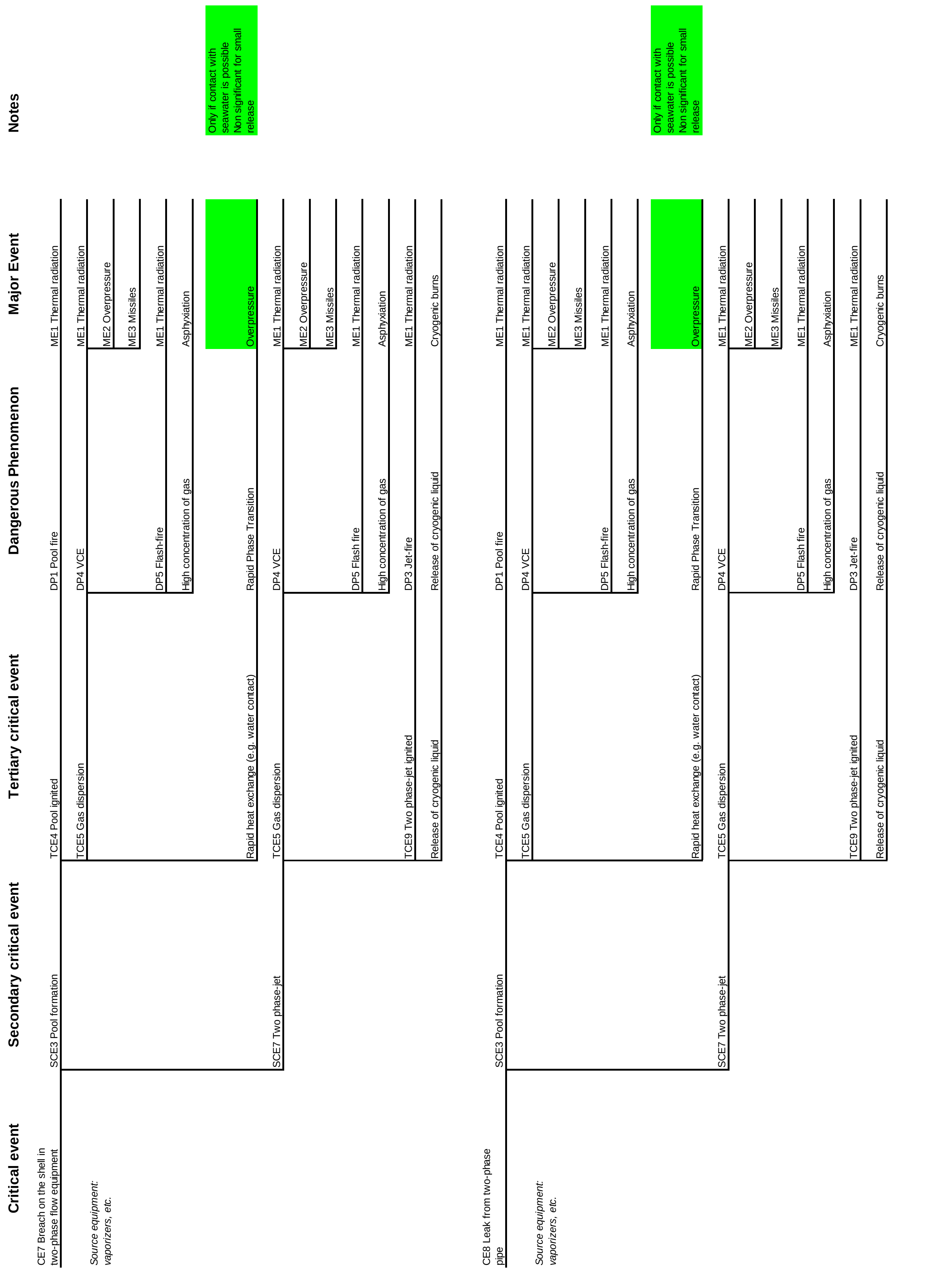


Figure 11 - Integrated event tree for LOC of LNG/CNG mixtures.

7.2. Gap analysis

In the following, the models available for the scenarios identified in task 2.2 will be screened for gap analysis.

7.2.1. Liquid release through rupture/breach

Release dynamics of LNG, referring to instantaneous, continuous or semi-continuous release scenarios, may vary substantially depending on:

- the physical properties of the material at process or storage conditions during containment and during release;
- the amount of mass, momentum and energy stored or processed in the system where a release is examined;
- the way the (accidental) loss of containment takes place, and,
- the subsequent mechanical and physical interaction with the environment.

For the calculation of the amount and the rate at which LNG can be released from an opening in a closed LNG system, all possible controlling mechanisms involved in the heat and mass transfer processes at the source, should be thoroughly examined. Depending on whether the duration of release is much smaller or larger than the characteristic time of the successive phenomena (dispersion, fire), it can be made a classification between instantaneous releases or continuous release with different consequences.

Reviews on LNG spills include works by (Prince, 1983), (Thyer 2003), (Luketa-Hanlin, 2006), (ABS Consulting, 2004) and (Hightower et al. 2004). However, until now there have been very few researches on the source term (outflow model) of LNG spills. Source term description has therefore to be based on classical models used for the release of other materials, such as the one described by Lees (Lees, 1996) and “Yellow Book” (CPR14E, 2005).

LNG is usually stored at atmospheric pressure but may be pumped between storage vessels under pressure. In case of leakage from small holes in tank or pipe, the liquid outflow rate can be predicted by Bernoulli's theorem (orifice model), otherwise, in case of flash within the pipe, through a Homogeneous Equilibrium Model (HEM), based on the resolution of the combined balance equations and stoichiometric relationships.

Flashing may also occur upstream the release in a pipe between vessel and loss of containment; several models are available in the literature for predicting two-phase flow in pipes, as summarized by (Melhem, 1993) to which the reader is referred for more details. The main parameters identified as important in defining the reliability of a given model are the ratio of pipe length to pipe diameter (larger or lower than 50), the initial vapor fraction (larger or lower than 0.01), and the ratio of the initial sub-cooling to the temperature (larger or lower than 0.1). In general, each model is reliable only in a specific window of the aforementioned parameters.

The available models can be broadly classified as:

- Quasi-one-phase models: the two-phase-flow is approximated by relations for liquid flow with an average density related to the vapor fraction;
- Homogeneous equilibrium models (HEM): assume equal flow velocities of both phases as well as thermodynamic equilibrium between the liquid and vapor phase allowing for vapor mass fraction estimation from thermodynamic relations only;
- Non-homogeneous models: do not assume equal flow velocities of liquid and vapor phases, allowing for phase slip;
- 'Frozen' models: assume equal flow velocities of both phases as well as a constant ratio between the vapor and liquid fraction of the flowing fluid.

The homogeneous equilibrium jet model (see for a detailed description of one of these models, TPDIS, (Kukkonen, 1990), which implies consideration of release temperatures up to the saturated vapor temperature at the pressure of the release, seems to be suitable for LNG discharges (Cleaver et al., 2007), even if very few experimental validations have been carried out. Generally speaking, there is not a fully agreement on the predictive capabilities of HEM: someone (e.g., Nyren, 1987; Leung, 1990; Leung and Nazario, 1990; Morris, 1990; Nielsen, 1991) report good agreement between HEM and experimental data, while others report underpredictions (e.g., Nielsen, 1991; Giot, 1994). In general HEM should give reasonable predictions if the vapor fraction is larger than 1%. Note that about 100 mm pipe length is required to establish thermodynamic equilibrium between vapor and liquid phase (Melhem, 1993); this means that in case of saturated liquid upstream and pipes longer than 0.1 m HEM may be applied.

One area of uncertainty is the chain of events that might occur following the creation of a hole in LNG ship at or below the water line. The lack of experimental data on incidents and holes in the tanks of LNG carriers enables to process submarines releases only through a theoretic-physical approach. Pitblado et al. (2004) addressed this situation and provided some predictions for the chain of events: if both the inner and outer containment are breached a complex series of phenomena may occur depending on breach size, location and on the relative levels of water and LNG in the tank. These phenomena involve heat exchange between water and LNG (both by direct contact and through the tank surface), water ingress in LNG tank, LNG egress from the tank, tank pressurization, etc. Detailed modeling studies of this type of issue have been addressed also by Fay (2003). Furthermore, as shown by the work of Woodward (2007), the release scenario can change during the emergency, with the flow directed into the double hull, out in the sea water, or into the LNG tank, depending on the conditions established and also on possible interactions between the two fluids.

The test data currently available for LNG spills are unsuitable for application to source term validation. Hence, the applicable models have all been developed and validated for a substances different than LNG. This represents the main gap identified for describing the release through rupture/breach.

It should be mentioned that the definition of suitable models for the source term is complicated by the fact that there are many different mechanisms by which the LNG can be released. This situation points out the desirability of having more experimental data in just about all areas, including data taken at larger scales.

7.2.2. Two-phase jet dispersion

A leak from a pressurized pipeline or the base of a large tank may lead initially to a jet release. In particular, if LNG is released from a small hole occurring in a pressurized section of the regasification plant, it can lead to a release in the form of continuous jet, with high probability of fragmentation into droplets that can lead to a flash within the tube or once downloaded from the orifice, when the LNG reaches atmospheric pressure.

Experimental data (Cleaver et al., 2007) have shown that if the release is not blocked a jet will be generated. In the presence of obstacles, part of the LNG falls to the ground (rainout) to form a pool. Factors that influence the phenomenon are: temperature and pressure of the discharge, size of the discharge, flow regime in the pipes upstream of the discharge, weather conditions (speed and wind direction), and geometry of the surrounding environment.

For the case of an unobstructed jet a large fraction of the LNG may vaporize in the air before the liquid rains out (Cleaver et al., 2007; Kneebone and Prew, 1974). The amount of vaporization depends on the ambient temperature, the pressure and temperature of the LNG, the initial velocity of the liquid, the orifice size and shape, the fluid trajectory, atomization of the liquid spray and the entrainment rate of fresh air. The following three cases can be broadly distinguished (Hocquet et al., 2002):

- stable liquid jet: the liquid is below the ambient pressure boiling point and emerges as an intact liquid jet. The liquid jet exchanges little heat with surrounding air and it remains liquid until it encounters a solid or liquid surface, when the rapid heat transfer will produce a rapid boiling and a pool may form;
- mechanically fragmented jet: the liquid is below the ambient pressure boiling point and emerges as a spray of droplets. Droplets from mechanical break-up are generally large enough to fall to the ground, even if the heat transfer from the air may be sufficient to vaporize at least a part of them before they hit the ground and form a pool may;
- two phase jet: the liquid is at significant pressure and its temperature is above the ambient temperature boiling point. In this case the sudden depressurization causes rapid partial vaporization (flash) since the heat capacity of the liquid is usually enough to provide the heat required to vaporize a large fraction of the liquid very quickly and to shatter the liquid into a very fine aerosol spray.

The first two cases have received relatively little attention in the literature, in particular with reference to mechanical and thermodynamic break-up (Witlox and Bowen, 2002). However, models of two-phase jets are available since they have been developed for hazard analysis of pressure-liquefied gases (such as LPG). When the pressurized liquefied is released it flashes, that is, a part of the liquid phase evaporates by cooling the liquid phase until boiling point.

When flash occurs only after the release, models of two-phase jets can assume homogeneous equilibrium between gas and liquid phases. There is a small zone just outside the release orifice in which the pressure decreases to the atmospheric value: in this zone it is usually assumed that no air is entrained and no heat is exchanged. The vaporization is thus considered to occur at constant entropy and in equilibrium conditions, therefore allowing the prediction of the flash fraction. After flashing, either a vapor jet with a droplet spray or a liquid jet with vapor bubbles can develop. A vapor jet with droplets entrains air leading to droplets evaporation. Some droplets may fall on the ground and form a liquid pool. A liquid jet with bubbles forms a pool, and the flashed vapor in the bubbles can be considered as originating from the pool.

Following a two-phase release or a single phase release with jet breaking, a two-phase jet enters the atmosphere. After the jet reaches ambient pressure, it still has high momentum and is very turbulent. Air entrainment models usually maintain the homogeneous equilibrium assumption, and as the partial pressure of the released material decreases it continues to vaporize and therefore to cool. A strength of homogeneous equilibrium models is that no knowledge is required of droplet sizes in order to predict the dynamics of the jet itself. The density is obtained from the liquid fraction, which evolves first as the jet depressurizes and then as air is entrained. However this strength is also a weakness: with no information about droplet sizes it is not possible to predict any rain-out of liquid from the jet. Atomization of the liquid can produce droplets so small that they do not rain-out and therefore the homogeneous equilibrium model is adequate. In the case of LNG, however, and depending on the thermodynamic state of the liquid just upstream of the release, atomization of the liquid may be less efficient and a more detailed model, involving droplet sizes, may be required to predict rain-out. Witlox and Bowen (2002) review jet formation and details of atomization in various thermodynamic circumstances, and make numerous recommendations for further research, but this area of modeling is still at a fairly embryonic stage, at least for LNG releases.

In order to describe in detail the whole evolution of the two-phase jet, separate models are required for several different following phenomena, namely:

- the flash or the breakage of the liquid phase;
- the droplet size of the liquid fraction, the droplets evaporation during sedimentation and the rain-out fraction;
- the evolution of velocity, concentration and width of the two-phase jet;
- the evaporation of droplets in the two-phase jet due to air entrainment and the thermodynamic state (temperature, density) of the mixture.

A two-phase jet can be considered as constituted by three main regions: flashing, which occurs after the exit until the mixture is cooled to the boiling point; air entrainment, droplets rain-out and/or evaporation due to the air heating; complete droplets evaporation and single-phase jet dispersion.

The flash fraction (and other quantities) at the end of the flashing stage after releasing can be calculated from the exit conditions by the equations arising from the conservation of enthalpy, momentum, and mass, together with an equation of state as the perfect gas law (see for instance “Yellow Book” CPR14E, 2005 for more details).

Droplet diameter after flashing depends on the breakage mechanism. A liquid jet (flashing or not) may break-up mechanically (capillary or aerodynamic break-up) or thermodynamically (by flashing). For capillary and aerodynamic break-up there are several models and descriptions available; for instance, Tilton and Farley (1990) summarize drop size correlations together with correlations for the length before break-up (which is relevant to determine which process starts first, since a sub-cooled jet may break-up aerodynamically before being shattered by flashing, leading to larger drops). The initial drops formed in the jet may break further by aerodynamic forces. The maximum stable drop size can be determined using a critical Weber number, which value is in the range 5 – 100 (Wierzba 1990), even if values between 10 and 20 are often used (Tilton and Farley, 1990). For what concerns thermodynamic break-up, it seems to occur if the exit temperature exceeds a critical temperature such as $(T-Tb)/T > 0.1$, where Tb is the boiling temperature (Hague and Pepe,1990). Drop size estimation methods are reviewed by (Tilton and Farley, 1990). The calculation of the droplets trajectory is generally performed by assuming that the horizontal velocity of the droplet equals the horizontal jet velocity, and the vertical velocity (settling velocity) follows from the aerodynamic drag force. A simple approximate expression for critical the droplet diameter for which drying time and settling time to the ground are equal can be derived (Kukkonen et al. , 1989), giving the information that only droplets larger than this critical diameter can fall on the ground.

Equations describing the change of droplet mass up to the moment the droplet falls on the ground can be derived using the basic model principles and combined with an integral jet/plume model. All evaporated droplets are fed ‘back’ into the jet/plume model, which is usually assumed to behave like a pure vapor jet (Kukkonen, 1990). A rather complete twophase jet dispersion model has been proposed by Cleary et al. 2007 and Witlox et al. 2007.

The experiments involving the release of pressurized LNG sowed that, for unobstructed releases, all of the LNG remains inside the jet without any rain-out. However, if obstacles are present in the path of the jet, then some of the LNG rains out of the jet to produce a spreading pool.

The factors that have appeared to influence the jet behavior are:

- temperature and pressure of the release;
- size of the release;
- flow regime in any pipe work upstream of the release location;
- atmospheric conditions (wind speed and direction) and surrounding geometry (obstacles, surface type).

The horizontal jet experiments showed that for pressures of between about 3.5 and 7 bar, the flammable zone may extend a considerable distance downstream, with concentrations of over 5% being measured 80m downstream for the case of a mass flow rate of approximately 5 kg s^{-1}, released through a 25mm diameter nozzle. LNG droplets were also detected within the dispersing plume at similar distances downstream. The elevated releases in a vertically upward direction were very wind affected and in low wind conditions the flammable cloud could descend to ground level. The LNG droplets did not rain out close to the source.

There are many difficulties associated with validating source jet models for LNG spills since there are many different mechanisms by which the LNG can be released and there are very few data available. The gap analysis therefore identifies the lack of validation for LNG as the main limit in the currently available models.

7.2.3. Liquid pool spreading and evaporation

A liquid spilt of LNG onto the ground or water surface will spread and the pool will evaporate. Pool dimension is connected to the spreading of the liquid and the contemporaneous vaporization because of the various heat sources (heat flux from surface beneath, convected heat flux from air, long-wave solar radiated heat flux, solar radiated heat flux, evaporation flux) (Yellow Book, CPR14E, 2005).

As the liquid spreads, three flow regimes are recognized (Kukkonen, 1990):

1. gravity - inertia regime: gravitational acceleration of the descending liquid mass is counter-balanced by inertia,
2. gravity - viscous regime: in which the gravitational spreading force is opposed by friction at the liquid-subsoil interface,
3. surface tension - viscous regime: in which for very thin liquid films, surface tension replaces gravity as the driving force.

Often in the literature, cryogenic spills on water surfaces are considered as gravity-inertia governed.

Obviously, in case the liquid is caught in a bund, the spreading of the spill will be limited, and the maximum pool size will be the size of the bund. Of course, this will only be the case when the dimensions of the bund are well designed: if the bund is too small, the released liquid will simply spill over the dike.

For pools spreading, important things to account for are the gravity driving force, puddle formation, and how the vaporization rate affects the flow as the pool spreads. Resistance forces on land and water will be very different. A pool spreading on land experiences a greater friction effect over the whole of the bottom of the pool, while pools spreading on water have to push out the water displaced. Pools spreading on land may also typically encounter a bund or dike which constrains the spread. Pools spreading on land may also be channeled (deliberately or inadvertently) or run off down any slope. This can clearly strongly affect the resulting shape and area of the pool and hence the resulting dispersion characteristics from the spill. If pool spreading happens on water surfaces, moreover, other factors may affect the phenomenon, as waves, wind speed and direction and extension of water body (pool development will be different if release happens on sea surface or shallow water bodies). With regard to pool vaporization, the important features to account for in assessing vaporization are the temperature of the pool, the heat transfer to the pool from the surroundings, and heat removal from the liquid to provide the heat of vaporization.

The following list of candidate models was identified:

- Raj and Kalelkar   P.K. Raj and A.S. Kalelkar (1974)

- Opschoor G. Opschoor (1977), G. Opschoor (1980)
- SOURCE5 Atallah et al., 1993
- SPILL Briscoe and Shaw (1980)
- GASP D M Webber (1988)
- SUPERCHEMS Saraf and Melhem (2005)
- SAFESITE 3G Woodward (2007)
- CANARY Taylor (2007)
- PHAST Witlox and Oke (2007)
- Fay Fay (2007)
- ALOHA http://www.epa.gov/emergencies/content/cameo/aloha.htm
- LSM90/LPOOL Cavanaugh et al., 1994
- LSMS http://www.cerc.co.uk/
- ABS Consulting ABS Consulting, 2004
- LNGMAP http://www.appsci.com/
- FLACS Kim and Salvesen (2002)
- Brambilla & Manca Brambilla and Manca (2009)

In particular, the Gas Accumulation over Spreading Pools (GASP) model of Webber (1990) and Webber and Jones (1987) describes the spreading of evaporating or boiling liquid pools on land or water and is recommended in the TNO Yellow Book (Van Den Bosh & Weterings, 1997) which also provides details of the computational methods used to solve the governing shallow-layer equations together with sample applications. GASP predicts the vaporization rate of a circular liquid pool assuming that the underlying surface (land orwater) is flat (i.e. doesn't take into account surface waves or sloping effects). It doesn't consider multi-component liquids. The underlying surface can be given a prescribed roughness and the pool can interact with bund walls. Releases can be either instantaneous or continuous. The GASP model forms the basis of other LNG spill models including the LNGMAP and ABS Consulting models (ABS Consulting, 2004).

Fay (2007) suggests a rather simple standard inertial-gravity model for pool spreading, in which the phenomenon is governed by gravity. This kind of modeling proceeds by time steps, in order to couple at each step pool spreading and evaporation, as pool volume (and mass) changes during time.

For cryogenic liquids, such as liquefied natural gas (LNG), pool spreading is accompanied by evaporation of the pool fluid. The pool is heated from below by the water (which has a significantly higher temperature), and in addition may be heated from above if the pool vapor is burning as a pool fire. This is usually taken into account by calculating the volume evaporated per unit of time.

A good review of a number of experiments regarding LNG pool spread can be found in Luketa-Hanlin, 2006. A review is provided in IntegRisk (IntegRisk, 2010). There are many difficulties associated with validating source term models for LNG spills. In particular, there are many different mechanisms by which the LNG can be released. While there is some data available for some of these release mechanisms, in other cases there is very little available at all.

Regarding pool spreading model, Fay (2007) compared his standard and supercritical model with China Lake trials, even if no laboratory or field experiments that correspond to gravity flow from a cryogenic fluid storage tank onto the surface of water have been conducted. In these tests, volumes of the order of 3–6m3 were spilled at a fixed volume flow rate in a period of 30–250 s, during which a steady state pool fire was established. These tests replicated the startup process of a gravity-fed spill of long duration (duration of spill, t_s, is much smaller than duration of pool formation, t_d).

The experiments involved a discharge at a fixed volume flow rate for the full duration of the discharge. At or near the start, the vapor pool was ignited and a pool fire was established for the remaining duration of the discharge. After an initial period of spreading, a pool fire of fixed radius R_{eq} persisted until the outflow ceased. The recorded history of pool radius R{t} was compared with the supercritical and standard model values, the only parameters needed for this comparison being R_{eq} and U, the discharge velocity. These comparisons are presented in Figure 12, in terms of a dimensionless radius R{t}/R_{eq} versus a dimensionless time U_t/R_{eq}.

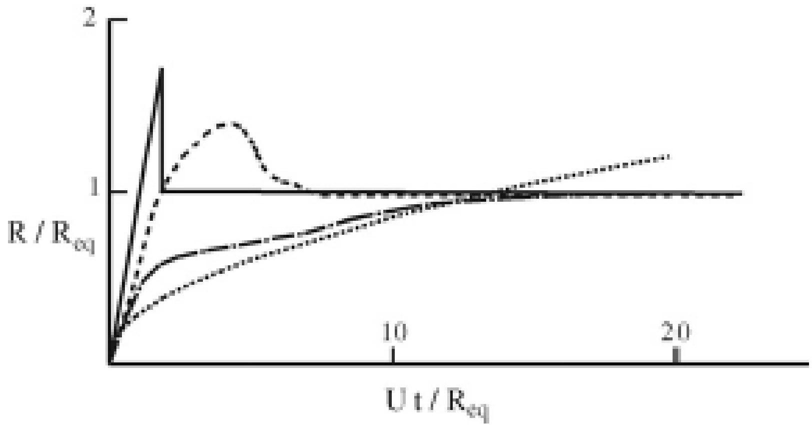


Figure 12 - Comparison between experimental and model results for LNG pool spreading.

The measurements of tests 5 and 12 are shown as dashed and dot-dashed lines, respectively. Test 12 has a lower U and higher R_{eq} than test 5, yet the initial spreading is noticeably different. At the very beginning, R increases linearly with t, but at a speed that is about (2/3)U. In test 5, R overshoots Req by 50%, while in test 12 it undershoots by the same percentage, as a steady state is approached. It seems unlikely that the inflow started instantaneously with the value U, as the supercritical model assumes, but ramped up to this value over the first few seconds, slowing the early spreading and delaying the time to a steady state by a factor of 2–4. On the other hand, the standard model under predicts the spreading rate, especially for test 5, and substantially over predicts the time to establish a steady pool fire. Nevertheless, it is certainly true that the measured spreading in both these tests lie within the limits of the two models.

LNG pool formation is very important to the final result – both for dispersion and subsequent pool fire. Feldbauer et al (1972) spilled 415kg of LNG on water giving a pool for 11s and a maximum diameter of 14m. In comparison, PHAST gave 15s to a maximum diameter of 18.5m. Koopman et al. conducted four experiments (Burro trials) spilling about 2000kg of LNG over a 60s time period. They observed that pools formed with a maximum diameter of 14 to 16m, which boiled off in about 90s. PHAST gave a maximum diameter of 22m with a boil-off time of 80s. DNV concludes that PHAST validates reasonably well, but gives conservative (i.e. larger) pool dimensions.

DNV ran the ten LNG water spill trials using, as close as possible, the specification of the experiments for discharge, stability, wind speed, temperature, humidity, and surface roughness. Other parameters were standard values inside PHAST and are based on its own validations against a wide range of spill experiments involving many liquefied gases and substrate types. Overall PHAST validated well. Specifically for the ten LNG trials, and looking for distance to Lower Flammable Limit (LFL = 4.4%), PHAST gave an average result slightly under-predicting the distance. Iterating with end-point showed that PHAST equally likely to under predict as over-predict distance, using 85% of LFL. This gave an average absolute error of about 20% and a standard deviation of about 30%. This is better than the often quoted factor of two either way for a good dispersion model. It should be noted that, other than running dispersion to an end-point of 85% of LFL, all the parameters used in PHAST are either normal defaults or values appropriate for LNG spills over water.

Some issues still stay open regarding LNG pool modeling. Among the others, wave influence understanding on pool spreading is still in progress, mainly because lack of experimental data about this. Even dispersion under more complex conditions (such as confined spaces, narrow water surfaces) should be investigated in more detailed ways, especially from experimental point of view.

In general, a lack of experimental data, especially on small and pilot scale is reported. Model validation, as said before, needs a big amount of data, and especially LNG matter needs a variety of release characteristics and mechanism and ambient conditions to be fully understood.

7.2.4. Vapor cloud dispersion

The hazardous materials released in the atmosphere are transported and diluted by atmospheric air (that is, by the wind). Modeling this phenomenon is of fundamental importance in risk analysis of LNG – related accidents since the assessment of the worst – case scenarios for LNG spills (in terms of potential damage distances) involve Vapor Cloud Dispersion (VCD) modeling.

Since LNG is a cryogenic liquid with a molecular weight lower than air (Luketa-Hanlin et al., 2007), it rapidly vaporizes when it is spilled onto land or water at a much higher temperature. The natural gas cloud is usually visible due to entrainment and consequent condensation of water vapor of the atmosphere. The evolving vapor propagates downwind at roughly the wind speed, depending on cloud size and atmospheric stability, and has a very low height to lateral dimension ratio due to the vapor density which is initially 1.5 times that of the air. Once vapors heat up, they become lighter than air (i.e., $\rho_{LNG} < \rho_{air}$). In fact, density decreases as air is mixed with LNG vapors, principally at the peripheral regions of the cloud so that the cloud's core will be at the lowest temperature and hence the highest density. Eventually the LNG vapor cloud will be completely mixed with air and will dilute. The only mechanism for the cloud to become buoyant under extremely low wind speeds and very stable conditions will be by contact with the ground or water surface allowing for the cloud to lift off the surface by the heat transfer. Natural gas vapors must be at 166K to be neutrally buoyant in air at 289K. As a consequence, the dispersion of LNG vapors is a very complex phenomenon influenced by several different factors, from wind velocity and large obstacles (which determine the mixing rate between LNG and air) to ambient and ground/water temperature (which determine LNG heating rate). In particular, the maximum distance to the LFL is mainly influenced by spill rate, atmospheric conditions, and the presence of obstacles or terrain features (Luketa-Hanlin et al., 2007). At a particular spill rate, initially the cloud will propagate downwind and the LFL distance will increase until a steady state is reached where the evaporation rate matches the spill rate. At this point the maximum distance to LFL is affected only by fluctuations in atmospheric conditions or obstacles. At a given spill rate, atmospheric conditions significantly affect dispersion distances. Typically, "stable" stratifications and low wind speeds will result in the furthest distance to the LFL. When obstacles or terrain features are present they can either enhance gravity flow, increasing LFL distance, increase mixing, or provide containment which reduce the distance to LFL.

Although each real LNG release is intrinsically non-stationary, for the purpose of modeling it is usually possible to simplify the modeling by comparing the characteristic time of release (t_R) and the characteristic time required by LNG to reach the target (t_F), and classify the release in continuous release (plume) and instantaneous release (puff), according to the usual practice in risk assessment (Lees, 1996).

In case of the dispersion of vapors and mists from LNG release the typical models for heavy gas dispersion are usually considered. General discussion on the available model for heavy gas dispersion can be found in classical references, such as Lees (1996), "Yellow Book" (2005) and Hanna and Drivas (1987). A selection is reported in Table 18 (Ivings et al., 2007). The proposed model can be roughly classified (according to their description of the physical phenomena and to complexity of the numerical solution) into four classes:

- *Distributed parameter models* (the so-called Navier-Stokes or CFD models): FEM3 CFD (Luketa-Hanlin et al. 2007), FLACS (Dharmavaram et al., 2005; Hanna et al., 2004), FLUENT (Gavelli et al., 2008), CFX (Sklavounos and Rigas, 2004), FEMSET, HEAVYGAS, ZEPHYR (Luketa-Hanlin et al, 2007), FDS (Chan, 1992), etc. FDS, CFX and FLUENT are general-purpose CFD codes that are not calibrated for dispersion problem; FEM3 CFD or FLACS were instead specifically developed for consequence modeling.
- *Shallow Layer Models*: e.g. TWODEE (Hankin and Britter, 1999).
- Lumped parameter models (the so-called Integral Models): EFFECT, DEGADIS, SLAB, PHAST, HEGADAS (Lees, 1996).
- Point source models: e.g. Gaussian Models.

Table 18 - List of dispersion models (Ivings et al., 2007)

Model's Name	*Model Type*	*Supported by*
ALOHA	Integral	Publicly available (CAMEO, EPA)
CANARY	Integral	Quest Consultants Inc.
CFX	3D-CFD	ANSYS
DEGADIS	Integral	Publicly available (e.g. Trinity consultants, Lakes Environmental)
DRIFT	Integral	ESR Technology , UK
FDS	3D-CFD	Publicly available, NIST
FEM3A	3D-CFD	University of Arkansas
FLACS	3D-CFD	Gexcon AS, Norway
FLUENT	3D-CFD	ANSYS
GASTAR	Integral	CERC, UK
HGSystem (HEGADAS)	Integral	Shell, UK
SLAB	Integral	Publicly available (e.g. EPA, Trinity consultants, Lakes Environmental)
SLAM	Shallow Layer	Risø, Denmark
SCIPUFF	Lagrangian	L3 Communications Titan Group, Trinity consultants
STAR-CD	3D-CFD	CD-Adapco
SUPERCHEMS EXPERT	Integral	IoMosaic
TSCREEN (Britter-McQuaid model)	Box	Publicly available (e.g. EPA, Lakes Environmental)
PHAST (UDM)	Integral	Det Norske Veritas (DNV), Norway
BREEZE (DEGADIS, SLAB)	Integral	Trinity consultants

Recent reviews fully covered the available LNG experiments (Luketa-Hanlin et al. 2006; Cleaver et al., 2006; Coldrick et al. 2009; Woodward, 2010), and the reader is referred to them for a detailed analysis. A few model validation tests are reported in the literature; the main ones are summarized in the following.

Simplified models vs experimental data

Fifteen hazardous gas models (integral models and point source models) were evaluated using data from eight field experiments. The models include seven publicly available models (AFTOX, DEGADIS, HEGADAS, HGSYSTEM, INPUFF, OB/DG and SLAB), six proprietary models (AIRTOX, CHARM, FOCUS, GASTAR, PHAST and TRACE), and two ''benchmark'' analytical models (the Gaussian Plume Model and the analytical approximations to the Britter and McQuaid Workbook nomograms). The field data were divided into three groups: continuous dense gas releases (Burro LNG, Coyote LNG, Desert Tortoise NH3-gas and aerosols, Goldfish HF-gas and aerosols, and Maplin Sands LNG), continuous passive gas releases (Prairie Grass and Hanford) and instantaneous dense gas releases (Thorney Island Freon). The comparative analysis was performed starting from the assessment (for continuous and instantaneous releases of heavy gas) of a set of statistical parameters as proposed by Hanna et al. (1993).

The dense gas models that produced the most consistent predictions of plume centerline concentrations across the dense gas data sets are the Britter and McQuaid, CHARM, GASTAR, HEGADAS, HGSYSTEM, PHAST, SLAB and TRACE models, with relative mean biases of about +/- 30% or less and magnitudes of relative scatter that are about equal to the mean. The dense gas models tended to overpredict the plume widths and underpredict the plume depths by about a factor of two. All models except GASTAR, TRACE, and the area source version of DEGADIS perform fairly well with the continuous passive gas data sets. Some sensitivity studies were also carried out. It was found that three of the more widely used dense gas models (DEGADIS, HGSYSTEM and SLAB) predicted increases in concentration of about 70% as roughness length decreased by an order of magnitude for the Desert Tortoise and Goldfish field studies. It was also found that none of the dense gas models that were considered came close to simulating the observed factor of two increase in peak concentrations as averaging time decreased from several minutes to 1 s. Because of their assumption that a concentrated dense gas core existed that was unaffected by variations in averaging time, the dense gas models predicted, at most, a 20% increase in concentrations for this variation in averaging time. Furthermore, the considerable variability observed comparing releases in different sites is attributed to the intrinsic randomness inherent the phenomena of dispersion (Hanna et al., 1996).

DEGADIS / SLAB vs Burro trials

The Burro series of LNG spill experiments measured the concentration at 57, 140, 400, and 800 m from the source. All tests were conducted over a desert range with a steep slope rising 7 m in elevation from the pond to 80 m downwind. Beyond 80 m the terrain was relatively flat. Of the eight Burro tests, tests number 3, 5, and 8 were selected for this evaluation. The other tests were excluded due to reported problems (Touma, 1994). The LNG was released from a cryogenic liquid storage tank. The spill pipe was directed straight down toward the water with a splash plate installed at a shallow depth below the spill pipe outlet. Consequently, after the LNG stream encountered the water, it was directed radially outward along the surface of the water. Although spread of LNG due to the spill plate probably resulted in sources of finite area and transient release rates, no information is reported on the size of the area source or variability of emissions for modeling. Gas concentrations were measured at 30 stations at heights of 1, 3, and 8 m above the ground. All concentration data were averaged to 10 s for the study. Release duration was assumed as 166.8, 190, and 107 s, for tests 3, 5, and 8, respectively. Meteorological data were collected at 2 m above the ground. Average values for test duration for temperature, humidity, Pasquill stability class, and Monin-Obukhov length were taken from the Burro data report. The stability class and wind speed assumed for tests 3, 5, and 8 were B and 5.4 m s-1, C and 7.4 m s-1, and E and 1.8 m s-1, respectively. The surface roughness value was about 0.02 cm.

The statistical evaluation of model performance compares observed and predicted maximum centerline concentrations at each receptor arc and a plume half-width indicator at each arc. The plume half-width is defined as the lateral distance between the maximum concentration and the location at which concentrations have decreased to 50% of the maximum. For measured concentrations, the two half-width values on either side of the maximum were averaged. Model performance is displayed in several graphical formats using the observed and predicted values. A combined fractional bias was determined by arithmetically averaging the results of the individual tests; for Burro the average values are computed using just two test results. Because the number of data points provided in each dataset is small, the results should be viewed cautiously.

For Burro tests DEGADIS exhibits fairly extreme overpredictions, while SLAB show relatively little bias. Data on plume half-width were examined to gain additional insight into the performance of the models. It appears that the models as a group perform better in predicting the plume half-width than they do in predicting maximum concentrations. In particular, DEGADIS for maximum concentrations gave large overprediction at 57 and 140 m but showed smaller overprediction bias at 400 and 800 m. The model underestimated plume half-width especially at the farthest distances. On the other hand, SLAB provided relatively good agreement with observed maximum concentrations at 140,400, and 800 m with overprediction by a factor of 1.6 at 57 m. The model showed relatively large overestimation especially at the farthest distances.

DEGADIS / SLAB / PHAST vs various experimental data sets

The Integrisk Project reports (IntegRisk, 2010) reports a validation of three popular simulation models, namely DEGADIS, PHAST, and SLAB, with available experimental models. Particular attention was given to their ability in calculating the extension of the flammable cloud following a LNG release onto water. The assessment was performed in two steps: an evaluation of LFL concentration predictions by comparison with field dispersion data; an estimation of the sensitivity of the models predictions to some input parameters. The three models were validated against twelve field experiments, selected from Burro (Koopman 1982), Coyote (Goldwire, 1983) and Maplin Sands (Colenbrander, 1980) series of trials consisting of LNG releases onto water. These trials cover a wide range of meteorological conditions and source properties. The models were run by specifying the available values of LNG discharge rate, release duration, ambient temperature, wind speed, stability class, humidity, and surface roughness and assuming that the released substance can be treated as pure liquid methane and that the emission rate is equal to a given constant value for the whole release duration.

The performances of the models were assessed by comparing observed and predicted maximum plume centerline concentrations at ground level as a function of the downwind distance. The available field experimental data allowed to evaluate heavy gas dispersion models over a wide range of concentrations, from very high (heavy gas region) to very low (neutral gas region) (Ferrario, 2007).

The results show that DEGADIS, SLAB and PHAST predict experimental data within a factor of two. SLAB presents the best value of geometric mean bias but it is the model with the highest geometric variance. The high value of VG is mainly due to random scatter rather than to mean bias, and this implies that in some cases predicted values could be not as reliable as its mean bias value showed. PHAST and DEGADIS Geometric Variance is lower than the SLAB one and the scatter of variance is more dominated by the mean bias. However, with respect of DEGADIS, PHAST has a lower

Geometric variance and, on average, model predictions are closer to the experimental values. DEGADIS resulted the most conservative model for risk assessment purposes, as it tends to over-predict the flammable concentrations (at a fixed distance) while SLAB and PHAST tends to under-predict them.

Similar results can be obtained by comparing the models considered by Hanna et al. (1993) in connection with several heavy gases different from LNG (in particular, data derived from Desert Tortoise which involve pressurized ammonia releases and Goldfish pressurized Hydrogen Fluoride releases over a desert surface). Apart from the UDM model implemented in PHAST, for which the different versions of the code could account for some of the observed differences, the results suggested that model performances can change significantly depending on the heavy gas considered.

A further validation analysis, using the same twelve field experiments, has been carried out comparing the observed and predicted LFL distances (fixed concentration value of 5% vol. for methane). While DEGADIS and SLAB confirmed the behavior shown in the previous analysis, the distances predicted by PHAST are very close to the observed values. In other words, PHAST can give the most reliable prediction of the LFL distances in eight trials out of twelve. It can be concluded that the mean performances of PHAST, previously evaluated over a wide range of concentration values, are penalized by its lower ability to predict data in the low concentration region. In this low concentration region (roughly below 3.5% vol) the model substantially under-predicts all the measured concentrations.

Both DEGADIS and PHAST use as a transition criterion from the density stratification phase to the passive dispersion phase the bulk Richardson Number. DEGADIS sets the transition when the Richardson number drops below a critical value set equal to 1, while in PHAST the default value for the transition to occur is equal to 15. An early transition to the passive behavior of the cloud implies an overestimation of the air entrainment rate (which is inhibited by the density of the cloud) and of the lateral cloud dimensions with consequent underestimation of gas concentrations with distance. This can explain the poorer performance of PHAST in the low concentration region. Since SLAB does not separate the dispersion phases it does not present the problem of setting a correct transition criterion.

For what concerns the parametric sensitivity analysis carried out, its aim was to understand which parameters mainly influence model results. Sensitivity analysis was carried out both for continuous and short term releases in three different atmospheric conditions: neutral (D5), unstable (B3), and stable (F2). It was evaluated the sensitivity of four of the most important output parameters used in consequence analysis (downwind LFL and 1/2 LFL distances, crosswind LFL distance and maximum flammable mass) with respect to the following input parameters: wind speed, ambient temperature, relative humidity, pool diameter, source flow-rate, release duration. The sensitivity of a variable with respect to the input parameter was calculated applying the Finite Differences Method (Varma et al., 1999).

It has been found that for the models considered the ambient temperature is the most sensitive parameter, mainly due to the criteria implemented in the models for the transition from dense to passive phase dispersion; for all the models, sensitivity with respect to pool diameter is always negligible at constant source flow rate and the source flow rate plays a relevant role only when DEGADIS model is run at atmospheric stable conditions (a precise value of the release duration is important only for short term releases); DEGADIS and PHAST show a significant sensitivity with respect to relative humidity in stable conditions, while PHAST predictions are sensitive to small variations of wind speed in stable conditions.

In conclusion, DEGADIS, SLAB, and PHAST performance in predicting the plume centerline concentration for an LNG release onto water is reasonable good; models show a mean bias within a factor of two and a scatter of about two. SLAB is the model that on average shows the best performance but its reliability strongly depends on release conditions. On the contrary, even if DEGADIS was not the model with the best mean bias, it has a constant reliability and is always conservative. The ability of PHAST to correctly predict the LFL downwind distances is quite good, but at low concentrations (say below 3.5% vol.) downwind distances are always substantially under-predicted. All the models considered require the ambient temperature value being always carefully defined, while parameters describing environmental conditions and source flow rate have to be defined carefully only when simulating releases in stable conditions. Duration of the release is an important parameter only for short term releases.

CFX / Integral Models vs Coyote trials

CFX code has been utilized for the simulation of the Coyote Series large scale spill trials (Sklavounos and Fotis 2005), performed in 1981 by NASA. The objective was to determine the transport and dispersion of vapor from LNG spills, in addition to investigate the damage potential of vapor cloud fires. Coyote series trials involved liquefied natural gas release, dispersion and subsequent ignition and combustion of the flammable cloud. Ignition took place in sufficiently late times, so that the gas cloud had spread in substantial area and sustainable fire could develop around the igniter location.

The validation was performed by considering cloud dispersion until the time that combustion was initiated, complemented with the relative performance assessment between the CFX code and the two integral models DEGADIS and SLAB (Sklavounos and Fotis 2005).

Computational results of the CFX code regarding gas concentration histories were compared against the trial records showing a reasonably good agreement, whereas the dispersion behavior of the natural gas cloud as a heavy one was captured, proving that CFDs may effectively estimate the atmospheric dispersion of cryogenic gas releases. For the intercomparison, the statistical performance measures of fractional bias (FB), geometric mean bias (MG), geometric mean variance (VG), mean relative square error (MRSE) and normalized mean square error (NMSE) (Duijm and Carissimo, 2002) were used. The statistical measures showed that the CFX code yielded more accurate results compared to those of SLAB and DEGADIS. Both the CFX code and integral models overestimated gas concentrations with geometric mean bias in the range between 0.5 and 1, and experimental concentration predictions up to a factor of 2.

In some tests, DEGADIS model appears to overestimate gas concentration, whereas SLAB model seems to provide concentration estimations closer to those of CFX than DEGADIS model. It is also evident that all models calculate a maximum concentration which remains constant while the cloud passes through the receptor. On the contrary, experimental temporal concentration variation presents large fluctuations. Probably, wind speed changes as well as random changes in the blow direction may affect locally the turbulent mixing of gas with air, thus causing substantial concentration changes.

Cloud dimensions and cloud shape calculated by the code are in good agreement with those observed from the experiments. Furthermore, high concentration values near the ground indicate a heavy rather than a light gas dispersion behavior. The calculated performance measures show that all models provide conservative estimations. A clear overestimation of the measured concentration values by DEGADIS and SLAB models, while CFX code predictions show a less scattering. Although there is a considerable difference between integral models and CFX, the statistical indicators considered in the study show that they all were able to predict gas concentration within a factor-of-two.

Fluent vs Falcon trials

When considering spills into an impoundment, as opposed to spills over water or flat terrain, it is important to consider the effect on vapor dispersion and mixing due to the impoundment walls and the LNG storage tank or process equipment within the impoundment. Only the Falcon test series of large-scale LNG spill tests accounts for the effect of large obstacles. The Falcon tests were heavily instrumented to measure: air temperature, pressure and humidity, wind speed and direction, turbulence intensity, heat flux from the ground, and gas concentration. The sensors were located both within the fenced area, to record the behavior of the constrained LNG cloud, and downwind of the fence, to observe the dispersion of the LNG vapor that spilled over the fence. Sensors were located up to 250m downwind of the trailing edge of the vapor fence. These tests used a realistically complex geometry that represents conditions likely to be present at or near an LNG release. The vapor fence simulates the effect of the impoundment walls, and the barrier was placed upwind of the spill to introduce additional turbulence, in a manner similar to the effect that containment tanks, buildings or even ships would have on an actual spill. These types of surface features and realistic flow complexity test the capability of the CFD model to accurately predict dispersion in the flow patterns formed in complex geometries. A predetermined amount of LNG was spilled into an impoundment at a prescribed rate, and the flammable vapor cloud was then tracked as it was carried downwind and dispersed in the environment. Therefore, the Falcon tests provide data on the entire LNG vapor cloud dispersion scenario.

Falcon-1 test was chosen as the benchmark case as it combines low wind speed conditions (1.7 m/s at 2m elevation) with other challenging conditions from an analysis standpoint among the Falcon tests: most stable atmosphere, largest spill volume (66.4m3) and spill flow rate (28.7m3/min). Also of interest is the fact that DEGADIS model predict the vapor cloud to remain confined inside the vapor fence, unlike what was observed during the experiment. Therefore, any model that can accurately simulate the Falcon-1 test data must be able to account for physical phenomena other than vaporization, in order for the cloud to overflow the impoundment and disperse downwind. The Falcon tests gas concentration data was averaged over 5 s time intervals. The CFD tool Fluent is a Reynolds-Averaged Navier–Stokes (RANS) based model and predicts a smoother and more slowly-changing behavior of the methane cloud. The results shows a very good agreement between experiments and predictions.

FLACS tests

With support from Norsk Hydro, Total, Statoil, and Petroleum Safety Authority Norway (PSA), and in cooperation with DNV, a LNG-development and validation project for FLACS has been recently carried out. The first phase of the project was a validation activity in which 8 tests from Burro and 3 tests from Coyote experiments performed at China Lake (USA), and 4 tests from Maplin Sands (UK) have been simulated. Predicted downwind maximum gas concentrations at various distances have been compared to experiments showing good correlation (Hansen et al., 2007). Additional models have been also developed to extend the pool simulation capabilities to allow the simulation of the formation and spread of a pool with local evaporation rates based on heat from ground, wind speed, local vapor pressure (Hansen et al., 2007).

FDS tests

FDS (Fire Dynamics Simulator) is a CFD code created by NIST (National Institute of Standards and Technology) (McGrattan, 2005) to compute fire and smoke propagations. It allows Large Eddy Simulations (LES) of dispersions. Yee and Biltoft (2004) performed a validation trial successfully modeling LNG (Chan, 1992) releases by using a dedicated procedure for the aerosol release.

Open issues

The open issues in modeling dispersion originated from LNG release include the effects of surface roughness and site obstacles, the formation of a vapor 'blanket' over a spreading pool and its mixing rate with ambient air, heat transfer effects and the transition to passive behavior. For instance, large scale test data for releases on variable terrain and in an urban environment would be very useful (Koopman and Ermak, 2007), as well as experiment showing the influence of large obstacles. In this respect, the limitation related to the use of integral models is evident for geometrically complex situations. Field tests of the series Falcon in particular highlight the importance of correctly modeling the gas-air mixing: the basin containment, which under the assumption of absence of mixing should have to contain all the steam released, is resulted not sufficient (Havens and Spicer, 2005).

For the Navier–Stokes models, higher order turbulence models, such as the widely used k-epsilon models, are a potential improvement (over K-theory models) because they do not assume local equilibrium and allow for the creation, transport, and destruction of turbulence. Similarly, large eddy simulation models would be useful in estimating concentration fluctuations and peak concentration. However, these more advanced turbulence models must also include the effects associated with the dispersion of cold, denser-than-air vapor clouds. Moreover, they must be able to reproduce the well known Monin-Obukhov similarity profiles in different atmospheric stratification conditions.

In recent years, Navier–Stokes atmospheric dispersion models have been used to study trace gas dispersion in the urban environment around structures and buildings for detailed planning studies and to study meteorological coupling with larger scale models to provide more appropriate initial and boundary conditions for local scale dispersion models. The extension of this work to include large LNG releases would be appropriate for similar high risk scenarios. In addition, fast-running dense gas dispersion models that include parameterized cold, dense gas effects, complex terrain (mountains, valleys, etc.), and three dimensional meteorology are needed for emergency response applications. As a consequence, fast and easy geometry importation procedure from existing geo-referred databases should be developed to represent realistic urban environments.

7.2.5. Pool fire

An LNG pool in presence of ignition results in a pool fire. The largest LNG pool fires are expected to be from LNG impoundment sumps or containment basin around its storage tanks, or an unconfined spill from a tank of a LNG carrier (Woodward and Pitblabo, 2010). For LNG releases over water the shape and size can be affected by environmental conditions, such as wind, waves, and currents. The first and main hazard arising from a pool fire is due to thermal radiation which is largely determined by the visible flame size and flame brightness that vary with pool diameter. The burning rate is a critical parameter that determines the amount of thermal radiation: according to Baik et al. (2005) the burning rate value of methane on water is about 2.5 times greater than the burning rate on land.

In literature, two approaches can be identified to model pool fires: semi-empirical models and field models (or Computational Fluid Dynamics Models).

Semi-empirical models characterize the geometry and radiative characteristics of a pool fire using correlations based on dimensionless modeling. The correlations used in semi-empirical models are derived from a wide range of experimental data and give reasonable predictions if they are not used outside their range of validations.

Field models solve the Navier-Stokes equations of fluid flow and, in order to predict fire behavior, they incorporate sub-models which describe the chemical and physical processes occurring in fires. Many of these sub-models are empirical and therefore validation of CFD codes is as important as it is for more simple modeling techniques.

In general two types semi-empirical approaches are described to calculate the heat flux to a target from a pool fire: Point Source Model and Solid Flame Model.

Point Source Models

In the Point Source model the radiation is assumed starting from a point in the middle of the flame. The heat flux in the near field cannot be predicted adequately and the presence of objects interacting with the flame cannot be modeled.

By their very nature, these models introduce very simplified assumptions (e.g. ignoring flame geometry, ignoring variation of SEP with the flame, ignoring effect of obstacles and atmosphere) and it is known to give result which are good only for a first approximation evaluation also in pool fires from conventional material; this will be furthermore true in the case of LNG fires. An example of point source model applied to LNG is present in 49 Code Federal Regulations 193 (US federal regulations for onshore LNG terminals).

Solid Flame Models

Solid Flame Model assumes the flame like a cylinder whose emits thermal radiation uniformly from the surface and at a specified constant rate. Base, height, and tilt angle of the cylinder are determined according to the diameter of the pool and other parameters (e.g. wind speed) (Brown et al., 1974; Ray and Atallah, 1974; Lautkaski, 1992; Johnson, 1992).

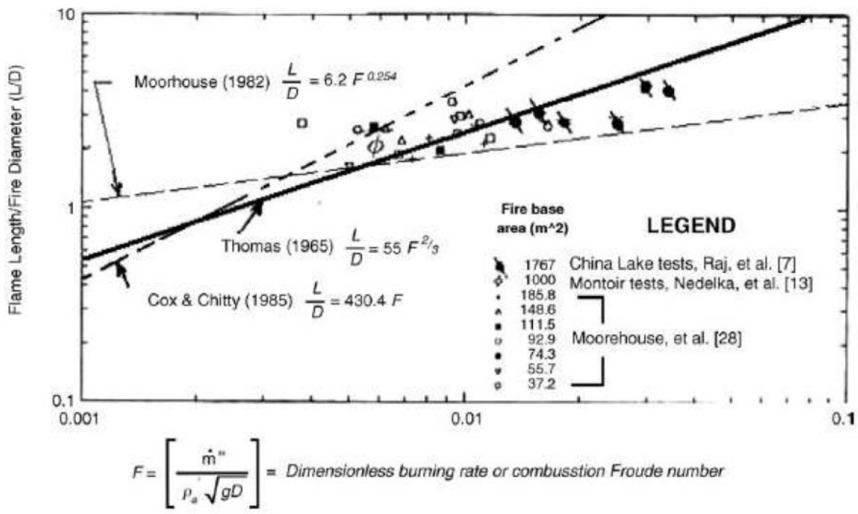
A critical parameter in the model is the Surface Emissive Power (SEP): typical values for the SEP used in solid flame models applied to LNG pool fires range between approximately 175 and 325kW/m^2. Different options exist to model the non uniform SEP of a burning pool fire (Gavelli, 2008):

- single zone models; (Beyler 2002) in which the entire flame height is assumed to be unobscured by smoke (clear flame);
- two-zone models (FERC, 2004), in which the lower part of the cylinder is assumed to be a clear flame, while the upper part is assumed to be partially obscured by smoke;
- three-zone models (Ray, 2007) in which the base of the flame cylinder is assumed to be unobscured, the middle portion of the flame is anchored to the base and intermittently obscured by smoke and the upper region of the flame is separated from the base into stretching flame puffs, which are substantially or totally obscured by smoke.

The SEP and the smoke shielding parameters are factors defined so as to approximate a set of highly complex phenomena.

The thermal radiation emitted by a fire is partially scattered and/or absorbed by the atmosphere: this phenomenon is common to all the pool fire models and its modeling is well described in the literature Ray (2007).

As for the dimensions of LNG pool fires, the plume length-to-diameter ratios from field LNG pool fire tests and the predictions from different correlations were reported by Ray, 2006 (Figure 13).



$$F = \left[\frac{\dot{m}''}{\rho_a \sqrt{gD}}\right]$$

Figure 13 - Comparison of experimental data on fire height-to-diameter ratios with correlations for use in models (Raj 2006).

LNGFIRE3, developed by the Gas Technology Institute in Chicago, is a dedicated model for LNG fires which consist of 3 sub-models: confined pool fires, unconfined pool fires and jet fires. It calculates the radiant flux levels at user-defined points downwind of an LNG fire. For confined and unconfined pool fires, it is used a solid flame model in which the fire is represented by a cylindrical fire with uniform emissive power. The LNGFIRE3 model are described by Atallah & Shah (1990).

A number of limitations and shortcomings of the LNGFIRE3 model stand out when compared with data from experiments involving large LNG pool fires on land. The main limitation is the use of a constant emissive power for the entire surface of the idealized fire; it is known that for increased fire dimension the radiative characteristic change significantly. Other limitations of the LNGFIRE3 model are reported by Ray (2006b).

From the series of LNG pool fire tests carried out thus far, the flame brightness, or Surface Emissive Power (SEP), appears to have reached a plateau, about 170 kW/m2 for the largest diameter tested so far (35m Montoir tests, see Johnson, 1992). There is uncertainty how the SEP might vary thereafter for bigger pools, but there is strong theoretical evidence that there would be no further increase in SEP and indeed the SEP might start to decrease due to the shielding by soot from incomplete combustion. The lower limit seems to be about 20 kW/m2 typical of hot smoke. Pool fires larger than 35m diameter would be required to confirm this trend (Chamberlain, 2006)

The height of the flame depends on how well the flame can entrain air for combustion. For methane Chamberlain (2006) provides applicable equations for calculating flame length in the intermittent fire and mass fire regimes as function of the square root of the Froude number. The way to determine the transition from a burning regime to another is not easy. Many authors suggest that the mass fire regime will not be reached even for extremely large spill sizes. A large LNG spill therefore is predicted to burn in the intermittent fire regime (Chamberlain, 2006).

Raj et al. (1979a/b) report, for the largest LNG pool fire experiments on water, burning rates, m, of 0.0004 to 0.001 m/s (assumed LNG density equal to 411 kg/m3); as this range is larger than the values measured for land-based pool fires, a sensitivity study was carried out by varying the burning rate between from 0.00035 to 0.001 m/s reaching the same conclusion: a large LNG spill is predicted to burn in the intermittent fire regime.

In the pasts 30 years several LNG pool fire tests have been conducted to understand the fire characteristics and the thermal radiation emitted (Raj, 1982); the most important tests were:

- 1962 The US Bureau of Mines (Burgess and Zabetakis, 1962)
- 1969 Esso tests (May and McQueen, 1973)
- 1973 The American Gas Association (AGA, 1974)
- 1974-76 United States Coast Guard (Ray and Atallah, 1974; Ray et. Al., 1979a)
- 1976 Japan Gas Association (JGA, 1976)
- 1980 British Gas (Moorhouse, 1982)
- 1980 Shell Reasearch (Mizner and Eyre, 1982)
- 1981 Tokyo Gas (Kataoka, 1981)
- 1987 Gaz de France (Nedelka et al., 1989)
- 2009 Sandia Large LNG Pool Fire on Water (Luketa-Hanlin and Freitas, 2009)

The fire sizes have ranged from about 2m to 35m in diameter on land but some tests are planned for the future to validate fire models on a large scale experimental data simulating releases on water up to 100 meters.

It should also be noted that validation tests are also hindered by uncertainties present in the experimental data from tests. While several LNG pool fire studies on land and water have been conducted to determine thermal radiation, burn rate, and flame speed, there is a lack of data for large LNG pool fires on water. The most complete data set for a LNG pool fire on water is from the one on a 15m diameter pool from the U.S. Coast Guard (Ray 1979b, Schneider 1979).

The SEP seems to not increase for pool diameters large than 35 m and, on the contrary, after attaining a maximum value the SEP would expect to decrease with further increases in diameter due to smoke shielding. Experiments are needed for confirm this trend. Many have theorized that there is a limit in a pool diameter at which the flame break up in multiple fires (mass fire). That limit have to be checked because occurrence or not of a mass fire influence (reducing) the quantity of heat received by an object at a fixed distance (see (Zukoski, 1995; Corlett, 1974; Cox and Chitty, 1985; Heskestad 1991/1998; Delichatsios, 1987).

A validation comparison of a three-zone SEP model is reported by Raj (2007) using the so called PoFMISE model. The results show good agreement of measured and predicted SEP, but are limited to a small number of test cases.

The Solid flame Models assume that heat is radiated from the surface of a solid object with a simple geometry and represents a fire as a surface emitter of radiant heat energy. The change of fire shape with time, complex complex and/or irregular fire shapes and changes in the SEP cannot be modeled. For large LNG fire (D>30m), the use of Thomas correlation may be questionable due to Froude number and evaporation rate decrease resulting from soot formation. Finally, the use of different SEP calculation methods may create inconsistencies (among those calculated with radiometer data and actually observed flame radiating surfaces and those calculated with radiometer using Thomas correlation).

In general it is possible to state that both Point Source model and Solid Flame model over-predict the measured heat flux at various distances at crosswind, upwind, and downwind locations; see Luketa-Hanlin (2006) for a comparison.

Field Models

Many studies have been developed (Smith et al., 2003; Malalasekara et al., 1996; Hostikka et al., 2003) to investigate the possibility to model the fire characteristics by the use of the Computational Fluid Dynamics codes which would be able to simulate the net effect of many different parameters as turbulence, reactions, soot formation and the effect of thermal radiation on the substrate. Examples of applicable CFD Models include FDS (Public Available, NIST see McGrattan et al., 2009a/b) and VULCAN (Proprietary, SANDIA).

Field models are based on Navier-Stokes equations for fluid flow. They attempt to simulate combined effects of turbulence, reaction chemistry, generation of combustion products (e.g. soot), and thermal radiation. The uncertainties related to the use of these models are higher than the ones associated to the corresponding dispersion models, due to the need to simulate the combustion kinetic. The modeling of all the involved physical phenomena may not be complete/adequate within the practical timescales required for calculation. The models should be validated with experimental data but currently experimental data are limited and the calculation time can be significant.

The gap analysis of pool fire models has therefore concluded that, while some models are available, the development and experimental validation of models is still needed for this scenario.

7.2.6. Flash fire

The spill of flammable liquefied gases (such as LNG) and its subsequent evaporation leads to the formation of a dense gas cloud at ground level that may be ignited far from the release point. When the environment is either partially confined or congested the main hazard following the cloud ignition is related to overpressures generated by a Vapor Cloud Explosion (VCE). On the contrary, when the gas cloud spreads over a non-congested area its ignition leads to a combustion without generation of damaging overpressures, which is called Flash Fire or Vapor Cloud Fire. In this case, the main consequences are related to the thermal radiation from the burning of the cloud (Rew et al., 1995).

Heavy gas clouds arising from continuous releases (e.g., pool evaporation) assume a “cigarlike” shape, that is, with height much less than width or length. Following an ignition at the edge of the cloud, three different stages can be identified (Pula et al., 2005). In the first stage of the cloud combustion, premixed turbulent flames spread radially from the ignition point until the portion of the cloud whose concentration falls between the upper and the lower flammable limit (UFL and LFL, respectively) has burnt. As soon as flames reach the UFL boundary, they slow down and become diffusive, much higher and more visible, assuming the shape of a crosswind wall of flames that moves towards the release point. This phenomenon was named burn-back and it is longer and more emissive than the first phase.

Finally, when the flames reach the source of release, a pool fire or a jet fire, depending on the characteristics (duration, momentum, etc.) of the emission considered, may follow the Flash Fire. However, while the latter is a steady-state fire scenario, the whole process involved in a Flash Fire is transient and quite fast. This is the reason why in the frame of the Quantitative Risk Analysis (QRA) the area caught within the cloud’s LFL boundary is usually considered at risk for people lethality while no hazards are expected beyond the edge of the cloud. However, a question arises concerning the reliability of this assumption since a large Flash Fire could be expected to cause appreciable damages not only within the burning cloud region, but also from the exposure to the thermal radiation generated.

Flash fire models used for the purpose of risk assessment are usually based on gas dispersion modeling combined with the probability of ignition (e.g. Considine et al 1982, Clay et al 1988). In these models the boundary of the fire is defined by determining the contour of the gas cloud with lower flammability limit concentration (Lees, 1996). Such approach offers conservative estimates of fatalities caused by flash fires and is applicable to flash fires from LNG vapors as well.

More detailed modeling has been undertaken by e.g. Raj and Emmons (1975) and Rodean et al. (1984) based on incorporating a flame propagation rate and using standard view factor techniques to calculate thermal radiation external to the fire (Lees, 1995). This model has been discussed, also with reference to LNG Flash Fires, by Rota et al. (1998).

Considine and Grint flash fire model (1985) predicts the hazard range of the fire in a form of graphs of the distance to particular level of fatal injury (Lees, 1995). Their results are derived from a Flash Fire model where the flame is assumed to travel radially away from the ignition source. They distinguish the results for a vapor cloud with concentrations between the upper flammability limit (UFL) and the lower flammability limit (LFL), and LFL and another pair.

More complex models developed in the frame of Computational Fluid Dynamics (CFD) can be also used, as discussed in more details for jet fire and atmospheric dispersion phenomena (Rigas et al., 2006).

Several experimental works on the vapor cloud combustion following large scale spills of LNG have been carried out (China Lake, Maplin Sands, Lawrence Livermore National Laboratory, Gaz de France, TRW, AGA, Shell Research) and they are deeply discussed in the literature (Ray et al. ,1977; Little et al. ,1979; Ermark et al., 1983; Lees, 1995; Blackmore et al., 1982; Eyre et al., 1982; Hirst and Eyre, 1983; LLNL, 1983 and 1984; Rigas and Sklavounos, 2006; Havens, 2009; Raj, 2009 and 1979; Gaz de France, 1972; TRW, 1968; AGA, 1974; Mizner and Eyre, 1983; Raj, 2007) where all details can be found.

The vapor cloud fire models based on lower flammability limit, do not explicitly calculate the physical effects of fire, simply assuming a thermal radiation within the lower flammability limit contour high enough to results in fatal injuries and outside these contour thermal radiation is based on the surface emissive power at the edge of the cloud (Lees, 1995). These kind of approach provides generally conservative estimates of the affected area.

More detailed (e.g. Raj and Emmons, 1975; Rodean et al., 1984), which incorporate a flame propagation rate and use standard view factor techniques to calculate thermal radiation from the fire, require the knowledge of the physical and chemical processes which occur during wind/flame interaction, which are currently not well understood.

The simulation of Coyote series trials conducted by Lawrence Livermore National Laboratory (LLNL) in 1981 involved the release, dispersion, ignition, and combustion of unconfined natural gas clouds in the open-air (Rigas et al, 2006). The simulation is done by using CFD code CFX 5.7 with the standard three-dimensional Navier–Stokes equations, which incorporates the k–ε model for turbulence modeling, the Eddy Dissipation model for combustion, and P1 model for radiation transport modeling. Computational thermal radiation histories were compared with experimental data from totally four trials showing a reasonably good agreement for several locations in the field. Discrepancies were in overestimation of the thermal radiation at a certain location within a factor-of-two of the observed values. Furthermore, the low levels of overpressure obtained through the simulations, and also observed in the experiments, proved that the ignition and combustion of a vapor cloud on the open air results in flash fire rather than a Vapor Cloud explosion.

7.2.7. Vapor Cloud Explosion

The deflagrative combustion of a large cloud of fuel air mixture in the open atmosphere with the production of severe pressure waves is named in the literature Vapor Cloud Explosion (VCE). VCE is a very complex phenomenon due to the influence and the mutual interactions of many physical, chemical and fluid-dynamic parameters. Within industrial risk framework, it is largely accepted that

VCE identifies the gas or vapor explosions in unconfined environment, thus excluding the effects of thermodynamic pressurization due to confinement. Furthermore, detonation regimes are nowadays ruled out. As regard the reactivity of the fuel mixture, which is a key parameter in the definition of the VCE effects, it is important to note that methane, the main component of LNG, is a relatively low reactivity fuel, but increasing amounts of higher and more reactive hydrocarbons in the commercially available LNG (e.g. ethane and propane), though at very low content, may affect the overall reactivity of the mixture.

The consequence modeling of VCE regards essentially the estimation of the peak pressure and impulse of the blast wave produced by the explosion as a function of the distance from the source.

The body of literature regarding VCE modeling is large and referred either to empirical models, lumped parameter models, and distributed parameter models as Reynolds Average Navier-Stokes (RANS) code, generally named Computational Fluid Dynamics (CFD) codes. All main books on industrial safety, as Lees (1996), or HSL guidelines (2002) in UK, report the main empirical and lumped parameter models on VCE, whereas they lack in detailed information on CFD models and codes, as their application to industry is relatively recent and only applied in very specific sectors such as offshore oil and gas production, where VCE risks are severe and likely.

Semi-empirical models which take into account at least some of the physical and geometrical parameters cited above have been proposed and largely adopted in the industrial sectors, at least for far-field effect of VCE and land-use assessment. Examples of empirical models include: SCOPE model by Shell (Puttock, 2000), CLICHE model by British Gas (Advantica Technology Ltd, however based on work of Fairweather and Vasey; 1982 and Chippett; 1984). Examples of semi-empirical models include: Multi-Energy Method also referred as MEM (Van den Berg, 1985), Multi-Energy Method plus Guidance for Appliance of Multi-Energy also referred as MEM + GAME Method (Van den Berg and Eggen; 1996), Baker and Strehlow Method also referred as BS Method (Tang and Baker; 1999), Congestion Assessment Method also referred as CAM Method (Cates and Samuels; 1991).

The Multi-Energy Method and Baker and Strehlow Method are certainly acceptable in the far-field for LNG explosion, while more accurate analyses are necessary when near-field effects are analyzed. In the specific case of VCEs the main difficulties lay in the definition of the initial explosion strength (or more specifically in the peak pressure reached by the flame propagation in the premixed flame) and in the pressure-time profile. Indeed, as for any complex transient, scale dependent, turbulent reactive phenomenon, the prediction of the peak overpressure (and the total duration of blast wave) has to be simplified, thus introducing relevant uncertainties in the analysis.

On the other hand, RANS Computational Fluid Dynamic (CFD) is the only option for detailed analysis of VCE. However, the computational burden (and the required skill) when large scale VCEs are investigated is generally so high that the industrial application is hindered by economical considerations. Furthermore, very large uncertainties are still intrinsically produced by the several assumption on the combustion phenomena when using RANS and results can be only adopted by assuming a number of conservative options. Examples of CFD models include: FLACS, AUTOREAGAS, CFX, CFD-ACE+, STAR-CD, EXSIM, COBRA, FLUENT, etc. Many CFD codes are included in other commercial package (e.g. Autoreagas in ANSYS) or should be considered multi-purpose even if they have been applied successfully in the simulation of VCE.

Up to now, research on LNG explosions has been principally carried out on a laboratory/small scale and few actual field tests have been performed to analyze the behavior of large scale release of LNG when ignited, as the Burro and Coyote test series, (Koopman, et al., 1982a, 1982b, Koopman and Ermak 2007). However, no VCE was observed in any test, considering pressure wave characterized by high intensity in the far field.

Vapor Cloud Explosion is an unclear phenomenon which is still under investigation. Open issues are strictly related to the prediction of interaction among fluid-dynamic and chemical phenomena as in the deflagrative explosions. The development of CFD based on Large Eddy Simulation (LES) could be the next future for numerical simulation of this complex phenomenon also for LNG VCE. Large scale tests for VCE are still missing, mainly due to the high cost of experiments. However, some physic could be resolved by medium scale tests as those produced in US by Texas AM University in pools.

7.2.8. Rapid phase Transition

Rapid Phase Transition generally represents the explosive evaporation of a cryogenic liquid in contact with a large source of heat, such as in the case of LNG and sea water. Since the vapor develops very rapidly, localized overpressure is possible. This is a purely physical phenomenon, does not involve any ignition, fire or other chemical reactions, and has been confirmed by different experimental tests reported in the literature (see for a general overview Atallah, 1997). Due to the importance of this issue, several reviews on the risks related with the release of a large amount of LNG are reported in the literature (Schubach and Bagster, 1996; ABSG, 2004; Sandia, 2004; Shaw et al. 2005; Luketa-Hanlin, 2006; Melhem et al., 2006; Koopman and Ermak, 2007; Bubbico & Salzano, 2009). These papers or guidelines may be the main reference for RPT analysis. Two main aspects are investigated my models: the possibility of RPT occurrence and the blast wave generation and propagation.

Possibility of occurrence models

Due to the many modalities with which the RPT phenomenon can develop, the conditions that allow an actual explosive evaporation to occur are still unclear. Furthermore, it has also been recognized that not always an RPT occurs under seemingly identical conditions (Fredheim et al., 1995; Cleaver et al., 1998). As a consequence, different analyses and models of the mechanism have been proposed in the literature (ABSG, 2004; Atallah, 1997; Conrado & Vesovic, 2000; Havens & Spicer, 2006, Woodward, 2007), and up to now no appropriate methods are available for the calculation of the blast effects from a rapidly expanding vapor or gas volume.

It is generally accepted that RPT likelihood and the corresponding overpressure basically depend on the amount of cryogenic liquid spilled and the velocity of its evaporation, i.e. in other words on the accident scenario in general. Both the above two terms will depend on a number of more specific parameters: the amount of liquid spilled, the localization of the release source (above or below the sea level), the vessel configuration and the operating conditions within that vessel and those outside it, the duration of the release. Most of the scenarios described in the literature, mainly refer to above-water releases. In the case of underwater releases the dynamics of the phenomenon can be more complex. As a general rule, an underwater spill greatly affects RPT occurrence (McRae 1982; 1983, McRae et al. 1983; 1984a; 1984b), even though Atallah (1997) claims that for a 30 cm underwater release, the equivalent explosive mass is between 0.01 and 0.001 times the actual explosive mass.

Both the occurrence of the physical explosion and the calculation of the generated overpressure are based on thermodynamic considerations and in particular on the concept of the superheat limit temperature (Lees, 1996; Katz, 1972; Katz and Sliepcevich, 1971). From the phase diagram of the substance involved, the initial pressure and the maximum theoretical energy involved in the explosion can be evaluated: the maximum energy dissipated during the expansion for pure methane (from 24.6 to 1 bar absolute) is estimated as 56.2 kJ/kg. This value is then reduced by about 50% to give an actual suggested average explosion energy value of 28.1 kJ/kg. A similar treatment is applied to LNG mixtures, and an average value of 37.75 kJ/kg is suggested for the explosion energy.

The composition of the mixture will not only influence the energy involved in the explosion but also the occurrence of the explosion itself. In fact, based on the heat transfer rates under the different boiling regimes, when the temperature difference between the spilled LNG and the sea water is too high, the film boiling regime will establish and the vapor film generated at the interface between the two substances reduces the heat transfer rate and the corresponding evaporation rate. During this initial period of the evaporation phase, methane is preferentially depleted from the liquid LNG, which will progressively enrich in higher hydrocarbons. When the water cools enough and/or the LNG bubble point temperature gets high enough, due to the consumption of methane, the faster (more than one order of magnitude) nucleate boiling heat transfer regime will establish, and an explosive rapid phase transition can occur. Less than 20% of methane and more than 50% of ethane by weight are required for generating a RPT, while it is clearly stated that no RPT is possible with pure methane. This behavior is confirmed (sometimes indirectly) also from some experimental investigation (Fredheim et al., 1995; Cleaver et al., 1998). Garland and Atkinson (1971) found that the presence of a hydrocarbon film on water increases the probability of RPT occurrence. Similar limit contents for methane and ethane (40% and 20%, respectively), are reported from the experimental runs at ESSO (Enger and Hartman, 1972a-d). RPTs characterized by different conditions and strength are reported by the Gas Research Institute (1982) and Porteous and Reid

(1976), however the addition of small amounts of methane (as little as 10 mol %) inhibited RPTs and none were ever obtained with methane concentrations in excess of 19 mol %.

The degree of mixing between LNG and water likely affects the evaporation rate of LNG and thus increase the likelihood of an explosion; conversely, an extensive formation of ice, can markedly reduce the heat transfer rate between the two phases, and thus hinder the generation of an RPT. Besides this effect, ice formation can also interfere with the flow of water or LNG through the hole. Despite these two variables will most probably play a fundamental role in determining the conditions for an explosive evaporation to occur, no information on their influence is available yet, neither from a theoretical point of view, nor from experiments.

Blast models

Due to the inherent complexities in the modeling of the physical phenomenon and to the uncertainties in the scenario evolution, the quantification of overpressure generated by even simpler events is still quite uncertain.

In most cases the overpressure produced by the fast evaporation is calculated conservatively assuming that the whole amount of stored LNG is involved in the expansion, and, a more than conservative explosion model, such as the TNT equivalency model, is also typically adopted. With both these conservative assumptions hazard distances well below those obtainable for other dangerous events linked to an LNG release (e.g. flash fire or vapor cloud explosion), are found. In summary, the hazard potential of RPT can be severe, but is highly localized in the proximity of the spill area.

When the TNT equivalency model is adopted, an explosion efficiency (or yield) is introduced in order to fit the calculated overpressures to the experimental data, when available. Of course, the quantification of this coefficient is highly uncertain and questionable. In some cases values obtained from different processes can be used (Lipsett, 1966; Anderson and Armstrong, 1974), however their applicability to RPT has not been demonstrated yet. Schubach and Bagster (1996), found that in the case of steam explosions the maximum energy yield of RPT is limited by the superheat energy of the cold fluid involved and that only a small fraction of the available superheat energy is transferred into the shock wave. Hence, in terms of energy production, RPTs are less efficient than higher explosives at generating blasts. In this regard, it must be noted that despite it has sometimes been stated that physical explosions provide sharper pulse than deflagrations, TNT is not likely to be a proper model to evaluate the explosion energy and overpressure associated to such a kind of physical expansion. In fact the evaporation rate plays a fundamental role in the dynamics of the phenomenon. Nonetheless, if a proper efficiency coefficient is introduced, values of overpressure relatively close to the actual ones can be obtained. The problem is that, as it has already been observed in different literature sources (see for example IChemE 1994, Strehlow and Baker, 1976), the efficiency factor strongly depends on the explosion typology and circumstances.

Conrado & Vesovic (2000), presented a detailed analysis of the problem, with specific reference to the effect of the mixture composition on the vaporization rate of LNG (and also LPG), as compared with that of pure methane (and propane). It can be noted that their results are in contrast with other results obtained from similar analyses available in the literature (e.g. Melhem et al.; 2006, Luketa-Hanlin; 2006; etc.). Even if the initial assumptions (constant boiling regime, constant heat transfer coefficient) are removed, the qualitative finding does not change much and the vaporization rate of the LNG mixture, even if slightly higher than in the first case, still remains lower than in the case of pure methane. In this model, the main influence on the results is due to the total differential latent heat, so that the effect of a higher content of ethane during the evaporation process results in a drastic decrease of the vaporization rate in the latter stages of the spill. The higher content of ethane in the vapor phase results only in a small increase of the vaporization rate. This result is also in contrast with experimental findings (see next section), where RPTs where observed even for quite smaller contents of higher hydrocarbons.

Independently on the specific value assigned to the explosion efficiency for the TNT equivalency method, its assumption is definitely uncertain and questionable. An alternative approach is to adapt some gas-dynamic model to the calculation of the physical expansion of a gas in the surrounding environment. Such approach has been principally adopted for the analysis of the so-called BLEVE accident (van den Berg et al., 2004) after the catastrophic rupture of pressurized vessels. However no adequate comparison with experimental data has been provided so far. Furthermore, large uncertainties are present in the definition of the volume source strength, i.e., the exact liquid release rate from the vessel and the exact evaporation rate of the flashing liquid as a function of time. In the case of a RPT, these parameters are replaced by the LNG release rate and the evaporation rate after mixing with water. Following this approach, and starting from the fundamental work by Lighthill (1978), Bubbico and Salzano (2009) have recently proposed an acoustic-based model for the assessment of the explosion overpressure and the total energy produced by the RPT of LNG on sea water. These alternative gas-dynamic models require the knowledge of different parameters to characterize the strength of the volume source. They has been validated against experimental data relative to BLEVE accidents (Giesbrecht et al., 1981) and it was found that in the case of a release time of about 0.01 s, a good agreement is obtained. However, in case of RPT the heat transfer phenomena have characteristic times larger than the mechanical equilibria involved in BLEVE, and further validation is necessary.

Model validation

Experimental research on LNG/water physical explosions has been principally carried out on a laboratory/small scale and few actual field tests have been performed to analyze RPTs along with other characteristic dangerous phenomena. A list of reports about some of these experimental tests is reported by Luketa-Hanlin (2006), Gas Research Institute (1982). Partially with the exception of the Coyote test series, practically no specific experiments have been carried out for the study of the RPT phenomenon only. So general reference can be made to the well known experimental research available in the literature and referred to the other dangerous events associated with the use or storage of LNG.

Up to date no theoretical model is able to properly and thoroughly represent of all the many different phenomena occurring during an RPT. Due to the initial simplifying assumptions made by each author when devising a model for an RPT, most of the models available in the literature mathematically correctly represent the influence of only some specific parameters, but when compared with the experimental data, some disagreement is always found. With reference to the experimental data themselves, it must be observed that they not always give clear information on the effect of the different parameters describing the scenario of an RPT, sometimes even providing trends which are in contrast each other.

Furthermore, most of the models are focused on the occurrence of the explosion and not on the consequences of it; i.e., they preliminarily try to identify the conditions which are required to generate a RPT, such as the LNG composition, the temperature of the water, the temperature difference with LNG, etc.

At present no reliable model is available for the calculation of the overpressure associated with the explosive expansion of the vapor generated during an RPT. In the rare cases this attempt is made, the traditional model of the TNT equivalency is adopted. However, a number of fundamental differences exist between the expansion of a vapor, though very fast, generated by heat exchange between two liquid phases, and the detonative reaction of a high explosive. Because of the heat transfer step, RPTs will necessarily occur at much lower velocity than TNT detonations (maximum sonic velocity vs. supersonic velocity). Moreover, the accuracy of the calculations in the near-field by TNT method is well known to be highly questionable.

In the case of submerged releases, the situation is even worse, because the influence of the liquid head produced by the sea water above the release point has also to be taken into account (Shaw et al., 2005).

7.2.9. Burst/BLEVE of the unit

Mechanical explosions are originated by the sudden rupture of a vessel containing high pressure, non-reactive gas. A vessel rupture is coupled with the release of its content and the release of the internal energy. The sudden release of energy may give rise to blast waves and high velocity fragments. In the case of LNG terminals, the significant amounts of internal energy can be released upon burst only by those units which handle pressurized LNG at temperatures higher than its normal boiling point (e.g. recondensers, high pressure canned pumps). Units operated at atmospheric pressure or handling sub-cooled liquids are expected to have only moderate and local effects upon burst.

The calculation of the available internal energy is usually based on the isentropic expansion of the gas phase in the former “vapor space” of the vessel and on the flash of the former liquid phase

(BLEVE). Suitable models for calculating the expansion energy a reported by (TNO Yellow Book) and Baker (1997).

However, the effective release of energy by instantaneous boiling (BLEVE) may only occur if the temperature of the released material is between the superheat and the boiling temperature of the material (Venart et al. [1992]).

The possibility for pressurized vessels containing LNG to produce a BLEVE has been discussed in the literature (Planas et al., 2015; Pitblado, 2007), concluding that the scenario is possible if the accidental conditions are such that adequate superheating of liquid can be reached. Planas-Cuchi et al. (2004) describe an accident occurred in 2002 in Tivissa, Catalonia (Spain) where a BLEVE scenario took place for an LNG road transport truck. Planas et al., 2015 describe another BLEVE accident in Zarzalico, Murcia (Spain) occurred in 2011.

The blast wave events following the release of energy can be modeled by the typical consequence models applied for blast events. These have been introduced in “3.1.7 Vapor Cloud Explosion” and their applicability to blast waves from phenomenon of mechanical energy release (such as the vessel burst) has been extensively discussed in section “3.1.8 Rapid phase Transition”.

The burst of a vessel may be couple with its fragmentation and consequent missile effects. Several methods were proposed for calculating the initial fragment velocity and trajectory. Discussion of the methods is reported elsewhere (Van Den Bosh & Weterings, 1997). Only recently methods were proposed for the prediction of the number of fragments to be expected or the distributions of mass, velocity and range of the fragments (Gubinelli & Cozzani, 2009; Tugnoli et al., 2014). The main input required by these models is again the estimation energy released by the burst/BLEVE.

No specific large scale test is known for studying BLEVE in equipment handling LNG. The only relatively well documented large scale occurrence are the aforementioned accident in Tivissa (Planas-Cuchi et al., 2004) and Zarzalico (Planas et al., 2015) for road transportation trucks.

As evidenced above, no specific consequence models exist for BLEVEs of LNG and no specific validation for LNG has been carried out so far. The validity of the models for LNG is therefore only theoretical.

7.2.10. Fireball

A fireball occurs when a given amount of flammable vapor or gas, previously confined at relevant pressure, is suddenly released into the atmosphere due to a catastrophic rupture of the vessel, and is ignited. For LNG, this scenario is possible as a consequence of the release form a pressurized equipment which undergoes a catastrophic failure in the same conditions described above for the BLEVE (superheated liquid) plus the presence of an ignition source (e.g. flame).

Fireball from LNG equipment ha received moderate attention in the literature, since the enabling conditions for its occurrence are present only in few equipment unit or accidental conditions. The generic fireball models described in TNO Yellow Book (Van Den Bosh & Weterings, 1997), Lees'handbook (Mannan, 2005) and CCPS Guidelines (CCPS, 2012) can be applied to this scenario. An example is presented by Zhang and Liang (2013).

No specific large scale test is known for studying fireball from equipment handling LNG. The only relatively well documented large scale occurrence are the aforementioned accident in Zarzalico (Planas et al., 2015), where a fireball followed a fired BLEVE of a road transportation truck.

No specific consequence models exist for BLEVEs of LNG and no specific validation for LNG has been carried out so far. The validity of the generic fireball models for LNG is therefore only theoretical.

7.2.11. Note: Jet fire

A jet fire may be defined as a flame which "occurs when flammable gas issuing from a pipe or other orifice, with a significant momentum, is ignited and burns on the orifice" (Lees, 1996; Van Den Bosh and Weterings, 1997). As such, only a release containing and high fraction of vapor/gas can originate a jet fire. This is generally not the case for the release through an orifice of cryogenic LNG, and therefore the scenario is not further detailed in this section. A gap analysis of the modeming of this scenario has been carried out within the actifities of the Integrisk Project (Integrisk, 2010). Though consolidated and validated models exist for natural gas jet-fires, the following open issues were identified: molecular gas radiation properties (e.g. heat transport parameters, radiative properties), effect of soot (natural gas jet flames can be considered non-sooty flames but the radiative contribution of soot should be further investigated in detail and quantified), modeling flame impingement on structures (simulation of the effect of possible flame impingement, total heat flux on the structure, etc.).

7.2.12. Summary of the results

In the following table the results of the gap analysis carried out above are briefly summarized.

Table 19 - Results of the scenario gap analysis for LNG terminals.

Scenario	Model Availability	Model Validation
Liquid release through rupture/breach *Into air:*	**GREEN** Alternative models available: • Quasi-one-phase models • Homogeneous equilibrium models (HEM) • Non-homogeneous models • 'Frozen' models	**ORANGE** Validated for different substances Validated in different conditions (T, P)

Into water:	**RED** Only theoretical studies available	**RED** No conclusive validation available
Jet dispersion	**GREEN** Models available for: • Flash or the breakage of the liquid phase • Droplet size, evaporation and the rain-out • Concentration and size of a two-phase jet	**ORANGE** Few validation tests available, incomplete analysis of all the conditions
Liquid pool spreading and evaporation *Pool on land/still water:*	**GREEN** Several models for spreading and evaporation	**ORANGE/GREEN** Some validation experiments carried out and validated some models (more confirmation tests are needed)
Pool on non-still water:	**RED** No model available to account the effect of waves, wind, etc.	**RED** No validation available
Vapor cloud dispersion	**GREEN** Alternative models available: • Distributed parameter models (CFD models) • Shallow Layer Models • Lumped parameter models (Integral Models) • Point source models (Gaussian)	**ORANGE/GREEN** Good predictions in certain ranges of parameters (e.g averaging time, weather conditions). More uncertainty beyond the range (further validation needed: e.g. large scale tests with obstacles)
Pool fire	**GREEN** Alternative models available: • Semi-empirical models • Field models	**ORANGE/GREEN** Some validation tests available, more tests/data needed for complete validation Field modes require more work validation (complexity in describing phenomena involved)

Flash fire	**ORANGE** Alternative models available: • Dispersion based models (low detail) • Diffusive flame models (low detail/limited data for applicability) • CFD models (high complexity/high need of reliable input data)	**ORANGE** Limited validation (few cases). Further tests/validation trials needed
Vapor Cloud Explosion	**GREEN** Alternative models available: • Empirical models • Lumped parameter models • Distributed parameter models	**RED** No VCE observed in a large scale test.
Rapid phase Transition *Above water release:*	**RED** Few theoretical approaches; incomplete modeling of phenomena involved (e.g. ice formation, interaction with waves)	**RED** Few occurrences in field tests. No validation trial available.
Under water release:	**RED** No model (theoretical speculations only)	**RED** No test
Burst/BLEVE	**ORANGE** Burst and BLEVE models developed for other materials (simplified assumptions present in original models)	**ORANGE** No test for LNG (Validation of models based on other substances/conditions)
Fireball	**ORANGE** Fireball models developed for other materials (simplified assumptions present in original models)	**ORANGE** No test for LNG (Validation of models based on other substances/conditions)

8. Emerging Risk 2 – Biogas Production

8.1. Scenario identification

The configuration of anaerobic digestion facilities for biogas production varies according to several factors such as the nature and the quality of the fed substrate, the bacteria species involved and the final requirements for the resulting biogas, either to be burned in a Combined Heat and Power (CHP) generation unit or to be upgraded to biomethane.

A large variety of organic substrates can be used as feedstock in order to obtain biogas. In agricultural installations, the substrates used are mostly animal manure and energy crops. In addition, organic wastes may be suitable for biogas production. The main difference is the methane content that can be achieved in the biogas, which is highest for wastewater (68% by volume), followed by livestock (60 % by volume) and food waste (50 % by volume).

Despite the kind of feedstock, the main steps for biogas production are the following:

- anaerobic digestion, which takes place in the digester, which is the core component of the plant. The digestion can be carried out in a single stage, or in two stages according to the substrate handled and to economic considerations about the desired yield in biogas and the retention time;
- hydrogen sulfide removal, which is usually carried on within the digester itself. In some case, however, this is impossible due to the characteristic of the type of digester used and the hydrogen sulfide content is thus reduced by means of a dedicated scrubbing column; this might be also the case for substrates producing biogas particularly rich in H_2S;
- drying, that is generally achieved by cooling the biogas stream by means of a chiller.

The biogas demand can vary during the time. For this reason, it is necessary to store it in a gasometer. In most of cases, this is done directly onto the top of the digester itself by covering it with an elastic membrane able to handle the fluctuation in both biogas demand and production.

Figure 14 shows some alternative reference schemes considered for hazard identification in biogas production. The configurations have been based on several existing installations an on an extensive literature survey (Scarponi et al., 2015). The main difference between the schemes proposed and summarized in Figure 14 is the type of feedstock used: feedstock from agriculture similar can be used in Schemes A, B and C; feedstock from the agricultural processing industry such as food waste can be used in Scheme D; and wastewater can be used in Scheme E.

- Scheme A shows the basic reference scheme for biogas production: single digester with internal desulfurization.
- Scheme B is a single digester with external desulfurization; it is used to produce biogas as in Scheme A but hydrogen sulfide is removed in a dedicated bio-scrubbing column.
- Scheme C is a characterized by two digesters with internal desulfurization: the primary digester has a fixed roof, and the secondary digester is of the type used in Scheme A. In this case, the desulfurization takes place in the secondary digester, using the same technology as in Scheme A.

- In Scheme D waste from food industry is used and this type of substrate produces a stream less rich in methane, the inventory of biogas in the digester is higher with respect to all the other configurations, in order to maintain constant the production of energy at the CHP unit.
- Scheme E is an example of Upflow Anaerobic Sludge Bed reactor (UASB), which represents a technology diffused worldwide in wastewater treatment plants in which the methanogenic bacteria form a sludge that is suspended in the water to be treated. The wastewater flows from the bottom of the reactor upwards through the sludge of bacteria, producing a biogas particularly reach in methane, which is then transferred to a desulphurization column by means of a blower and finally dried.

Biogas upgrading to biomethane is the operation in which the methane content of raw biogas coming from the production phase (desulfurized and dried) is raised to meet the quality requirements for final utilization. For what concerns this process, five different reference processes were considered (Figure 14):

- Pressure Swing Absorption (PSA), in which CO_2 present in desulfurized biogas is adsorbed in zeolites or activated carbon at different pressure levels. This technology requires desulfurized gas to avoid the poisoning of the adsorption material. For this reason, a desulphurization stage precedes the adsorption columns. The upgrading technology consists of four adsorption columns filled with adsorption bed. Each column alternates four operative cycles: adsorption (i.e. take-up of H_2O vapour and CO_2 at a pressure of 8 bar), desorption (by pressure relief), evacuation (i.e. further desorption by flushing with raw gas or product gas) and pressure build-up. The reference scheme is thus composed by a compressor, a desulphurization unit and the four adsorption columns.
- Amine Absorption (AA), in which the CO_2 present in biogas is adsorbed in a solution of amine and water. There are several types of amine that can be used for this purpose such as monoethanolamine (MEA), diethanolamine (DEA), methyldiethanolamine (MDEA), etc. The absorption is carried on in a packed column as well as the regeneration of the amine. The upgraded biogas is than dried. The reference scheme considered here consists of a compressor (absorption pressure 1 barg), the absorption and regeneration columns and a dryer.
- Membrane Separation (MS), in which biogas is separated in CO_2 and CH_4 because of the specific selectivity of membranes modules. In this case, the presence of H_2S is detrimental since it can degrade the membrane. For this reason, a desulphurization unit is required before the biogas stream enter the membrane module. The reference scheme is composed by a compressor (operating pressure was assumed of 19 barg), a desulfurizer and the membrane module.

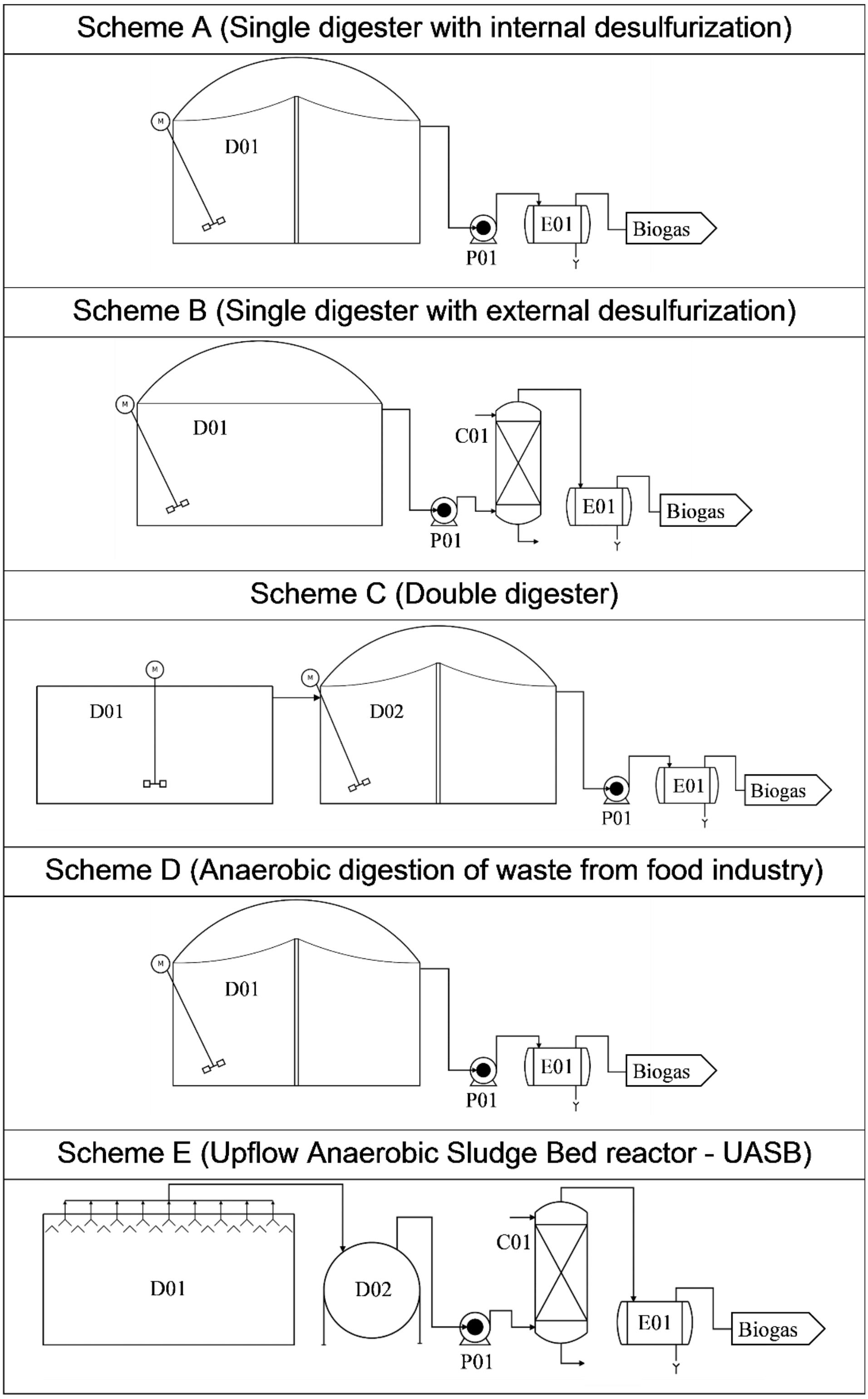


Figure 14 - Reference process schemes for biogas production from different feedstock.

- Water Scrubbing (WS), in which CO_2 present in biogas is dissolved in water at medium pressure (8 bar were considered in the present study). Biogas is compressed up to 8 bar and enter the scrubbing column where is put in contact with water. The resulting gaseous stream is then dried. The outflow water, rich in carbon dioxide, is regenerated in a stripping column with air at atmospheric pressure. The reference scheme encompasses a compressor, the absorption and stripping columns and a dryer.

- Cryogenic Separation (CS), in which CO_2 is separated from CH_4 by cooling the stream at high pressure (e.g. 80 bar and - 45 °C). Condensed carbon dioxide is removed in a separator and is further processed to recover dissolved methane which is recycled to the gas inlet. The gas is cooled further to approximately - 55 °C by heat exchangers. The cold gas undergoes an expansion through a Joule-Thomson nozzle into a flash vessel. The pressure in the vessel is 8 bar and the temperature approximately - 110 °C. The carbon dioxide freezes and is separated from methane. The reference scheme is composed by a multistage compressor, 6 heat exchangers, a separator vessel and a flash vessel.

For what concern the last step of the supply chain, i.e. final use, three main alternative processes can be considered:

- raw biogas combustion in a CHP unit,
- injection of the biomethane in the natural gas grid, and
- compression of the biomethane to be used as fuel for transportation purposes.

The first alternative is achieved by installing a combustion engine after biogas drying and desulfurization sections. This solution currently represents the reference technology for biogas final use, being the default option presently installed in the wide majority of the existing biogas production sites. Part of the energy produced in the CHP unit is directly used on site to produce the steam to keep a constant operating temperature in the anaerobic digester.

If injection in the national gas grid is considered, the stream has to meet the requirements of the grid in terms of inlet pressure and composition. Tasks as adjustment of the heating power by propane dosing are usually needed.

Finally, if the use as fuel for transportation purposes is considered, biogas has to be compressed and stored at a pressure from 200 to 260 bar. The reference scheme defined is thus composed by a compressor and a storage tank.

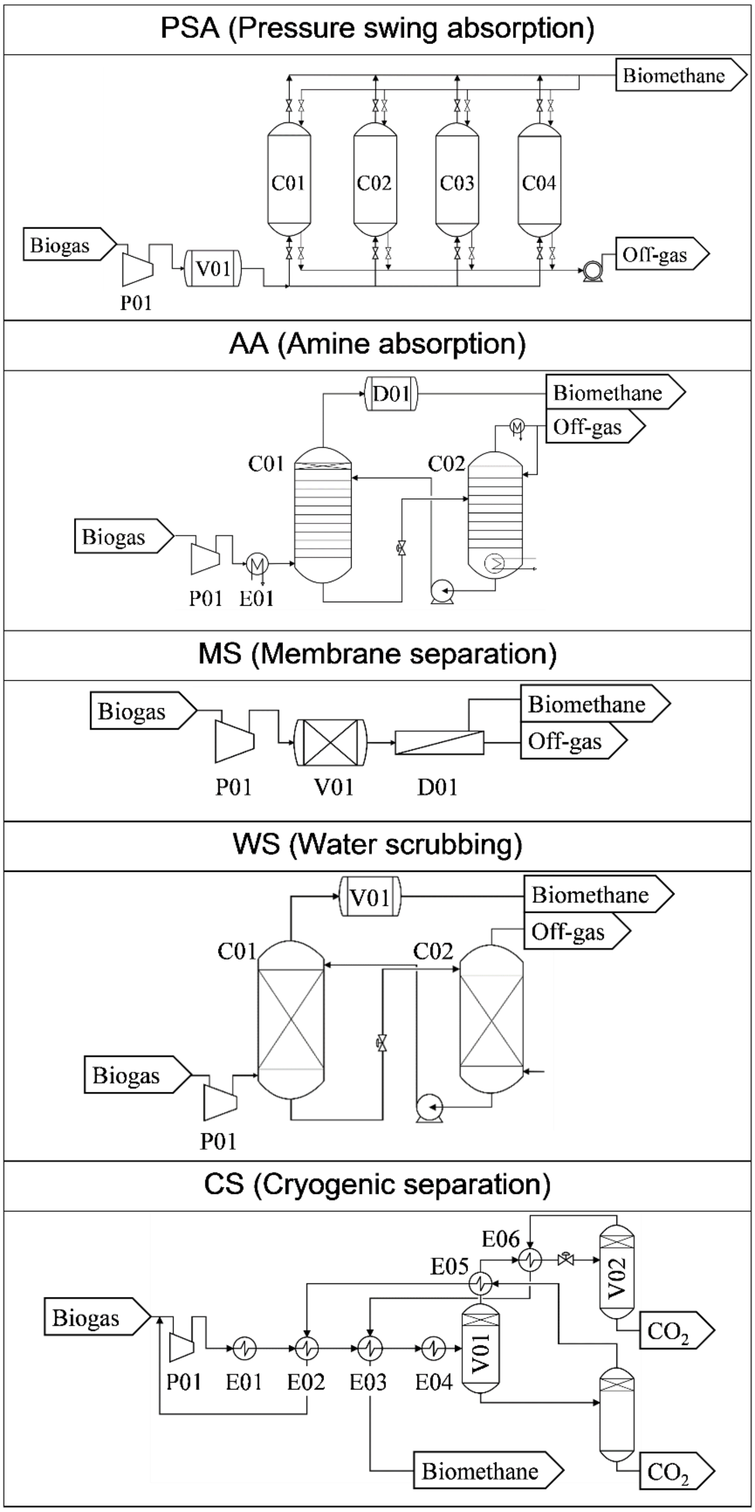


Figure 15 - Reference process schemes for biogas upgrading.

The reference schemes identified above were the basis of a hazard identification effort aimed at the identification of the accident scenarios of concern for this kind of installation. The following hazard identification techniques were applied:

- **Survey of past accidents occurred in biogas facilities (past accident analysis)**: data on past accidents were obtained from different accident databases with the purpose of identifying the critical issues related to this technology and the new possible threats. The analysis of these data has shown that the main causes of accidents are (in order of quantitative importance): equipment failure, meant as a set of components; component failures; maintenance errors, defined as operations carried on during maintenance that caused an incident, or the lack of maintenance itself; operational errors; design errors; others (e.g. malicious acts).
  The scenarios associated with accidents at biogas production facilities are mostly related to fire, explosion and release of raw biogas from the digester (i.e. still containing hydrogen sulfide). However, accidents due to access in confined space leading to asphyxiation are also reported. With respect to the release of biogas, raw biogas was released together with slurry from the digester. In most of these cases, biogas was dispersed in air with no further consequences. However, in a significant number of unignited release events the presence of hydrogen sulfide in the raw biogas caused several fatalities, due to its inhalation by unprotected operators. Thus, on the basis of these data it seems reasonable to assimilate the hazard posed by unignited raw biogas dispersions to that posed by toxic releases.
  The categories of causes identified were used to apply Multi Correspondence Analysis (MCA) (Rivière and Marlair, 2010) in order to evaluate possible influence of the accidental causes on the resulting scenarios. The results of the MCA showed that:
  - "Release" of biogas is mainly caused by: (1) Equipment failure, (2) Component failure, and (3) Operational error.
  - "Explosion" is mainly caused by: (1) Maintenance errors, and (2) Design errors.

- **MIMAH methodology (Methodology for the Identification of Major Accident Hazards)**: the bow-tie analysis, applied according to the MIMAH methodology (Delvosalle et al., 2006), allowed the identification of the critical events associated to each process scheme. Three main type of loss of containment were identified: catastrophic rupture of the equipment with biogas hold up (a), leak from pipe (b) (small to large), and breach on the shell (c) (small to large).
  The generic fault and event trees proposed from MIMAH had to be substantially modified and integrated to adapt to the case of biogas. The piece of equipment that needed more modifications was the digester that, according to the methodology, was classified as a reactor. As mentioned before, the gas dome (gasometer) is made of two membranes and serves as gas storage: this peculiarity does not have anything similar in the MIMAH methodology. Furthermore, according to the study published by Casson Moreno et al. (2015), the rupture of the gasometer seems to be a relatively common critical event. Since gasometer and digester are integrated, the fault tree for the CE "Catastrophic rupture" of

the digester includes both the catastrophic rupture of the digester itself and the catastrophic rupture of the gasometer.

Being essentially units at atmospheric pressure, the release of hazardous material in gas state occurs as a consequence of catastrophic ruptures. The expected scenarios in this case are the one related to release and possible ignition of a gas cloud (flash fire, vapour coud explosion, toxic cloud dispersion), while minor breaches/pipe failures are expected to lead to minor consequences. In the case of digesters, a scenario of confided explosion in the digester is also possible as consequence of the formation of a flammable mixture: this may lead to overpressure generation and missile ejection.

The comparison of the event trees obtained for the alternative upgrading technologies evidences great similarity among the results. For each unit, a pressurized gaseous release from a breach in the shell/connected pipework may potentially lead to VCE, flash-fire, jet-fire and toxic dispersion (if relevant, as e.g. for H_2S presence). This confirms that the similitude in the material properties and operative conditions (pressurized equipment with low inventory handling hazardous gas) inherently influence the hazardous scenario that may be originated.

Finally it should be noted that some specific hazards may originate if additional hazardous materials are present: this is the case of upgrading options involving amine solutions, where formation of toxic clouds from liquid leaks should be considered.

The results, in terms of critical event (top-event or loss of containment event) obtained from the hazard identification techniques listed above were integrated and homogenized in a single set of reference results for a generic biogas production and upgrading installation. Moreover the results refer solely to the release of biogas/biomethane and do not include accident scenarios related to the presence of auxiliary materials (e.g. ammines).

It should be noted that these results refers to generic installations, missing the specific issues and hazards that may characterize actual plants. Specific assessment by relevant hazard identification methods is complemented, but not substituted by the list. Moeover, the results presented in the following refer to potential hazards, irrespectively of their actual possibility and/or credibility for a given plant. As such, it ignores protection and prevention measures (even inherent and passive) that may exclude the occurrence of scenarios or causes in actual plants.

Table 20 lists and compare the critical events identified for the alternative schemes considered for biogas production and upgrading units. It should be noted as, with a few exceptions (digester failure), the release events are qualitatively similar among all the units considered.

Table 20 - Critical events identified for reference layouts for biogas production and upgrading equipment (see Table 16 for codes of the critical event).

Unit class	CE	Atmospheric / Pressurized Service
Anaerobic Digester (Primary or Secondary)	CE6, CE9, CE10	atmospheric
Blower	CE9	atmospheric
Dryer	CE9	• atmospheric • pressurized (amine absorption and water scrubbing)
Desulfurization column	CE6, CE9, CE10	• atmospheric • pressurized (PSA)
Compressor	CE9	pressurized
Absorption column	CE9	pressurized
Regeneration column	CE9	pressurized
Membrane module	CE9	pressurized
Scrubbing column	CE6, CE10	pressurized
Heat exchanger	CE9	pressurized
Flash	CE6, CE9	pressurized

Figures from Figure 16 to Figure 18 shows the set of event tree associated to the critical events identified above. As evident from the figures, a number of different accident scenarios is possible depending on the condition of the material before release, of the releasing equipment, of the location, of the type of release.

	Critical Event	Secondary Critical Event	Tertiary Critical Event	Dangerous Phenomena
a)	Leak from gas pipe (CE9)	Gas jet / low velocity release	Gas dispersion	VCE
				Flash fire
				Toxic cloud
				Environmental damage
			Gas jet ignited	Flare
				Toxic cloud
				Environmental damage

Figure 16 - Event tree for the critical event Leak from pipe for blower and drier (if operated in atmospheric conditions).

	Critical Event	**Secondary Critical Event**	**Tertiary Critical Event**	**Dangerous Phenomena**
a)	Catastrophic rupture (CE10)	Confined Explosion	Confined Explosion	Missiles ejection
				Overpressure generation
		Gas puff	Gas dispersion	VCE
				Flash fire
				Toxic cloud
				Environmental damage
			Gas puff ignited	Toxic cloud
				Flash fire
				Environmental damage

	Critical Event	**Secondary Critical Event**	**Tertiary Critical Event**	**Dangerous Phenomena**
b)	Leak from gas pipe (CE9)	Gas jet / low velocity release	Gas dispersion	VCE
				Flash fire
				Toxic cloud
				Environmental damage
			Gas jet ignited	Flare
				Toxic cloud
				Environmental damage

c)

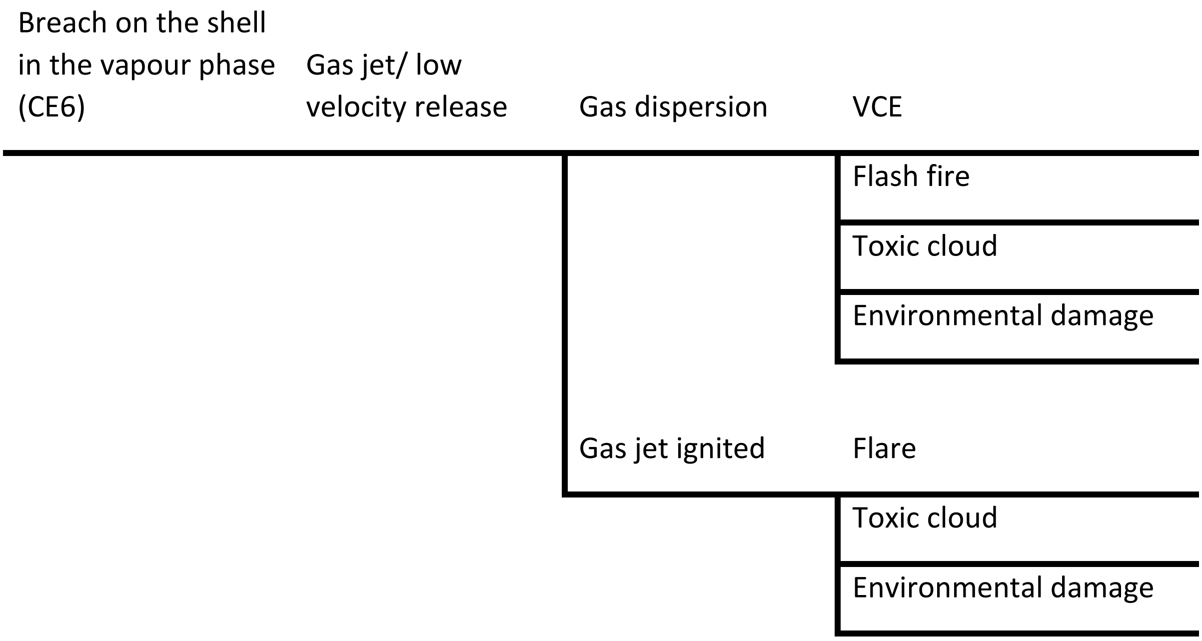


Figure 17 - Event trees for the critical events: a) Catastrophic Rupture; b) Leak from pipe; and c) Breach on the shell for anaerobic digester and desulfurization column (if operated in atmospheric conditions).

	Critical Event	Secondary Critical Event	Tertiary Critical Event	Dangerous Phenomena
a)	Catastrophic rupture (CE10)	Catastrophic rupture	Catastrophic rupture	Missiles ejection
				Overpressure generation
		Gas puff	Gas dispersion	VCE
				Flash fire
				Toxic cloud
				Environmental damage
			Gas puff ignited	Toxic cloud
				Flash fire
				Environmental damage
b)	Leak from gas pipe (CE9)	Gas jet	Gas dispersion	VCE
				Flash fire
				Toxic cloud
				Environmental damage
			Gas jet ignited	Jet fire
				Toxic cloud
				Environmental damage

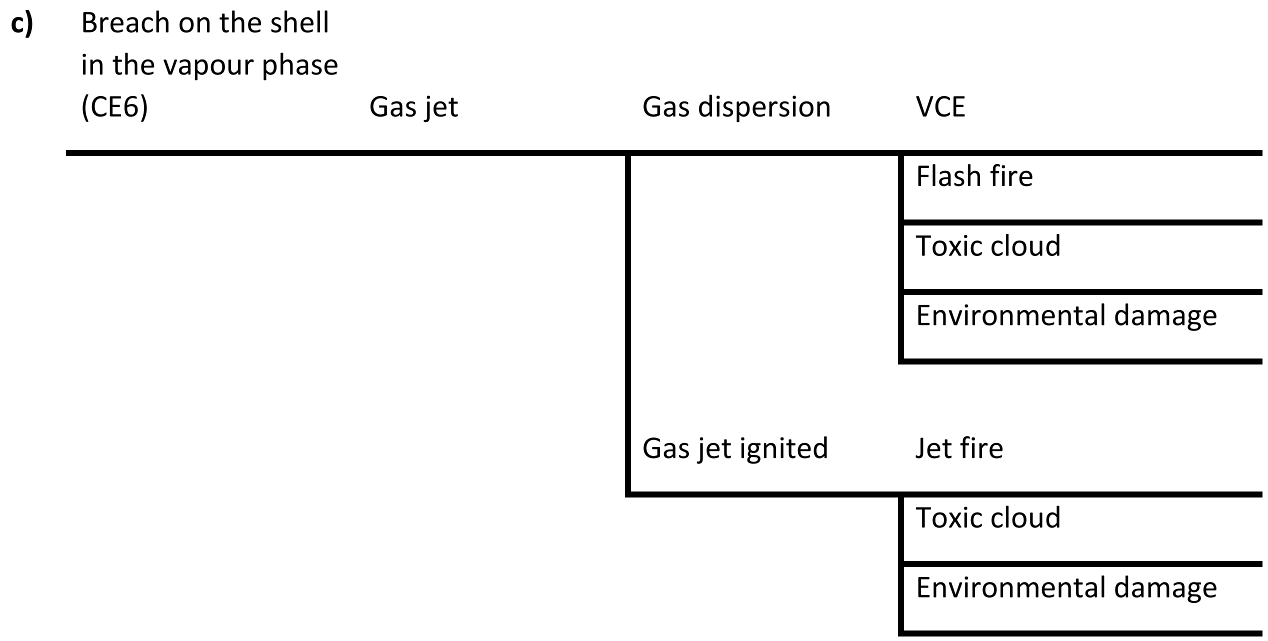


Figure 18 - Event trees for the critical events: a) Catastrophic Rupture; b) Leak from pipe; and c) Breach on the shell for pressurized equipment (only the relevant CE apply as specified in Table 20).

Among the possible scenarios, the attention in gap analysis was focused only on the one that are originated form the release of raw or not-completely-treated biogas (digester, desulfuration unit, etc.) since in this phases the released biogas may present contaminants of upmost interest in the definition of the hazard profile (e.g. H_2S).

As a matter of facts, scenarios involving release of biomethane or methane/carbon dioxide mixtures are well known accident scenarios in the Oil&Gas and energy sector, for which consolidated models are available.

Hence, from the point of view of consequence modeling, the analysis of the scenarios in Figure 17 - Event trees for the critical events: a) Catastrophic Rupture; b) Leak from pipe; and c) Breach on the shell for anaerobic digester and desulfurization column (if operated in atmospheric conditions). identified the following phenomena to be screened for gap analysis (Task 2.3):

- Gas release (rupture/breach or quasi-instantaneous)
- Vapor cloud dispersion
- Vapor cloud explosion
- Flash fire
- Confined explosion of a digester

8.2. Gap analysis

In the following the models available for the scenarios identified in task 2.2 will be screened for gap analysis.

8.2.1. Gas release (rupture/breach or quasi-instantaneous)

Biogas installation can release hazardous gas mixtures which many compose of methane, carbon dioxide and water, plus some minor components (hydrogen sulfide, ammonia). As evidenced from the hazard identification in task 2.2, the release may occur from either pressurized or quasi-atmospheric equipment.

In case of release from pressurized equipment, the dynamic of the release phenomenon is mainly driven by the pressure inside the equipment. The modeling of continuous and instantaneous gas release of from pressurized equipment failure has been extensively discussed in the literature and consolidated models can be found in several references (Van Den Bosh & Weterings, 1997; Mannan, 2005). Per se, the components of the biogas do not present particular modeling issues (e.g. phase change) in the typical condition involved in the release. The release models typically need information on the average properties of the released gas mixture, that can be easily and reliably calculated from available thermodynamic models and constitutive equations.

The models of interest in the case of pressurized gas are:

- models for continuous release of a compressible gas through a hole (e.g. Yellow book model, DISC / ATEX model, Maytal model real gasses);
- models for continuous release of a compressible gas through a pipe (e.g. Wilson model, GASPIPE model);
- models for instantaneous release/expansion of a compressed gas (e.g. Gas expansion model).

These release models, may not have been explicitly validated for biogas mixtures, but extensive experience and validation exist for similar gases and they can therefore be considered sufficiently reliable.

In case of release from quasi-atmospheric equipment, the pressure inside the equipment is no more the only driver of the dynamic of the release, but also the velocity field in the receptor environment and the diffusive/turbulent-diffusive mass transport phenomena in the region of the release point can play a key role. For continuous releases, the use of the typical models for pressurized gas outflow (or even for liquid outflow, given the moderate effect of gas compressibility in low pressure releases) is possible only if the pressure difference between the equipment and the environment is considered as the only driving force. More accurate description of the phenomena require the application of fluid-dynamic codes (Computational Fluid Dynamics, CFD), which have the ability to describe such issues in reliable way. This has a well known burdens in terms of resources and time required.

In case of instantaneous release from quasi-atmospheric equipment (e.g. release from collapse of a digester roof), the use of a CFD code appears the only viable option for a modeling able to take into consideration the geometry of release phenomenon. The use of other over-simplistic models (e.g. considering at time t=0 the entire volume of gas to form a pure biogas cloud at the former location of the digester, i.e. application also in this case of the hypothesis of the instantaneous "gas expansion model") seem to be conceptually inadequate and not necessary more conservative (e.g. the initial shape and dimension of the cloud affects dispersion modeling).

Limited attention has been devoted to modeling of this kind of quasi-atmospheric, since mainly near-field consequences are expected from these scenarios. However he growing concern for safety of in-plant operators and for assent integrity (in-plant domino escalation) points out the need of adequate modeling of these source terms. In fact a correct evaluation of the release flowrates in these low velocity cases will strongly affect the modeling of the subsequent dangerous phenomena, such as dispersion of to toxic components of the mixture (e.g. hydrogen sulfide) or flare-like flames upon ignition. More effort is therefore needed in developing and validating suitable modes.

8.2.2. Vapor cloud dispersion

The release of an unignited gas mixture form a biogas facility is generally followed by an atmospheric dispersion phenomena. Several conventional models are applicable in this phase, mainly depending on the characteristics of release and released material:

- Free jet models are used to describe scenarios in which the released material have a high initial momentum (e.g. hole in a pressure vessel): e.g. Chen and Rodi (1980)
- Plume rise/rounding models are used to describe the early phases of atmospheric dispersion of a chemical, where both initial momentum and buoyancy forces influence dispersion (e.g. hot/cold gases with moderate outflow velocities): e.g. Hoot, Meroney and Peterka (HMP, 1973), Briggs (1969)
- Dispersion of neutral or positively buoyant clouds and plumes is described by passive dispersion models: e.g. Gaussian model, ALOHA, UDM (Unified Dispersion Model), Neutral Gas Dispersion model (Yellow Book third ed 2005)
- Dispersion of negatively buoyant (dense) clouds and plumes is described by passive dispersion models: UDM model (Witlox & Holt, 1999) DEGADIS (Spicer & Havens, 1989) HEGADIS (Colenbrander & Puttock. 1983), SLAB (Ermak (1990))
- Short distance / Complex Terrain dispersion models: CFD based models impended in various software, as e.g. FLACS, Ansys-CFX, Fluidyn-PANACHE, FLUENT, OpenFoam, QUIC.

Per se, none of these models is known to have been explicitly validated for gas releases from a biogas facilities. However, they are consolidated literature models for which validation with a number of gases is well established. Therefore the models may be generally considered reliable also for biogas releases.

Modeling the dispersion from a release in a biogas plant requires to describe the behavior of a mixture of gases. A typical biogas release from a digester may contain different components (methane, carbon dioxide, water, hydrogen sulfide, ammonia, etc.) whose atmospheric dispersion behavior can be different due to their different properties (molar mass, diffusivity, rain out, etc.) and due to their mutual interaction in the cloud.

In the usual practice, the dispersion modeling of a gas mixture is typically tackled introducing a reference substance: this is a “virtual” substance with properties that are an average of the properties of the actual components of the mixture, calculated at the composition of release. The dispersion is modeled for the “virtual” reference substance as if it was a pure material, and the spatial concentrations of the single components are back-calculated assuming that the overall composition of the initially released mixture is maintained in any point of the cloud. This is equivalent to say that all the single components of the mixture disperse without any separation phenomena. Considering that the components present in biogas may have significantly different properties (e.g. molar mass), separation phenomena in the cloud may occur, and the concentrations calculated with the model above may be an inadequate representation of the real behavior. The separation phenomena in the cloud are of particular interest for biogas release, since the different components present different hazard profiles (methane is flammable, hydrogen sulfide is toxic and flammable, etc.) and an incorrect representation of the cloud behavior may result in bias in the risk evaluation.

CFD codes are expected to be the best option for modeling this kind of separation problem: they have demonstrated in other fields of application (combustion modeling, turbine design, etc.) to be able to model the kind of phenomena involved in dispersion of gas mixtures. Nevertheless full validation for large scale biogas dispersion events is still missing.

8.2.3. Flash fire

The release and dispersion over a non-congested area of a gas mixture containing flammable components may result in a flash fire if substantial quantities of materials are in points with concentrations above the lower flammability limit and an adequate ignition source is provided. Since biogas is a mixture containing also non-flammable components (e.g. carbon dioxide), the effect of these components has to be appropriately taken into account in the flame modeling (i.e. effect on the stoichiometry of the combustion, on the flammability limits, on the combustion kinetics, etc.).

An extensive discussion of the models available for flash-fire and of their inherent limitations and drawback was provided earlier in the ”Flash fire” section of the “7. Emerging risk 1: LNG terminals” and are not repeated hare for sake of brevity. No specific issues of these models are identified for the case of application to biogas mixture.

No validation test of these models is known for gas releases from a biogas facility.

8.2.4. Vapor Cloud Explosion

The deflagrative combustion of a large cloud of fuel air mixture in the open atmosphere with the production of severe pressure waves is named in the literature Vapor Cloud Explosion (VCE). In biogas release, some components of the release mixture are flammable (methane, hydrogen sulfide, ammonia, etc.) and in case of ignition and other enabling conditions (e.g. partial confinement) VCE is possible. As regard the reactivity of the fuel mixture, which is a key parameter in the definition of the VCE effects, it is important to note that methane, the main flammable component of biogas, is a relatively low reactivity fuel, but increasing amounts of other more reactive compounds may affect the overall reactivity of the mixture.

The body of literature regarding VCE modeling is large and contains models with different level of detail (empirical models, lumped parameter models, distributed parameter models as Reynolds Average Navier-Stokes (RANS) code, generally named Computational Fluid Dynamics (CFD) codes). All the reference books on industrial safety, as Lees (1996), or HSL guidelines (2002) in UK, report the main empirical and lumped parameter models on VCE, whereas they lack in detailed information on CFD models and codes, as their application to industry is relatively recent and only applied in very specific sectors such as offshore oil and gas production. Examples of empirical models include: SCOPE model by Shell (Puttock, 2000), CLICHE model by British Gas (Advantica Technology Ltd, however based on work of Fairweather and Vasey; 1982 and Chippett; 1984). Examples of semi-empirical models include: Multi-Energy Method also referred as MEM (Van den Berg, 1985), Multi-Energy Method plus Guidance for Appliance of Multi-Energy also referred as MEM + GAME Method (Van den Berg and Eggen; 1996), Baker and Strehlow Method also referred as BS Method (Tang and Baker; 1999), Congestion Assessment Method also referred as CAM Method (Cates and Samuels; 1991).

The main drawbacks and limitations inherent to the model have been discussed in the ”Vapor Cloud Explosion” section of the “7. Emerging risk 1: LNG terminals” and are not repeated hare for sake of brevity. No specific issues of these models are identified for the case of application to biogas. Clearly enough, the effect of the presence of non-flammable components of the mixture has to be appropriately taken into account in the flame modeling (i.e. effect on the stoichiometry of the combustion, on the flammability limits, on the combustion kinetics, etc.).

No validation of these models is known for gas releases from a biogas facilities; this is also partially due to the fact the phenomenon is believed to be unlikely (low confinement levels are typical in biogas plants).

8.2.5. Confined explosion of a digester

Formation of a flammable mixture in a digester is possible as a consequence of procedural errors and/or control system failure. A confined explosion will result from ignition of such mixture inside the digester.

Confined explosion have been widely studied for a number of industrial applications (reactors operating near/within flammable range, equipment handling flammable dust, etc.) and specific models exist for the design of appropriate vent areas and for the estimation of the overpressure generated (Forcier and Zalosh, 2000; Whitham, 1956; Mannan, 2005).

The roof of a typical digester also works as a gasometer, and usually offers a minor resistance to overpressure generation, working as a large vent area. Hence, overpressure generation outside the digester is expected to be moderate and, in particular, quite low in the far-field. This makes usually not of interest the application to this scenario of the simplest models used for blast wave propagation (Baker-Strelow, MultyEnergy, etc.), which are only applicable in the far-field (see “Rapid Phase Transition” section of the “7. Emerging risk 1: LNG terminals”). In the near-field the overpressures, if of any relevance for safety, can be effectively modeled only by more complicate approaches (e.g. CFD).

The occurrence in the past of this accident (e.g. Daugendorf 16/12/2007) has also evidenced the possibility of significant loss of containment of the liquid sludge from the digester and of fragment projection form equipment failure. These scenarios need further investigation as no validated models are available for the biogas digester.

8.2.6. Summary of the results

In the following table the results of the gap analysis carried out above are briefly summarized.

Table 21 - Results of the scenario gap analysis for Biogas production.

Scenario	Model Availability	Model Validation
Gas release through rupture/breach or quasi-instantaneous *From pressurized equipment:*	**GREEN** Models available for: • Continuous release of a compressible gas through a hole • Continuous release of a compressible gas through a pipe • Instantaneous release/expansion of a compressed gas	**GREEN/ORANGE** Validated for different substances (no relevant difference is expected for biogas mixtures)
From quasi-atmospheric equipment:	**RED** No models available. CFD may be applicable.	**RED** No validation
Vapor cloud dispersion	**ORANGE** Models available for pure gases: • Free jet models • Plume rise/rounding models • Passive dispersion models (positively buoyant and neutral gas) • Passive dispersion models (negatively buoyant gas) • Short distance / complex terrain dispersion models (CFD) Models non applicable to gas mixtures if component separation occurs (except CFD)	**ORANGE** Models validated for pure gases on many substances No validation available for dispersion of gas mixtures
Flash fire	**ORANGE** Alternative models (non-specific for biogas) available: • Dispersion based models (low detail) • Diffusive flame models (low detail/limited data for applicability) • CFD models (high complexity)	**ORANGE** Limited validation. Validation available only for other materials.

Vapor Cloud Explosion	**ORANGE/GREEN** Alternative models (non-specific for biogas) available: • Empirical models • Lumped parameter models • Distributed parameter models	**ORANGE** Limited validation. Validation available only for other materials.
Confined explosion in digester	**ORANGE/GREEN** Models for venting confined explosion may be applicable CFD may be applied to model near-field effects	**ORANGE** No validation for biogas digesters is available.

9. Emerging Risk 3 – Carbon capture transportation and storage

9.1. Scenario identification

The potential hazards and accident scenarios coming from CCS technologies have been discussed in several studies. It is common agreement that the hazard profile of the CCS system depends on the details of the technology employed and on the design and layout of the plant. CCS introduces new processes for the capture of CO_2, the transportation and the storage. The review of CCS hazards studies proposed in IntegRisk Project is summarized in the following:

Early studies

Early identification of potential hazards was presented by Connolly and Cusco (2007). A high level HAZID was carried out by HSL for IEA Greenhouse Gas R&D Programme (Wilday et al, 2009) and identified a large number of hazards/emerging risks. From these a smaller number of key emerging risks have been selected, since of interest for consequence modelling purposes:

- Explosions (effect: overpressure & thermal). Examples of explosions include explosions due to: loss of containment of oxygen in the capture processes (oxi-combustion) and subsequent explosion with any available fuel; loss of containment of hydrogen or synthesis gas from the capture process (pre-combustion) and explosion with air; loss of containment of high pressure CO_2 leading to BLEVE (transport and storage). The first two examples of explosions would be exacerbated by confined/congested plant areas, due to the retrofitting of CCS into existing plant where there is limited space.
- Fires (thermal effects). Examples include fires due to release of flammable amines or other solvent used for CO_2 capture.
- Sudden Emission/Emanation of gas = CO_2 mixture (toxic effect). This would be from a major equipment failure, e.g. of a pipeline transporting CO_2 (expected to be up to 1 metre diameter at up to about 200 bar), from intermediate storage (potentially several thousand tonnes of CO_2 in semi-refrigerated tanks, particularly for transportation by ship), from a ship (potentially several thousand tonnes of CO_2 in semi-refrigerated tanks) or during injection.

Storage of CO_2 in underground saline aquifers, depleted oil and gas reservoirs, and/or coal seams gives rise to some process-related risks (e.g. due to the drilling and use of monitoring wells, failure of the capping of injection wells) but also to very long-term risks of the CO_2 escaping. These long-term risks are beyond current analysis.

Past accident analysis

While there is a considerable history of incidents involving CO_2, there is lacking specific experience with regard to CCS-related technologies: the oldest CO_2 injection site was initiated in Sleipner in 1996. A review by HSE-HSL on CCS safety is given as an Appendix to (Wilday et al, 2009). This includes a well blow-out incident in Hungary in 1998 where CO_2 with H_2S impurities was being injected for enhanced oil recovery: 2500 people were evacuated. There are also many incidents involving much smaller scale CO_2 fire extinguishing systems. In the USA between 1975 and 2000 there were 51 incidents overall resulting in 72 deaths. In 2008 over 100 people, including firefighters, were affected by a release of CO_2 from a fire suppression system as a result of a fire in a paint factory in Munchengladbach, Germany.

The main source of emerging risk from CCS for surface installations is the release of a large quantity of CO_2. Other risks have been identified and include fire/explosion involving oxygen, synthesis gas or the solvent used for post-combustion capture. However these are all existing types of hazard, albeit on a very large scale for CCS. Impurities in the CO_2 will modify the risk, including its toxicity and the thermodynamics of an accidental release scenario.

MIMAH and DyPASI analysis

In order to define major top events of CCS surface installations and their potential causes, the bow-tie methodology MIMAH (Methodology for the Identification of Major Accident Hazards) and complemented with results from the DyPASI methodology (Dynamic Procedure of Atypical Scenarios Identification). This requires the definition of reference schemes for the technologies involved in the CCS chain. The plants taken as references were the most common options of capture and transport technologies available in literature:

- Amine-based post-combustion capture technology (Fluor Econamine FG+) in a pulverised coal power plant;
- Two stage Selexol pre-combustion capture technology and ASU in an Integrated Gasification Combined Cycle (IGCC) power plant;
- Oxyfuel combustion technology and ASU in a pulverised coal power plant; this includes an air separation unit (ASU);
- CO_2 compression unit and transport pipeline

Figures from Figure 19 to Figure 25 report details on the reference schemes used.

Due to the complexity of capture plants considered and the repetitivity of results obtained, only representative equipment for each plant is here considered:

- Post combustion capture: CO_2 absorber
- Pre-combustion capture: CO_2 absorber and air separation unit (ASU) considered as a unique distillation column
- Oxyfuel combustion: Boiler/furnace, recycle pipe, ASU (same analysis performed for pre combustion capture)
- Transport: compressor and pipeline

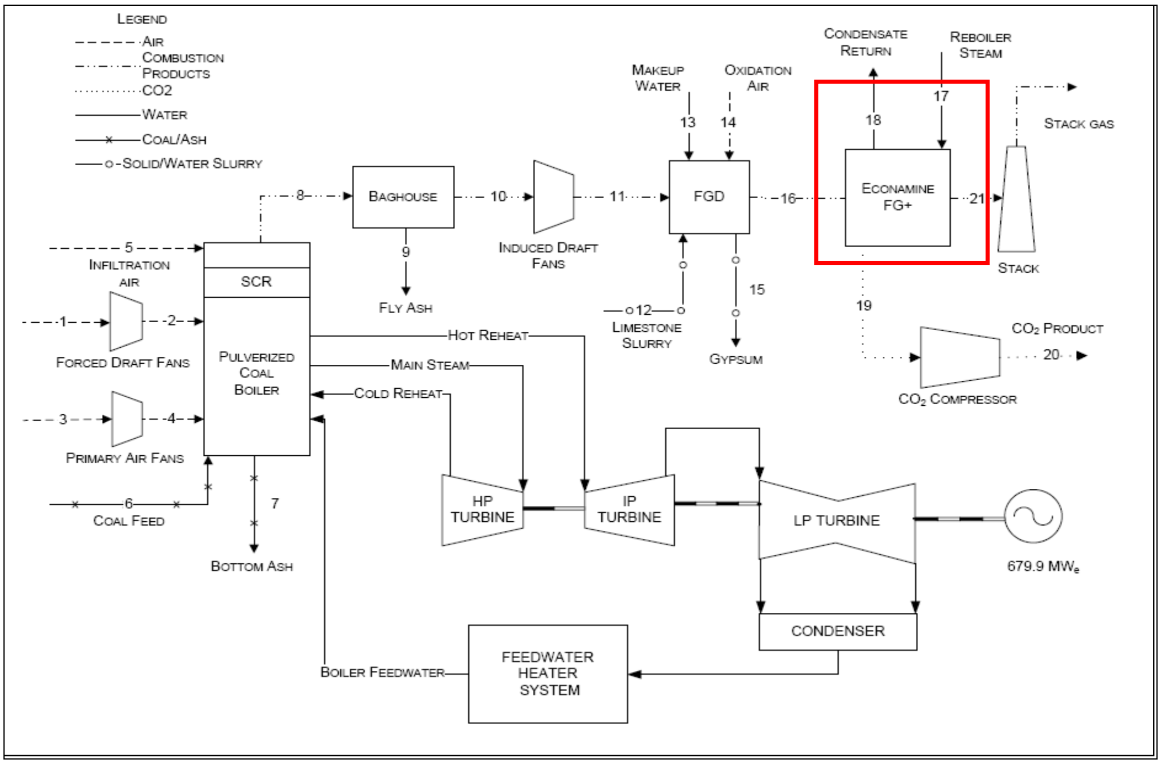


Figure 19 - Pulverised coal power plant block diagram, portion of plant considered highlighted in the red rectangle.

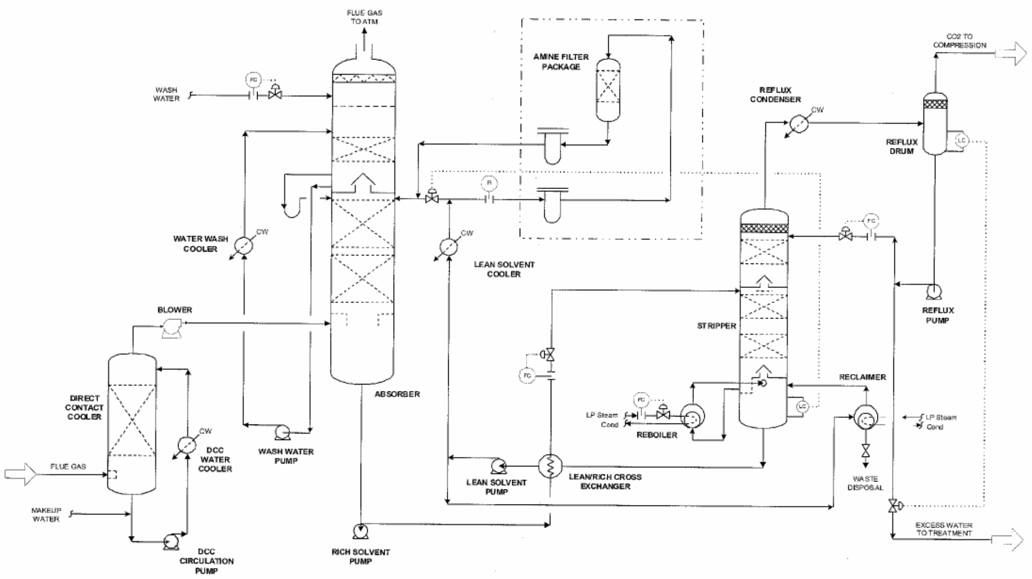


Figure 20 - Fluor Econamine FG Plus typical flow diagram.

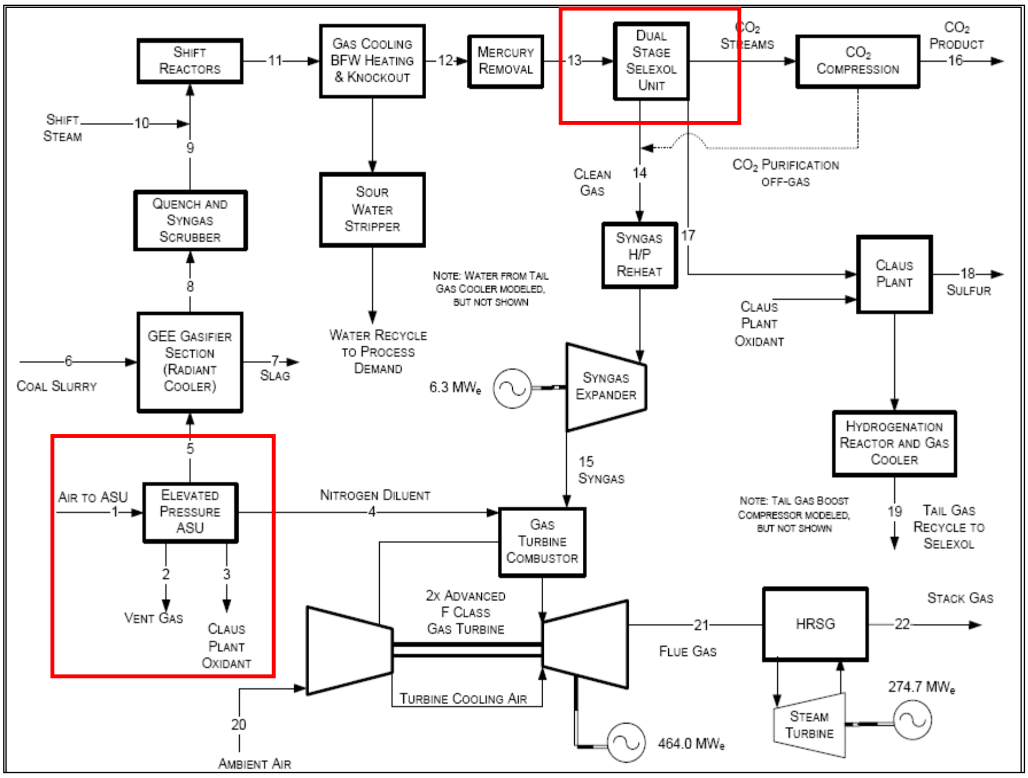


Figure 21 - IGCC power plant block diagram, portion of plant considered highlighted in the red rectangle

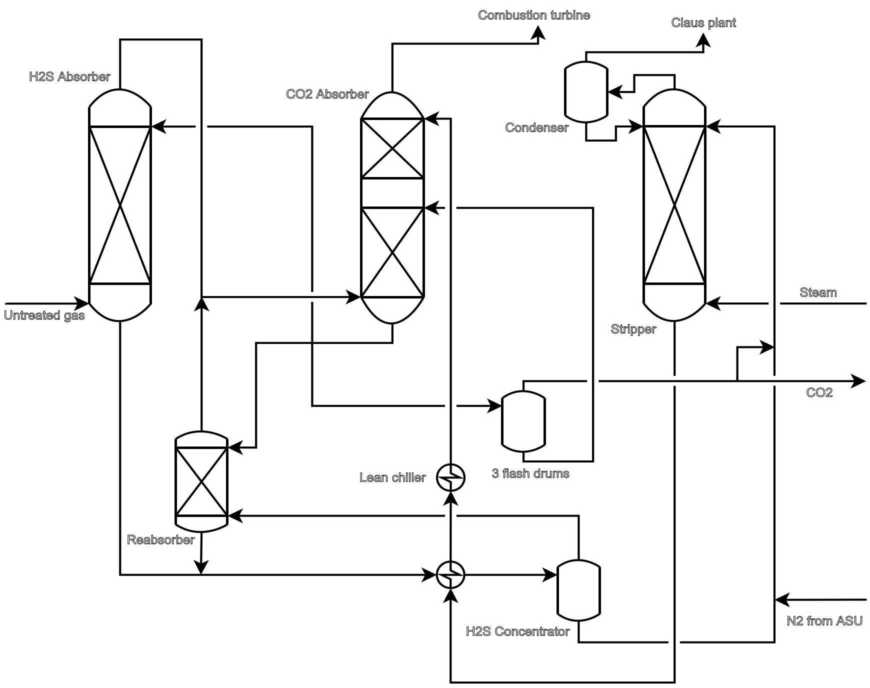


Figure 22 - Two-stage Selexol process flow diagram

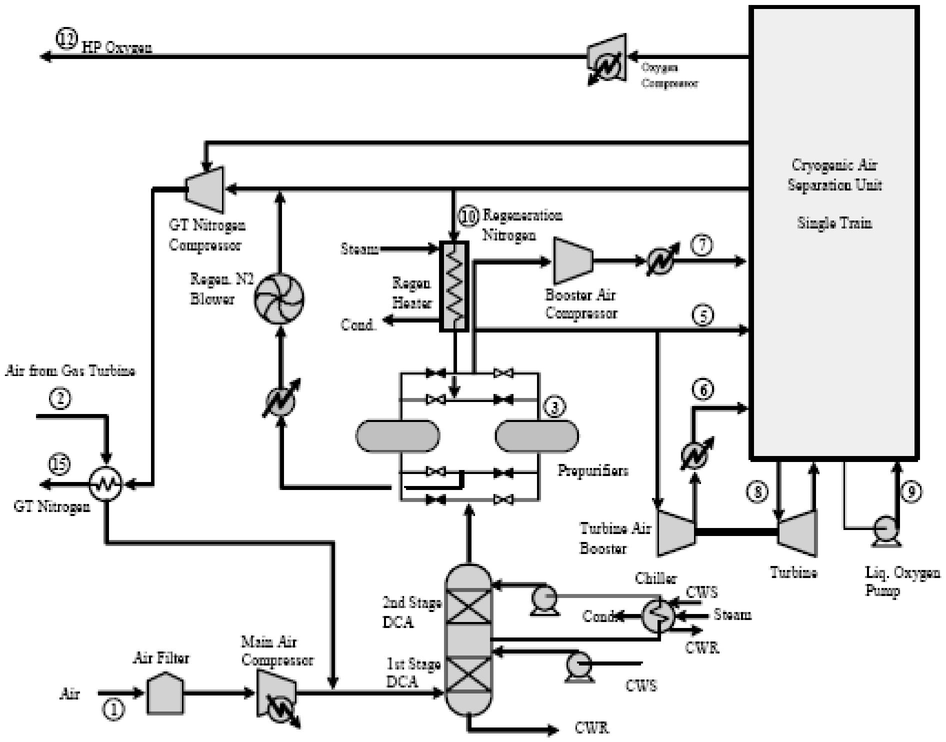


Figure 23 - Typical ASU process schematic

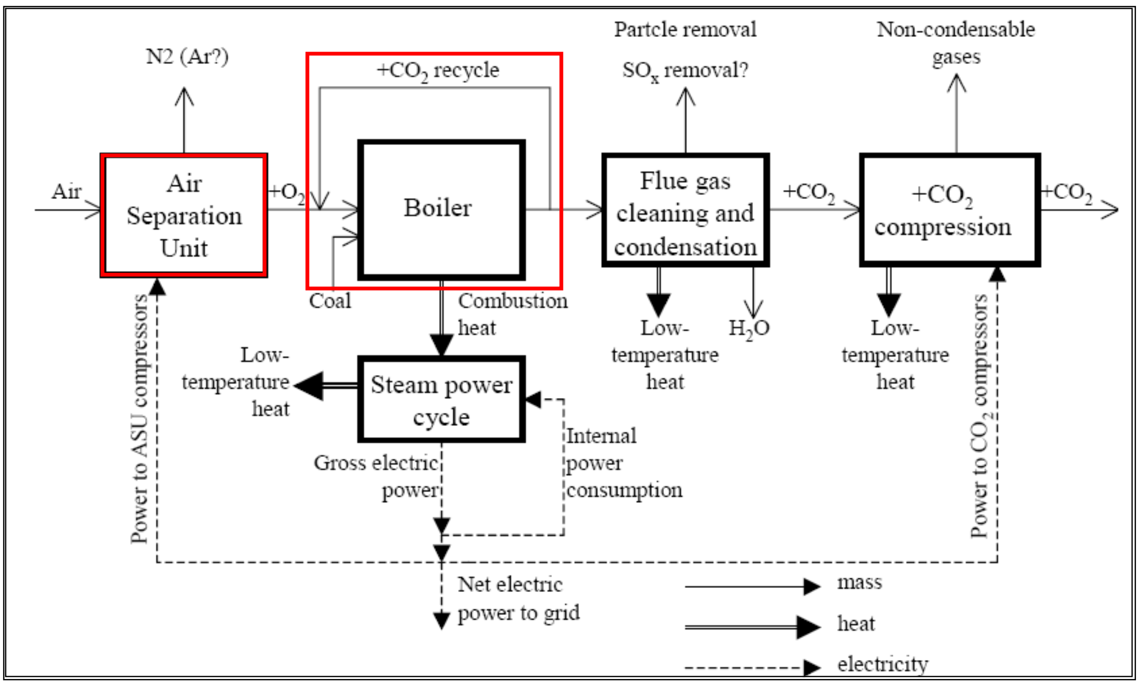


Figure 24 - Block diagram of a pulverised coal power plant with oxy-fuel combustion system, portion of plant considered highlighted in the red rectangle

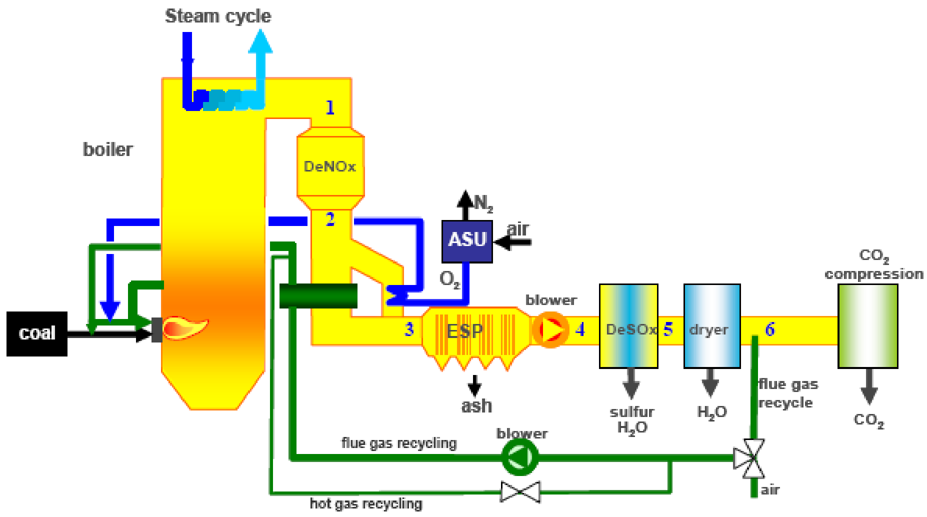


Figure 25 - Flow diagram of oxy fuel combustion system with recirculation after the CO_2 purification process

Table 22 summarizes the critical events obtained as results by the application of MIMAH and DyPASI methodologies. The result of the identified loss of containment is the release of the material contained in the unit (toxic effects for ammines and CO_2, fire effects for flammable gases and liquids, oxidant effects from oxygen).

Figures from Figure 26 to Figure 31 show the event trees identified for the different units:

- **Post-combustion capture – Absorber**: the potential consequences resulting are mainly the dangerous phenomena of toxic cloud and environmental damage, which mirror the toxic nature of both the substances considered (CO_2 and amines) and the toxicity to aquatic organisms of amines. Missiles ejection is only a consequence of catastrophic rupture.
- **Pre combustion capture – Absorber**: the main difference from the previous equipment is the presence of flammable substances (Rectisol solvent and hydrogen). The event of an internal combustion/explosion is, thus, considered as an event leading to CEs and the dangerous phenomena of Poolfire, VCE, Flashfire and Jetfire are taken into account as potential consequences. The toxic effects of a CO_2 release are still considered and gain even more importance because of the possible presence of impurities of H2S.
- **Pre combustion capture – ASU**: all the LOCs of oxygen considered in bow tie diagrams lead to the only consequence of domino effect (damage to other equipment). The LOC of oxygen is in fact resumed as direct cause of the critical event "start of a fire", together with "contact with a combustible". The source of combustible can be represented by a leak from a nearby pipe. However an oxygen-enriched atmosphere can cause materials not usually susceptible to burning in air to burn. If hair and clothing become saturated with oxygen, they may burn violently if ignited.

- **Oxyfuel combustion – Boiler**: the internal explosions in oxy-boiler/furnace may lead to a failure of the equipment. Moreover, leak of oxygen may result in the “start of fire” CE. Since in this case the only toxic hazardous substance handled is CO_2 (if impurities are excluded), the condition of high concentration has been introduced by means of DyPASI before the dangerous phenomenon of toxic cloud. This condition contrasts with the event of gas dispersion proposed by MIMAH and involves a certain level of containment. In fact only elevated concentrations of CO_2 have toxicological effects on the human body.
- **Oxyfuel combustion – Recycle pipe**: the slumping/low velocity release of CO_2 has been added to the bow tie diagrams of recycle pipe as a secondary critical event. This has been considered as a release alternative to gas jet because CO_2 is heavier than air and will tend to accumulate at lower levels. Previously it had not been considered for boilers because of high temperatures of gas CO_2 coming from boiler.
- **Oxyfuel combustion – ASU**: same as Pre combustion capture – ASU.
- **Compressor**: CE consequences generally mirror events previously outlined for equipment handling CO_2.
- **Pipeline**: Slumping/low velocity release is here again considered as release mode leading to high concentration of CO_2 if an adequate grade of containment is present. Since CO_2 is heavier than air, the containment can be represented by a low point such as a ground depression or a tunnel entrance.

Note: CO_2 BLEVE

Even if the event of BLEVE has not been mentioned in bow-tie diagrams, because not connected to the equipment analyzed, it should be noted that the occurrence of BLEVE (Boiling Liquid Expanding Vapour Explosion) is possible in case of catastrophic rupture of a storage tank containing dense phase CO_2. The outcome would thus be overpressure wave and missiles ejection.

Table 22 - Summary of critical events obtained by MIMAH – DyPASI.

CCS technology	**Equipment**	**Critical Event**
Post-combustion capture	Absorber	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
Pre combustion capture	Absorber	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
	ASU	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
		Start of a fire
Oxyfuel combustion	Boiler	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
		Start of a fire
	Recycle pipe	Large leak from pipe
		Medium leak from pipe
		Small leak from pipe
	ASU	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
		Start of a fire
CO_2 compression	Compressor	Large breach on shell
		Medium breach on shell
		Small breach on shell
		Catastrophic rupture
CO_2 transport	Pipeline	Large leak from pipe
		Medium leak from pipe
		Small leak from pipe

	Critical Event	**Secondary Critical Event**	**Tertiary Critical Event**	**Dangerous Phenomena**
a)	Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
		Pool formation	Pool evaporation and dispersion	Environmental damage
		Gas puff	Gas dispersion	Toxic cloud
				Environmental damage
		Aerosol puff	Gas dispersion	Toxic cloud
				Environmental damage
b)	Breach on shell	Gas jet	Gas dispersion	Toxic cloud
				Environmental damage
		Pool formation	Pool evaporation and gas dispersion	Environmental damage

Figure 26 - Event trees for Post-combustion capture – Absorber

	Critical Event	Secondary Critical Event	Tertiary Critical Event	Dangerous Phenomena
a)	Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
				Overpressure generated
		Pool formation	Pool ignited	Pool fire
		Gas puff	Gas dispersion	VCE
				Flash fire
				Toxic cloud
		Aerosol puff	Gas dispersion	VCE
				Flash fire
				Toxic cloud
b)	Breach on shell	Gas jet	Gas dispersion	VCE
				Flash fire
				Toxic cloud
			Gas jet ignited	Jet fire
		Pool formation	Pool ignites	Pool fire

Figure 27 – Event trees for Pre-combustion capture – Absorber

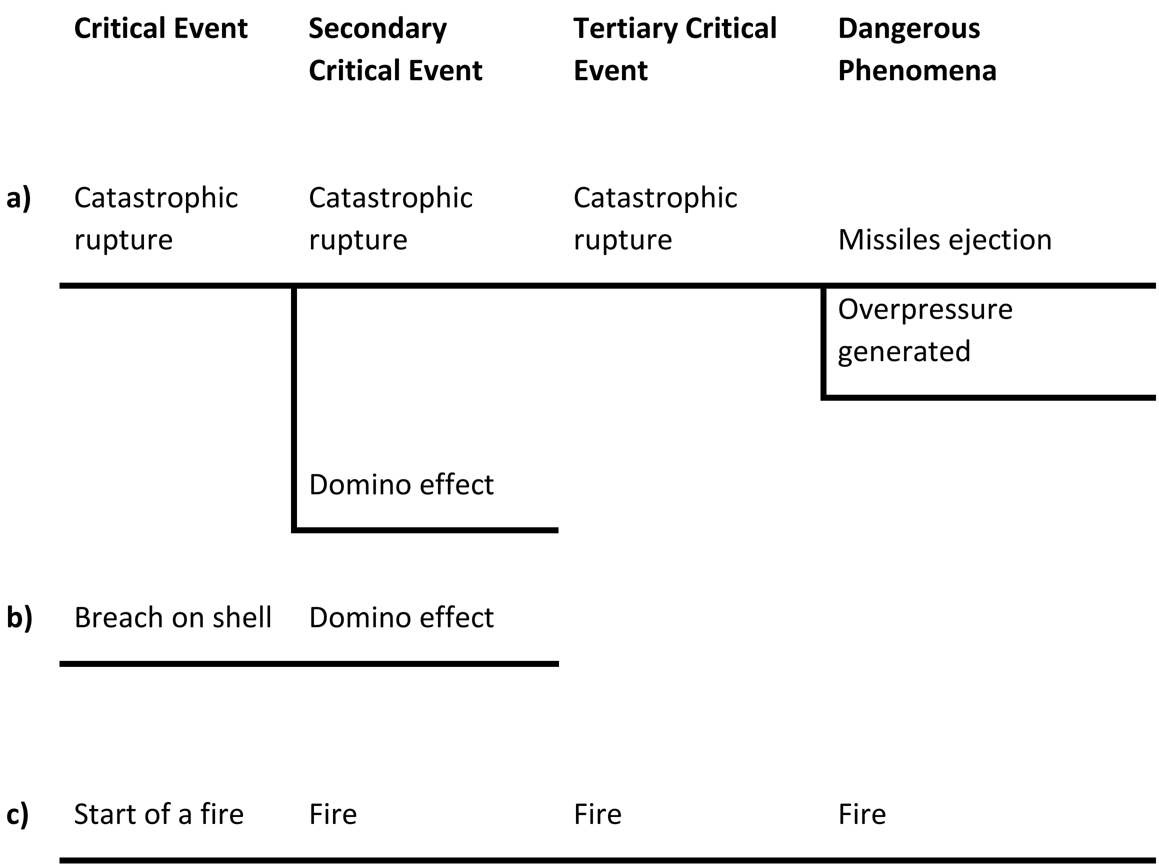


Figure 28 - Event trees for Pre-combustion capture – ASU and Oxyfuel combustion – ASU

	Critical Event	Secondary Critical Event	Tertiary Critical Event	Dangerous Phenomena
a)	Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
				Overpressure generated
		Gas puff	High concentration (CO_2)	Toxic cloud
		Domino effect		
b)	Breach on shell	Gas jet	High concentration (CO_2)	Toxic cloud
		Domino effect		
c)	Start of a fire	Fire	Fire	Fire

Figure 29 - Event trees for Oxyfuel combustion - Boiler

b)

Critical Event	**Secondary Critical Event**	**Tertiary Critical Event**	**Dangerous Phenomena**
Leak from pipe	Gas jet	High concentration (CO2)	Toxic cloud
	Slumping or low velocity release	High concentration (CO2)	Toxic cloud

Figure 30 - Event trees for Oxyfuel combustion – Recyle pipe and Pipeline

	Critical Event	Secondary Critical Event	Tertiary Critical Event	Dangerous Phenomena
a)	Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
				Overpressure generated
		Gas puff	High concentration (CO_2)	Toxic cloud
b)	Leak from pipe	Gas jet	High concentration (CO_2)	Toxic cloud
		Slumping or velocity release	High concentration (CO_2)	Toxic cloud

Figure 31 - Event trees for Compressor

<u>Massive and sudden release of CO_2 form underground storage</u>

The case of massive and sudden release of CO_2 form underground storage during injection and storage conditions has received a specific analysis within the IntegRisk project.

A possible accident involving the injection well is a failure of the pipework or tubing, which will lead to a well blow-out. This scenario is similar to the ones occurred in the past for hydrocarbon wells in oil & gas industry.

On the other hand, a massive and sudden releases may be the consequence of rather slow and long-term processes in the underground. With respect to these phenomena, some lessons can be learned from past occurrences:

- firstly, events in natural conditions, such as lake Nyos in 1986 and its 1700 casualties (Oldenburg and Lewicki, 2006);and

- secondly events with industrial anthropogenic features. At Hutchinson in 2001 in the USA, a sudden leak and a fire occurred at a distance of several kilometres from an underground storage of flammable gas (described in the ARIA database of industrial accidents or in Roux, 2009).

Hence the fault tree in Figure 32 was built. It shows as a sudden (and accidental) emanation at surface level may result from both surface or underground top events.

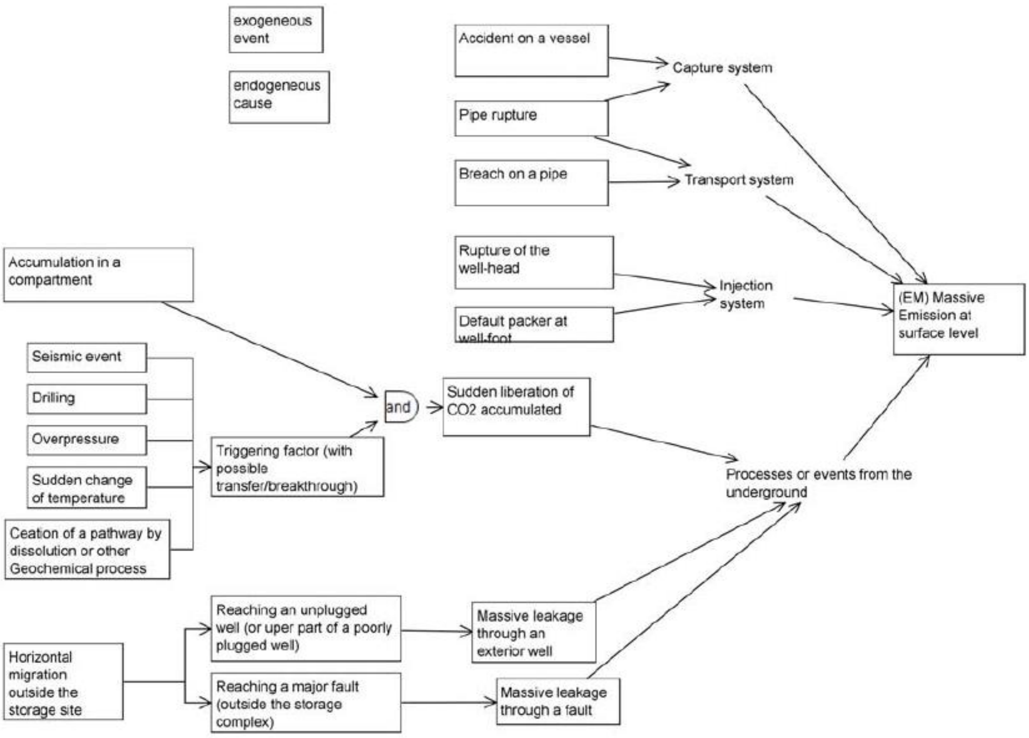


Figure 32 - Fault tree for underground injection and storage

The events following the identified critical event will be very similar to the ones already identified in the “leak from pipe” in the compressor (Figure 31): dispersion of dense gas jet. Underground water may be ejected as well with the CO_2, depending on the location and event condition of the specific failure scenario.

Selected scenarios

Among the possible scenarios identified above, the attention in gap analysis was restricted to the ones that are originated form the release of CO_2 alone. In facts, carbon dioxide is the material surely common to all CCS technologies and the one for which higher uncertainties in the consequence modeling are expected (cooling effects during release, formation/evaporation of dry ice, dense gas dispersion, etc.).

It is recognized that accident scenarios from other materials (oxygen, adsorption liquids, etc.), though commonly handled and modeled risks in industrial facility, would as well require dedicated analyses, given the growth in scale and number of CCS facilities. Nevertheless, they are very technology specific and should receive a second level priority (i.e. after the modeling of CO_2, which is inherent to the CCS technology, has been consolidated).

From the point of view of consequence modeling, the analysis of the scenarios in described above identified the following phenomena to be screened for gap analysis (Task 2.3):

- High pressure CO_2 release from rupture/breach
- Vapor cloud dispersion

9.2. Gap analysis

In the following the models available for the scenarios identified in task 2.2 will be screened for gap analysis.

9.2.1. High pressure (supercritical) CO_2 release from rupture/breach

Dense phase CO_2 (either supercritical gas or semi-refrigerated liquid) is expected to be the fluid handled in transportation and intermediate storage of a CCS system. According to the thermodynamics, a major release would lead to the formation of solid CO_2 (dry ice) as well as vapor phase. There are therefore issues in ensuring that any consequence model can adequately handle the thermodynamics and energy balance related to solid formation.

Witlox et al. (2009) suggests to use a conventional model (DISC or TVDI models, as implemented in DNV Phast) to simulate the outflow. Conventional models for source term estimation (outflow) were developed and validated either for single phase release (liquid or gas) or for a liquid-vapor two phase release. The role on the release rate of the formation of solid particles of dry ice has yet to be fully investigated, in particular in the case of a large size breach. No specific models are available up to now and no validation of more generic models have been yet disclosed.

It is known that the captured CO_2 stream from power plants will contain impurities such as SO_2 and H_2S. However, the impurities are expected to constitute a small proportion of the overall flow and it is assumed that the increase in toxicity will not be significant. Overall, the use of pure CO_2 in consequence modeling is considered a reasonable basis for determining an estimate of the hazards from loss of containment.

A particular case of CO_2 release is the one occurring during the blowout of an injection well. In this case, a two phase mixture of CO_2 and water can be released and a two phase flow regime with variable vapor fraction along the well needs to be modeled. Being similar to the case of oil&gas blowout scenarios the same models used for simulating those cases are applicable: these are typically based on multi-phase flow simulator codes (e.g. OLGA). No specific validation for CO_2 blowouts is however known.

9.2.2. Vapor cloud dispersion (from supercritical or liquefied source)

The possibility of solid phase formation in large CO_2 releases has important consequences of the subsequent jet and atmospheric dispersion. The main uncertainty up to know concerns the understanding of the conditions for the formation, growth and rain-out of the dry ice particles. Although, in the few experimental studies made to date, there has been little evidence of solid formation, the releases of these tests have all been of too short a duration for the environment to reach equilibrium at the low temperatures produced. In absence of a clear understating of the phenomenon, modeling is based only on theoretical speculations.

In many cases, the assumption of a 100% gaseous source term as the worst case for risk assessment has been suggested (Integrisk, 2010). This way conventional dispersion models (see relevant sections for other Emerging Risks) can be applied. However, such simplification is not acceptable when planning emergency response arrangements, since it is important to recognize and adequately predict the possible longer-term presence of CO_2 solid in confined spaces.

In the Integrisk Project, a preliminary application of a beta-version of the consequence modelling software DNV PHAST, which includes limited modelling of solid CO_2 formation, has been carried out. This version has been modified to include some of the most relevant thermodynamics for solid CO_2 as proposed by Witlox et al. (2009). However, the model still had some limitations (e.g. rainout of ice particles not considered).

The EC CO2PIPEHAZ project (UCL, 2010) is developing pipeline release and source term models, and will include experimentation.

For detailed design and risk assessment purposes, especially in complex geometries such as injection from offshore installations, computational fluid dynamics codes are likely to be required.

If rain-out can create significant deposits of dry ice, no specific model has yet been proposed for calculating the source term for dispersion from solid CO_2 sublimation.

Up to now, there remains a lack of experimental data for validation of any model involved in CO_2 dispersion from dense phase (supercritical or liquefied) outflows.

9.2.3. Note: BLEVE

In the Integrisk Project the possibility of CO_2 BLEVE for refrigerated storages has been also explored (Integrisk, 2010). Boiling liquid expanding vapor explosion is technically possible for vessels containing large inventories of CO_2 in pressurized liquid state (refrigerated storage). This is expected for intermediate storage tanks in a shipping facility. A CO_2 BLEVE can occur if there is catastrophic loss of containment of liquid CO_2 causing a very rapid loss of pressure. This can cause the liquid to become superheated and may exceed the superheat limit temperature at the final pressure (environmental pressure). If this occurs then homogeneous nucleation of vapour bubbles occurs throughout the liquid and can show and explosive behavior.

No specific models have been developed for calculation of the overpressure effects of CO_2 BLEVEs. However, the generic models provided by CCPS (1994) are deemed to be applicable also in this case.

No validation efforts are known for this scenario.

9.2.4. Summary of the results

In the following table the results of the gap analysis carried out above are briefly summarized.

Table 23 - Results of the scenario gap analysis for Carbon Capture Transposition and Storage.

Scenario	Model Availability	Model Validation
High pressure (supercritical) CO2 release from rupture/breach *Surface equipment failure:*	**ORANGE** Liquid outflow models are applicable No specific model is available (e.g. role of dry ice formation)	**ORANGE** Models validated for other materials/release conditions
Well blow-out:	**ORANGE** Models for well blowout in the oil&gas sector (e.g. OLGA)	**ORANGE** No validation for CO2/water mixtures
Vapor cloud dispersion	**RED/ORANGE** Models for pure gases are applicable if thermodynamics of dry ice formation is accounted No model available for dry ice rain-out and deposit sublimation.	**RED/ORANGE** Few field tests (still ongoing) No complete validation trial available.

10. Emerging Risk 4 – Hydrogen

10.1. Case definition and scenario identification

Description of the technology

Hydrogen Refuelling Stations have been selected as a case study to demonstrate emerging risk issues for the application of hydrogen. Layout and operating conditions of various (proto)types hydrogen refuelling stations have been described in literature, e.g. (HyApproval, 2008), (Moonis et al., 2010), (Nakayama et al., 2015), (Weeda and Elgowainy, 2015) and (LaFleur et al., 2015). The current subsection uses input from the Dutch Hazardous Substances Publication Series (HSPS) Nº 35 (HSPS, 2015). This is the Dutch technical standard for hydrogen refuelling stations, which was first published in 2015. This standard provides guidance for the design, construction, operation, testing and maintenance of hydrogen refuelling stations. The following types of hydrogen refuelling stations are included in HSPS Nº 35:

- HRS with supply of gaseous hydrogen by pipeline or by local production (Figure 33)
- HRS with supply of gaseous hydrogen from a tube trailer, either using a storage vessel (Figure 34), or not (Figure 35).
- HRS with supply of liquid hydrogen by road tanker, using a storage vessel or not and using a pump or not (Figure 36 to Figure 39).

Explanation of symbols for Figure 33 to Figure 39

1. liquid hydrogen storage unit	8. chiller	15. pressure regulator
2. gaseous hydrogen storage unit	9. dispenser	16. breakaway coupling
3. intermediate gas storage	10. safety valve	17. pressure build-up evaporator
4. evaporator	11. delivery hose	
5. emergency shutdown system	12. off-loading hose	LT level sensor
6. pump	13. fill	FT flow sensor
7. compressor	14. purifier	TT temperature sensor

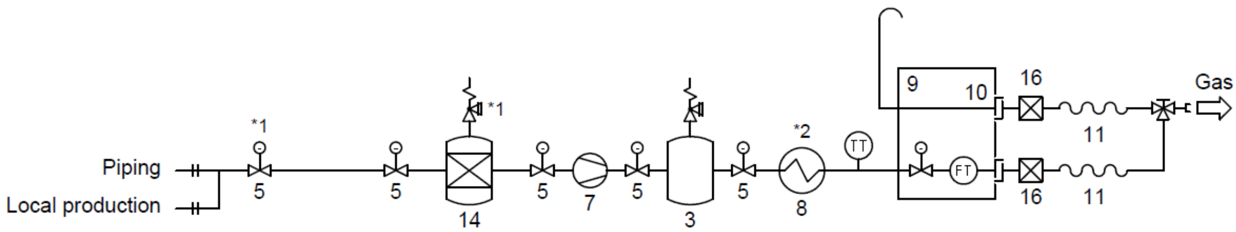


Figure 33 - HRS with supply of gaseous hydrogen by pipeline or by local production (reproduced from (HSPS, 2015)

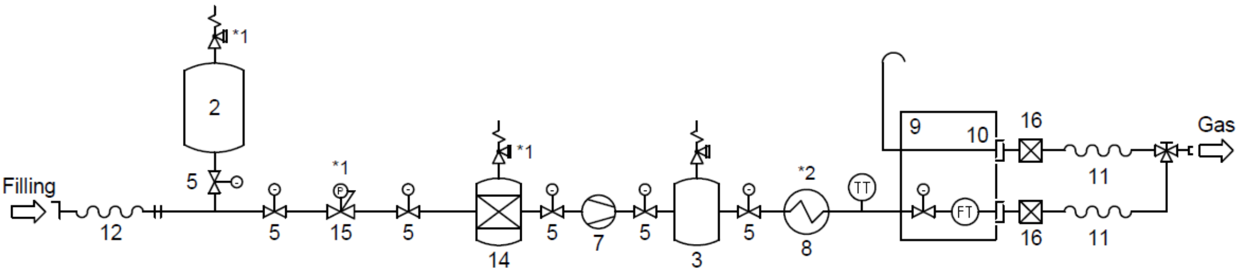


Figure 34 - HRS with supply of gaseous hydrogen from a tube trailer using a storage vessel (reproduced from (HSPS, 2015)

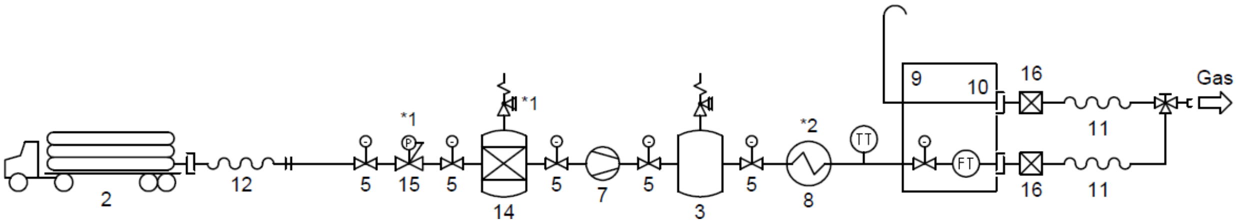


Figure 35 - HRS with supply of gaseous hydrogen from a tube trailer without storage vessel (reproduced from (HSPS, 2015)

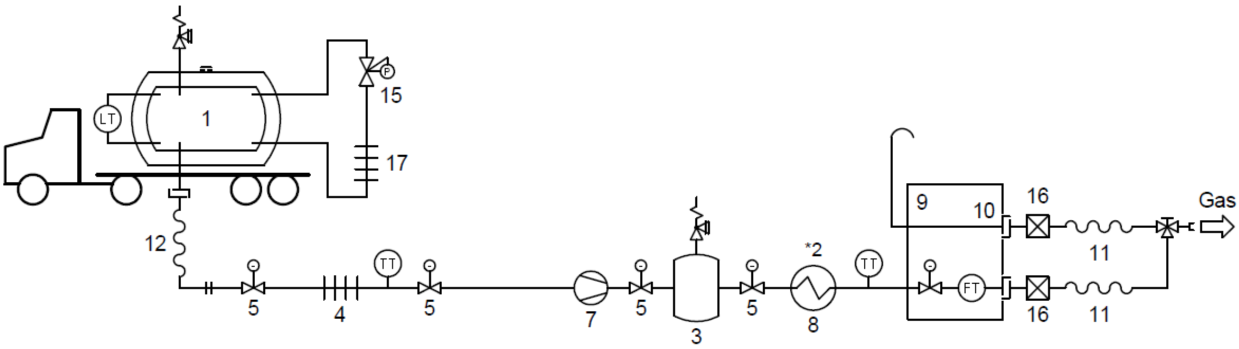


Figure 36 - HRS with supply of liquid hydrogen from a tanker, without storage vessel, without pump (reproduced from (HSPS, 2015)

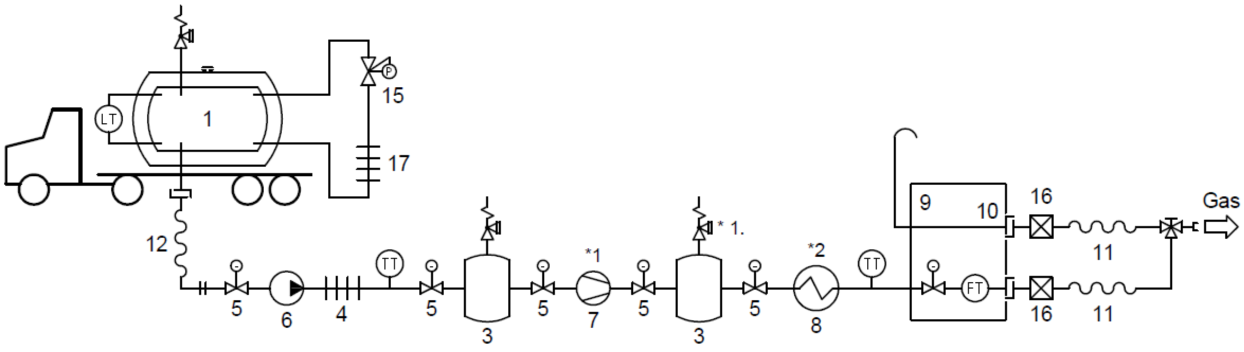


Figure 37 - HRS with supply of liquid hydrogen from a tanker, without storage vessel, with pump (reproduced from (HSPS, 2015)

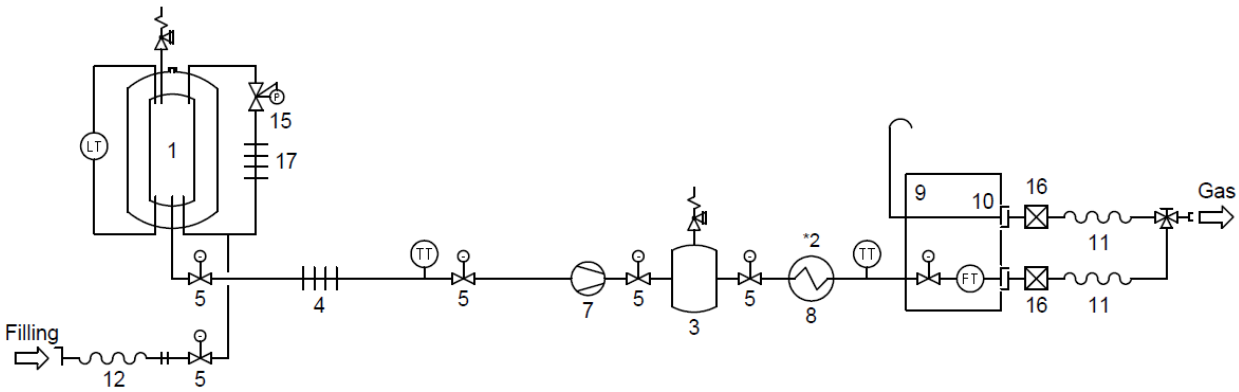


Figure 38 - HRS with supply of liquid hydrogen from a tanker, with storage vessel, without pump (reproduced from (HSPS, 2015)

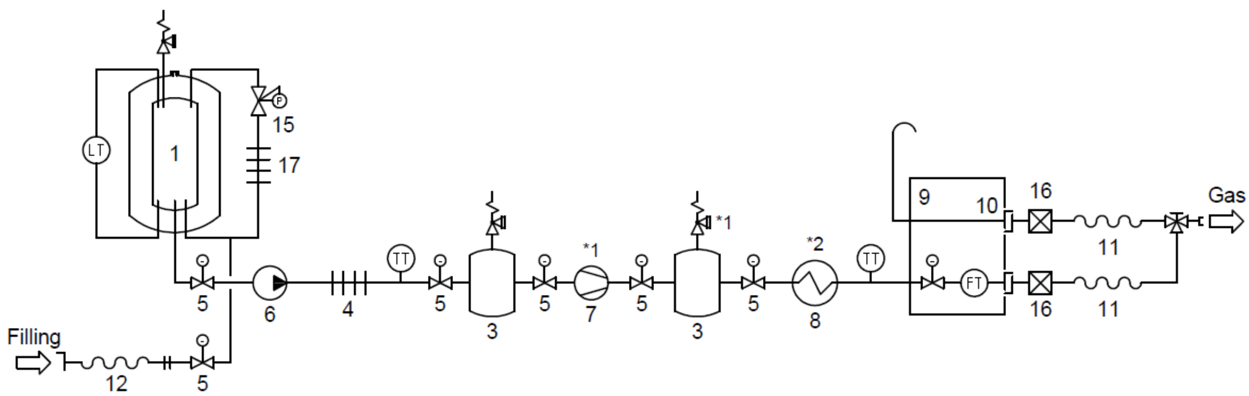


Figure 39 - HRS with supply of liquid hydrogen from a tanker, with storage vessel, with pump (reproduced from (HSPS, 2015)

Further clarification of system components, as provided in (HSPS, 2015):

1. Liquid hydrogen storage unit: Double-walled storage vessel, operated at a pressure between 4 and 8 bar. The storage unit can be stationary or mobile, e.g. using a tanker.
2. Gaseous hydrogen storage unit: Storage for gaseous hydrogen operated at a pressure between 200 and 1000 bar and a volume typically between 1 and 10 m^3 (water capacity). The storage unit can be stationary or mobile, e.g. using a tube trailer.
3. Intermediate gas storage: One or more high pressure vessels used to reduce charging times.
4. Evaporator: Produces gaseous hydrogen from liquid hydrogen.
5. Emergency shutdown system: Integrated system of valves, sensors and logic that can be used to isolate sections of the installation in case of an emergency. May be dual use; as process shutoff valves and safety valves. Additional manual valves are in place to isolate sections for maintenance.
6. Pump: For the transportation of liquid.
7. Compressor: For the compression of gaseous hydrogen to desired delivery pressures for receiving vehicles, typically between 350 and 700 bar.
8. Chiller: To cool gaseous hydrogen prior to dispensing it into the road vehicle.
9. Dispenser: System of delivery hoses, start and stop buttons and flow meters.
10. Safety valve: Pressure relief valve to prevent exceedance of maximum operating pressure.
11. Delivery hose: Hose for dispensing hydrogen into a vehicle with integrated safety function, warranting that hydrogen will flow if and only if the nozzle is connected.
12. Off-loading hose: Hose for supplying hydrogen from the transport unit into the storage vessel.
13. Fill: Supply of hydrogen from a tube trailer or road tanker.
14. Purifier: Removes impurities in the supplied hydrogen.
15. Pressure regulator: Sensor and control valve to monitor and maintain desired pressure levels.
16. Breakaway coupling: Device that automatically interrupts the hydrogen flow in case the road vehicle should drive away with the delivery hose still connected.
17. Pressure build-up evaporator: Evaporator that is used to maintain pressure in the storage vessel in times of hydrogen consumption.

The supply end of the refuelling stations differs between the different supply pathways. If gaseous hydrogen is supplied by a pipeline, or produced onsite, the supply side is typically limited to a purifier (item 14) that can be isolated by emergency shutdown valves (ESVs). If a tube trailer is used, a pressure regulator (item 15) is added upstream of the purifier. If liquid hydrogen is delivered by a tanker, the supply can either be directly from the tanker (without additional storage vessel) or from an in-between liquid storage vessel. In both cases, an evaporator (item 4) is used for the supply of gaseous hydrogen into the delivery system. Both intermediate tank and evaporator can be isolated by ESVs.

The dispenser side of the refuelling station consists of a compressor (item 7), an intermediate storage vessel (item 3), a chiller (item 8) and the dispenser (item 9). The compressor and storage vessel can be isolated with ESVs. A breakaway coupling (item 16) is integrated into the delivery hose (item 11), upstream of the dispenser (item 9) that is connected to the vehicle. A further safety valve (item 10) is added to prevent pressure exceedance.

MIMAH

The 'MIMAH' Methodology for the building of generic event trees (Delvosalle, 2006), that was defined in the ARAMIS project, was used to construct generic event trees for the equipment types described in the previous subsection. Following the MIMAH methodology, storage units, process units, pipes and transport equipment were selected for consequence analysis. The associated scenarios also cover releases from seals, connections (flanges and gaskets), valves and instruments integrated in these systems.

As a first step, the different equipment types described in the previous types were linked to associated equipment categories that are used in the MIMAH methodology (see Table 24). The associated critical events, secondary events and tertiary (critical) events, depend on the physical state of the product and on the hydrogen hazardous properties (defined by R-phrases).

- For cryogenic equipment, two states are selected: liquid and two-phase (Delvosalle, 2004a). Two-phase should be used if the critical event is caused by failure of the cooling system or by external heating. Liquid should be used for all other causes.
- Hydrogen is defined as extremely flammable (R12, see Table 10). Toxic impact and environmental damage do not need to be considered.

Using the above assumptions, the generic event trees can be generated (Delvosalle, 2004b). These are depicted in Figure 40 to Figure 45. Note: for storage vessels and transport units, the critical event 'leak from pipe' was renamed 'leak from connection' in order to avoid confusion with specific scenarios for pipes. For two-phase releases, gas dispersion from aerosol or jet release and gas dispersion from pool formation were combined into a single event gas dispersion, linked to both aerosol/jet dispersion and pool dispersion.

Table 24 - Overview of relevant equipment types and MIMAH categories

Equipment type	MIMAH equipment type	State	Event tree
Liquid hydrogen storage unit	EQ7 – Cryogenic storage	Liquid Two-phase	Figure 40 Figure 42
Gaseous hydrogen storage unit	EQ4 – Pressure storage	Gas	Figure 43
Intermediate gas storage	EQ4 – Pressure storage	Gas	Figure 43
Evaporator	EQ16 – Other facilities	Gas	Figure 43

		Liquid Two-phase	Figure 41 Figure 42
Pump	EQ16 – Other facilities	Liquid	Figure 41
Compressor	EQ16 – Other facilities	Gas	Figure 43
Chiller	EQ16 – Other facilities	Gas	Figure 43
Dispenser	EQ10 – Pipe	Gas	Figure 44
Delivery hose	EQ10 – Pipe	Gas	Figure 44
Off-loading hose	EQ10 – Pipe	Gas Liquid	Figure 44 Figure 45
Purifier	EQ12 – Separator	Gas	Figure 43
Tube trailer	EQ8 – Pressure transport unit	Gas	Figure 43
Road tanker	EQ8 – Pressure transport unit	Liquid Two-phase	Figure 41 Figure 42

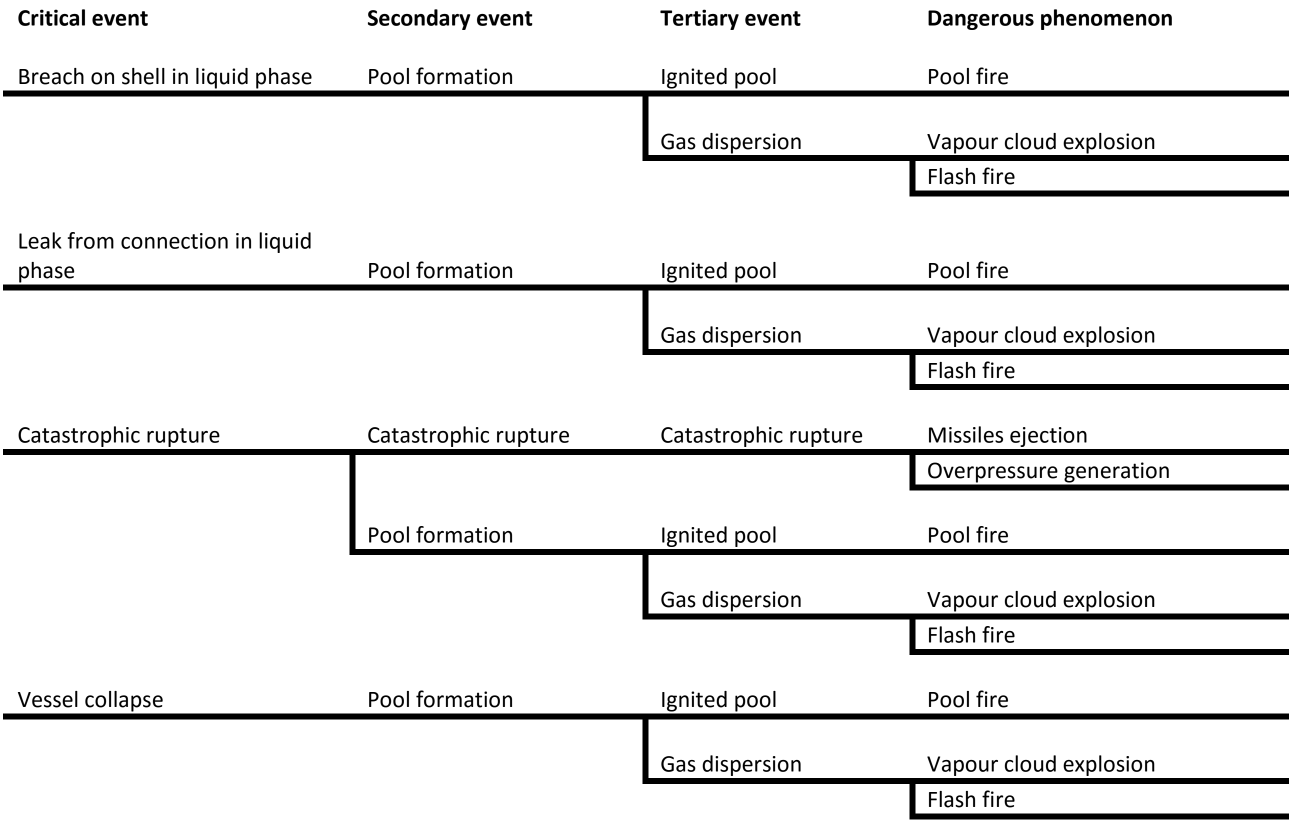
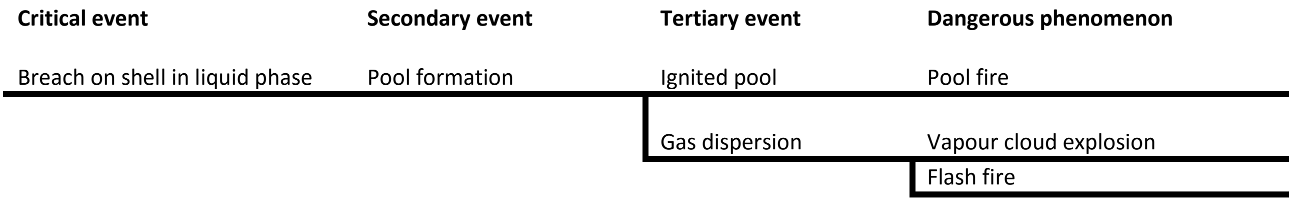


Figure 40 - Generic event tree for cryogenic storage (EQ7), for liquid hydrogen below boiling point



Leak from connection in liquid phase	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire

Figure 41 - Generic event tree for cryogenic installations other than storage (EQ8 and EQ16), for liquid hydrogen below boiling point

Critical event	**Secondary event**	**Tertiary event**	**Dangerous phenomenon**
Breach on shell in vapour phase	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
Breach on shell in liquid phase	Two-phase jet	Ignited two-phase jet	Jet fire
		Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
	Pool formation	Ignited pool	Pool fire
Leak from connection in vapour phase	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
Leak from connection in liquid phase	Two-phase jet	Ignited two-phase jet	Jet fire
		Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
	Pool formation	Ignited pool	Pool fire
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Aerosol puff	Ignited aerosol puff	Fireball
		Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
	Pool formation		

		Ignited pool	Pool fire

Figure 42 - Generic event tree for cryogenic installations (EQ7, EQ8 and EQ16), for two-phase hydrogen

Critical event	**Secondary event**	**Tertiary event**	**Dangerous phenomenon**
Breach on shell	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
Leak from connection	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Gas puff	Ignited gas puff	Fireball
		Gas dispersion	Vapour cloud explosion
			Flash fire

Figure 43 - Generic event tree for GH2 installations (EQ4, EQ8, EQ12 and EQ16)

Critical event	**Secondary event**	**Tertiary event**	**Dangerous phenomenon**
Leak from gas pipe	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire

Figure 44 - Generic event tree for GH2 pipework (EQ10)

Critical event	**Secondary event**	**Tertiary event**	**Dangerous phenomenon**
Leak from liquid pipe	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire

Figure 45 - Generic event tree for LH2 pipework (EQ10)

Accident databases and literature

Hydrogen accident databases were analysed to verify if all relevant release scenarios and critical events are covered by the generic event trees. The database study was complemented by a query on recent literature on accidents involving hydrogen using Scopus. The query was carried out on

31 December 2015 using the filter: TITLE (hydrogen AND accident*) AND (LIMIT-TO (PUBYEAR, 2015) OR LIMIT-TO (PUBYEAR , 2014) OR LIMIT-TO (PUBYEAR , 2013) OR LIMIT-TO (PUBYEAR, 2012) OR LIMIT-TO (PUBYEAR , 2011) . 63 publications were identified by this filter. Subsequently, all papers from the 2015 International Conference on Hydrogen Safety in Yokohama, Japan, and from the 2013 International Conference on Hydrogen Safety in Brussels, Belgium were added to the literature study. These publications were scanned for relevance and useful insights were integrated into the analysis below.

The **Hydrogen Incident and Accident Database (HIAD)** is a database from the Joint Research Centre of the European Commission that was initially developed in the HySafe project (2004-2009). The database can be accessed through a website (https://odin.jrc.ec.europa.eu/hiad/index.hiad). It aims to provide detailed information about hydrogen accidents to increase the understanding of hydrogen safety, and contained 275 data reports in February 2016. Input fields are in free format, resulting in large numbers of subcategories (e.g. Table 25). More detailed analyses reveal inconsistencies in the database, such as fires or explosions without ignition. Figure 46 suggests that the willingness to report decreased when the HySafe project finished in 2009. Analysis of Table 25 does not show principle events that are not covered by the generic event trees discussed in the previous subsection.

Table 25 - Distribution of 'principle events' in the HIAD database, selection of principle events with at least two occurrences (accessed 11 February 2016).

Principal event	**Occurrence**	**Ignition**		
		Yes	No	?
Explosion	117	26	15	76
Fire - hydrogen	63	17	3	43
Fire	33	13	1	19
Release of hydrogen	20	2	5	13
others / unspecified	9	1	0	8
Continuous release of hydrogen through faulty connections (tank fittings/valves/etc)	6	1	2	3
Collison with vehicle	5	0	0	5
Pipe rupture	4	1	1	2
Continuous release	3	1	1	1
Continuous release in partially confined atmosphere	3	0	1	2
Burst of tank	2	0	0	2
Cavitation	2	0	0	2
Continuous release (through valves) in open atmosphere	2	0	1	1
Continuous release in partially confined or totally confined atmosphere	2	0	0	2
Continuous release through faulty connections (tank fittings/valves/etc)	2	0	0	2
Instantaneous release in open atmosphere	2	1	0	1
Release from core/piping/fittings/etc.	2	2	0	0
Roll-over/overturn (after drive-off/collision)	2	0	0	2

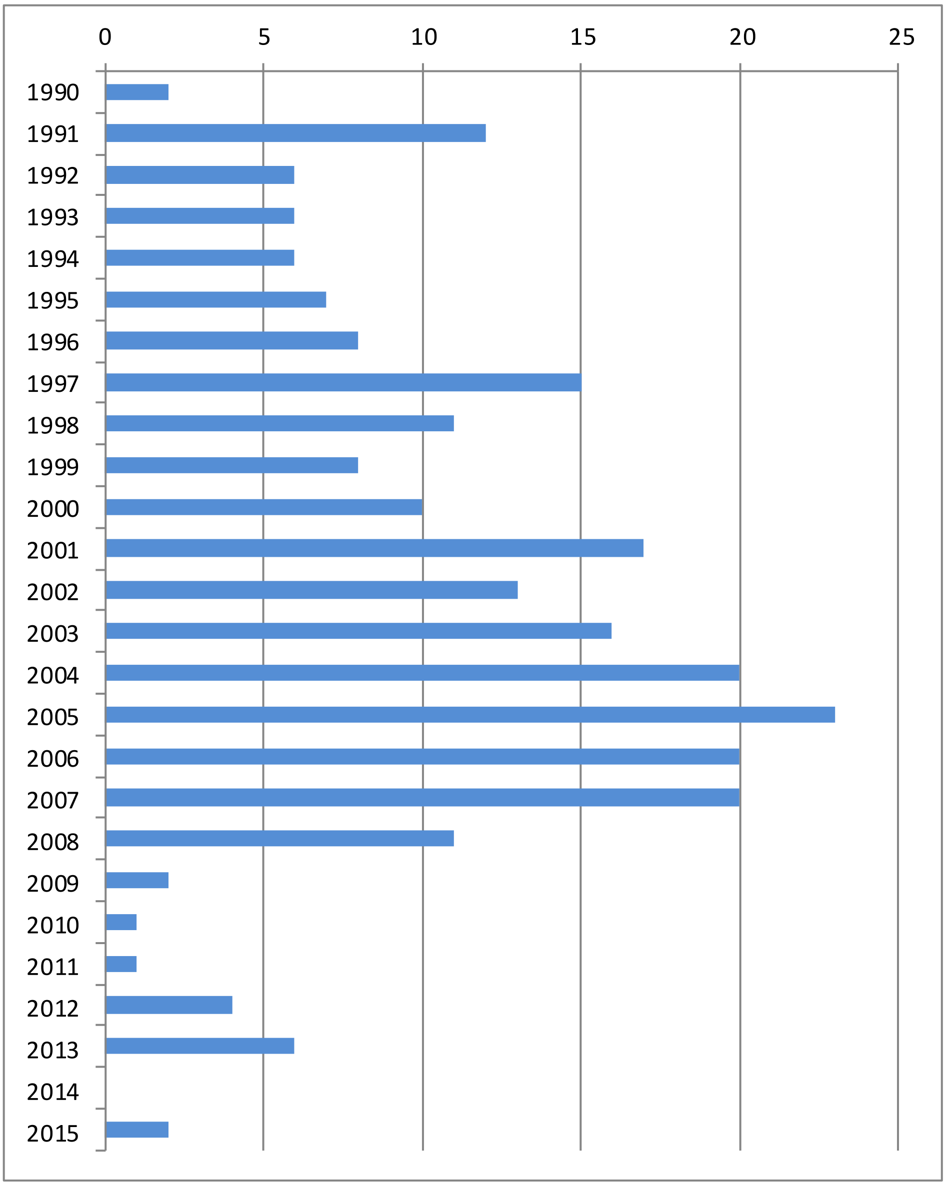


Figure 46 - HIAD database: reported accidents per year

H2tools Lessons learned (www.h2tools.org/lessons) is an initiative of the US Department of Energy's Office of Energy Efficiency and Renewable Energy (EERE) for learning from hydrogen accidents and incidents. Some of these incidents are near misses (no substance released). In February 2016, the database contained some 300 data reports. The database was previously known as the Hydrogen Incident Reporting Database (HIRD).

The following information is registered: type of equipment that failed, probable cause(s), contributing factors; damage and/or injuries, release (yes/no); ignition (yes/no). Some of these fields can be used to filter the data. The database does not contain specific information on release scenarios and consequence phenomena. Most accidents and incidents involve pipes and valves (see Figure 47). Except for electrical equipment and (laboratory) glass ware, all equipment types contained in Figure 47 are covered by the generic event trees discussed in the previous subsection.

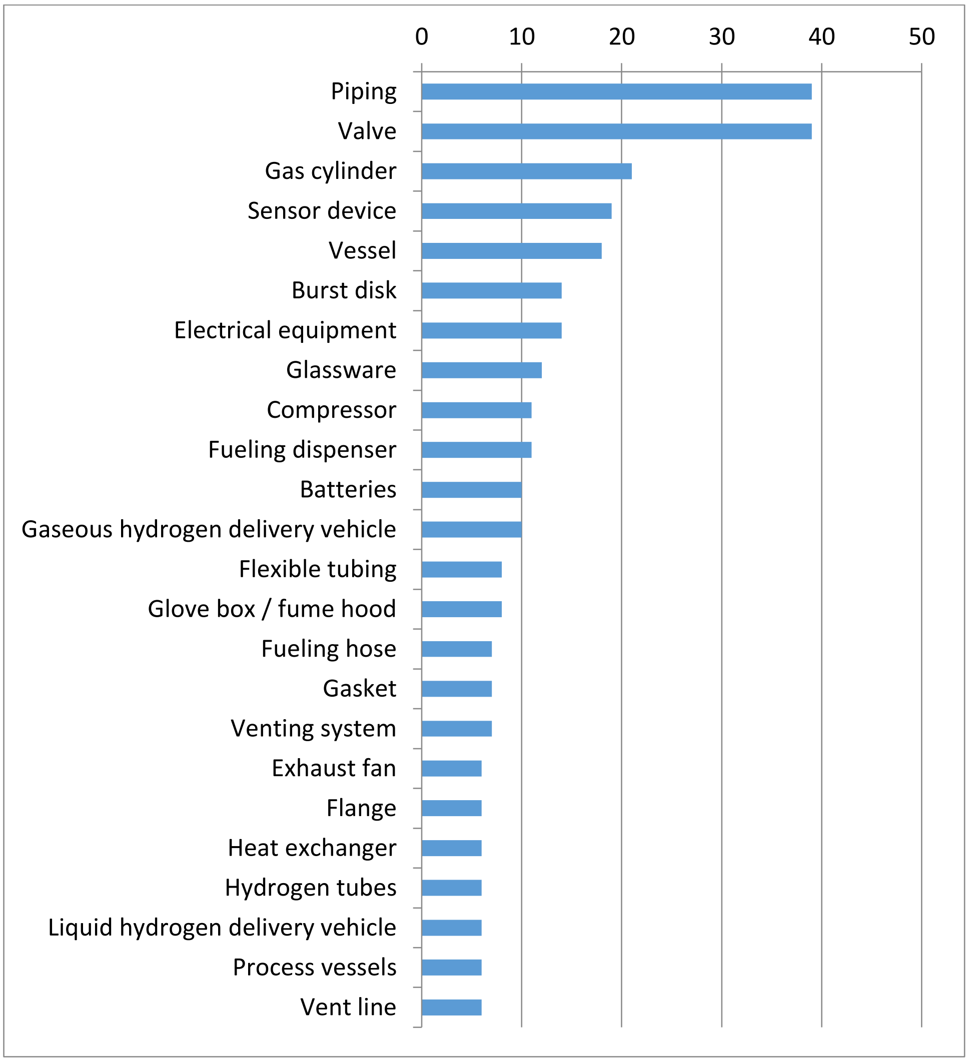


Figure 47 - Occurrence of equipment types in the h2tools database, selection of equipment types with 6 or more occurrences (accessed 11 February 2016)

Mirza et al. (Mirza et al., 2011) have analysed 32 accidents in the h2tools database in more detail. Releases had occurred from piping, vessels, valves, flanges, gaskets and miscellaneous equipment (e.g. sensors). From these 32 accidents, 14 had resulted in a fire without explosion, 10 resulted in explosion only, 5 resulted in fire and explosion and 3 accidents had no release and/or ignition. The outcomes depend of course on the types of accidents registered in the database and the accidents selected by Mirza et al. It should be noted that the selected accidents had taken place in a processing environment, not in a domestic environment or in a refuelling station.

Table 26 - Mirza et al.: Equipment involved and consequence outcomes for 32 selected accidents

Equipment type	Total	Fire only	Explosion only	Fire and explosion	No ignition
Piping	10	4	3	2	1
Miscellaneous	6	1	3	1	1
Storage vessels	5	2	2	1	0
Valves	3	2	0	0	1
Flanges	2	2	0	0	0
Gaskets	2	2	0	0	0
Process vessels	2	0	1	1	0
Safety devices	2	1	1	0	0
Total	*32*	*14*	*10*	*5*	*3*

One of the accidents in the h2 tools lessons learned database presumably involved a BLEVE: https://h2tools.org/lessons/liquid-hydrogen-tank-boiling-liquid-expanding-vapor-explosion-bleve-due-water-plugged-vent.

A release of hydrogen from a delivery truck in an urban environment has been described in detail by Venetsanos et al. (Venetsanos et al., 2003). The accident involved a release of gaseous hydrogen from two pressurised cylinder from a tube trailer in a street in central Stockholm in 1983. Ignition of the released hydrogen occurred after some 10 s (estimation) and resulted in a considerable explosion (reportedly 50 mbar overpressure at 90 m distance), 16 injuries, heavy damage to a nearby building and broken windows within a radius of 90 m. The corresponding critical event in the generic event trees is ‘leak from connection’ of ‘pressure transport equipment’ (EQ8), see Figure 43.

Hankinson and Lowesmith (Hankinson and Lowesmith, 2013) reviewed 18 accidents related to road transportation and 39 accidents related to liquefied hydrogen storage or hydrogen liquefaction. The majority of the transportation accidents involved a release from a burst disk or relief valve.

Literature on risk assessment and consequence evaluation

Several documents and publications exist in which risk assessment methods are described for the hydrogen fuel supply chain in general or for hydrogen refuelling stations in particular. Most articles focus on specific elements of the risk assessment and do not describe in full detail which release scenarios and consequence events should be used. Below, the relevant information related to consequence events is summarised.

- Rigas and Sklavounos (Rigas and Sklavounos, 2005) analysed hazards for gaseous and liquid hydrogen storage with a focus on consequence events. Ignition results in a fireball, jet fire or flash fire if the hydrogen cloud is in an open space, and in a confined vapour cloud explosion (CVCE) if the hydrogen enters a confined space. The CVCE can either be a deflagration or a detonation. Rigas and Sklavounos also discuss the impact of an engulfing fire on pressurised gas storage vessels or cryogenic liquid storage vessels. While the first would lead to tank rupture and subsequent fireball or jet fire, the latter would result in a tank rupture and Boiling Liquid Expanding Vapour Explosion (BLEVE).

- Matthijssen en Kooi (Matthijsen and Kooi, 2006), used generic Purple Book scenarios to analyse the risk of a medium sized hydrogen refuelling station to the surroundings. For instantaneous scenarios, they only considered flash fire, presuming that these occur 'in an open environment'. For continuous scenarios, jet fire, flash fire and vapour cloud explosion were considered to be relevant dangerous phenomena.
- Rosyid (Rosyid, 2006) described various safety aspects of the hydrogen fuel supply chain, including hazard identification (HAZID), fault tree analysis (FTA) and quantitative risk assessment (QRA). For hydrogen storage, the following release scenarios were selected: catastrophic rupture, continuous release of liquid or vapour through a hole on the tank, vapour release through relief valve, vapour release through rupture disc, full bore rupture of a vapour line and full bore rupture of a liquid line. For transportation by truck, the following scenarios were discussed: large release due to collision, leaks from pipes and fittings, failures of relief valves and rupture discs. For pipelines, rupture of pipeline and leak from pipeline was discussed.

  The considered dangerous phenomena for instantaneous releases were early explosion, fireball, late explosion and flash fire. Continuous releases can result in jet fire, late explosion or flash fire. The late explosion is a generic vapour cloud explosion event.

- Pritchard and Rattigan (Pritchard and Rattigan) discussed hazards of liquid hydrogen in general. Among others, they state that Rapid phase transition could be an additional relevant dangerous phenomenon that has received little attention until now. RPT might occur when cold liquid hydrogen comes into contact with a warm liquid, such as water. For hydrogen refuelling stations on land, RPT does not need to be considered. Pritchard and Rattigan also draw attention to possible solidification of oxygen in installations (due to air ingress) that can re-gassify when warmed-up (e.g. for maintenance), and create oxygen-enriched atmospheres with potential for heavy explosions. Cold burns are also discussed.
- Li, Pan, Meng and Ma (Li et al., 2011) studied safety distances to be used for a liquid hydrogen storage tank, and compared various consequence events for an instantaneous release and continuous release. Besides common dangerous phenomena such as fireball, jet fire, flash fire and vapour cloud explosion, they also analysed 'cold cloud' (cold burns). As in Rosyid et al., the vapour cloud explosion is a generic event.
- Moonis, Wilday and Wardman (Moonis et al., 2010) carried out a preliminary risk assessment for the hydrogen fuel supply chain, studying consequence distances for accident scenarios for hydrogen transportation, delivery, storage and dispensing. Effect distances were calculated for fireball, jet fire, pool fire, flash fire and vapour cloud explosion. The vapour cloud explosion is generic.
- Hankinson and Lowesmith (Hankinson and Lowesmith, 2013) describe the quantitative risk assessment procedure for liquefaction of hydrogen. Using the outcomes of two HAZID studies, 19 critical events were selected to assess risk. The dangerous phenomena considered include jet fire, generic vapour cloud explosion, pool fire, BLEVE, confined

vapour cloud explosion, internal tank explosion and explosion of solid oxygen and hydrogen within process equipment.

- LaFleur, Muna and Groth (LaFleur et al., 2015) illustrate how frequency and effect analysis of nine representative scenarios can be used to define design requirements for hydrogen refuelling stations. The nine scenarios are (i) jet fire from a leaking dispenser, (ii) rupture of a gas pressure vessel, (iii) deflagration in a confined space, (iv) detonation of an hydrogen/air mixture in a vent pipe, (v) release of liquid hydrogen from a liquid storage tank, (vi) a vehicle fire in the dispensing area, (vii) rupture of a pipeline, (viii) release of hydrogen with interlocks failing.

Table 27 provides a summary of specific release scenarios encountered in literature. Whether these scenarios should be used for a specific risk assessment, depends on the objectives and context of the risk assessment, and on the design of the installation considered.

Table 27 - Summary of critical events found in literature

Equipment type	**Critical events found in literature**
GH2 or LH2 vessel	• Internal tank explosion (initiating event) • Catastrophic rupture (initiating event) • Hole in the containment • Release from a relief valve or rupture disk • Detonation of hydrogen/air mixture in the vent pipe
GH2 or LH2 pipe, line or hose	• Full bore rupture of the pipe, line or hose • Hole in the pipe, line or hose • Internal explosion (e.g. due to solid oxygen regasification)
GH2 or LH2 transportation unit	• Catastrophic rupture • Hole in the containment • Release from a relief valve or rupture disk
Other equipment types (pumps, compressors, heat exchangers, separators, …)	• Catastrophic rupture • Leak
Seals and connections (flanges, joints, fittings,…)	• Failure of seal or connection (full diameter) • Leak from seal or connection (including leaks from gaskets).
Dispenser	• Release from the dispenser

The dangerous phenomena found in literature are listed in Table 28. An internal explosion is an explosion that occurs prior to rupture of a tank or pipe. Rupture of a tank or pipe on the other hand, is a more generic release type that could be the result of various causes (e.g. overpressure, collision, material defects, etc.). In order to show that, according to many, vapour cloud explosions can also occur in an unconfined space, a distinction is made between generic vapour cloud explosion and confined vapour cloud explosion. Whether the dangerous phenomena from Table 28 should be used in a specific risk assessment, depends on the objectives and context of the risk assessment.

Table 28 - Consequence phenomena found in literature

Release type	Release phase	Consequence phenomena found in literature
Internal explosion in tank or pipe	Not relevant	• Overpressure
Explosion in an open pipe or vent stack	Not relevant	• Overpressure
Catastrophic rupture of a vessel or tank	Gas	• Fireball • Generic vapour cloud explosion • Confined vapour cloud explosion (for confined spaces) • Flash fire
Catastrophic rupture of a vessel or tank	Liquid	• BLEVE • Generic vapour cloud explosion • Confined vapour cloud explosion (for confined spaces) • Flash fire • Pool fire • Cold effects (cold burns)
Release from an opening in a vessel or pipe (including full bore rupture of a pipe)	Gas	• Jet fire • Generic vapour cloud explosion • Confined vapour cloud explosion (for confined spaces) • Flash fire
Release from an opening in a vessel or pipe (including full bore rupture of a pipe)	Liquid	• Generic vapour cloud explosion • Confined vapour cloud explosion (for confined spaces) • Flash fire • Pool fire • Cold effects (cold burns)

Modification of the generic event trees

When comparing the release scenarios from Table 27 to those in the generic event trees (previous subsection), it becomes visible that two extra scenarios could be added to the generic event trees, in order to cover all relevant hazardous events related to hydrogen:

- For vessels: detonation of hydrogen oxygen mixture in the vent pipe connected to a storage vessel (if present). This scenario was identified by LaFleur, Muna and Groth (LaFleur et al., 2015). The scenario can be prevented by adequate dimensioning of the vent, as prescribed by codes and standards. Therefore, this critical event is not deemed relevant enough for modification of the (generic) event trees.
- For LH2 pipework: internal pipe explosion. Internal vessel and pipe explosions may occur for example due to solidification and regassification of oxygen, as described in more detail

in (Pritchard and Rattigan, 2010) and in (Hankinson and Lowesmith, 2013). Internal vessel explosions are already included in the generic event trees. Internal pipe explosions should be added.

When comparing the dangerous phenomena from Table 28 to those in the generic event trees, it becomes visible that the possibility of cold burns should be added. Cold burns occur if a person is exposed to cold unignited hydrogen. This dangerous phenomenon is relevant for cryogenic hydrogen spills. It could be noted that consequence distances for cold effects are generally lower than for fire phenomena (Li et al., 2011). The phenomenon is added to the generic event trees however, to illustrate that for cryogenic hydrogen dangerous phenomena can occur in absence of ignition.

Adding internal pipe explosion for GH2 and LH2 and cold effects for LH2 releases, leads to modification of several event trees. The event tree for release of liquid from a cryogenic storage vessel (Figure 40) is replaced by Figure 48. The event tree for releases of liquid from other cryogenic installations (Figure 41) is replaced by Figure 49. The event tree for two-phase releases from cryogenic installations (Figure 42) is replaced by Figure 50. The event tree for GH2 releases from gas pipelines (Figure 44) is replaced by Figure 51 and the event tree for LH2 releases from liquid pipelines (Figure 45) is replaced by Figure 52. The event tree for gas releases from GH2 installations (Figure 43) remained unchanged.

Users may choose to deviate from these general event trees, depending on the objectives and context of their studies. These deviations should be motivated.

Critical event	**Secondary event**	**Tertiary event**	**Dangerous phenomenon**
Breach on shell in liquid phase	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Leak from connection in liquid phase	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects

Vessel collapse	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects

Figure 48 - Modified event tree for cryogenic storage (EQ7), for liquid hydrogen below boiling point

Critical event	Secondary event	Tertiary event	Dangerous phenomenon
Breach on shell in liquid phase	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Leak from connection in liquid phase	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Pool formation	Ignited pool	Pool fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects

Figure 49 - Modified event tree for cryogenic installations other than storage (EQ8 and EQ16), for liquid hydrogen below boiling point

Critical event	Secondary event	Tertiary event	Dangerous phenomenon
Breach on shell in vapour phase	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Breach on shell in liquid phase	Two-phase jet	Ignited two-phase jet	Jet fire

	Pool formation	Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
			Cold effects
		Ignited pool	Pool fire
Leak from connection in vapour phase	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire
			Cold effects
Leak from connection in liquid phase	Two-phase jet	Ignited two-phase jet	Jet fire
	Pool formation	Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
			Cold effects
		Ignited pool	Pool fire
Catastrophic rupture	Catastrophic rupture	Catastrophic rupture	Missiles ejection
			Overpressure generation
	Aerosol puff	Ignited aerosol puff	Fireball
	Pool formation	Gas dispersion with pool evaporation	Vapour cloud explosion
			Flash fire
			Cold effects
		Ignited pool	Pool fire

Figure 50 - Modified event tree for cryogenic installations (EQ7, EQ8 and EQ16), for two-phase hydrogen

Critical event	Secondary event	Tertiary event	Dangerous phenomenon
Internal explosion	Internal explosion	Internal explosion	Overpressure
Leak from gas pipe	Gas jet	Ignited gas jet	Jet fire
		Gas dispersion	Vapour cloud explosion
			Flash fire

Figure 51 - Modified event tree for GH2 pipework (EQ10)

Critical event	Secondary event	Tertiary event	Dangerous phenomenon

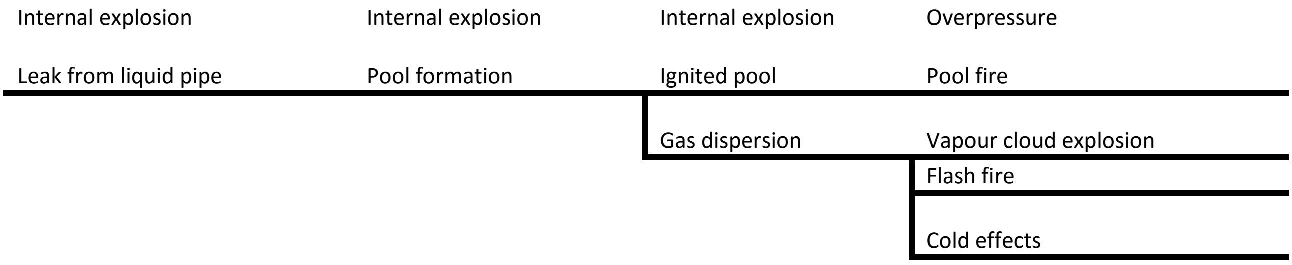


Figure 52 - Modified event tree for LH2 pipework (EQ10)

10.2. Gap analysis

In the gap analysis, we will discuss which physical phenomena need to be modelled, if models are available and if data for validating the models are available. Prior to the in-depth discussion per physical phenomenon, a few general remarks are made.

First of all, at least two recent/running initiatives have overlap with the current gap analysis.

- H2FC European Infrastructure (www.h2fc.eu) is a European Infrastructure Project funded by the European Commission for research and development on safe production, storage, distribution and application of hydrogen. One of the objectives of H2FC is to construct a "Database of High Quality Experimental Reference Data", for release, dispersion, ignition, jet fire, deflagration and detonation (H2FC, 2014). Allegedly, a first version of the database can be accessed by H2FC partners. In 2014, it was intended that a later version would be open to the public. It appears as if this disclosure to the general public will now be realized through the SUSANA project (see next item).
- More recently, the SUSANA project aims to develop a Model Evaluation Protocol for using Computational Fluid Dynamics models to analyse safety of hydrogen technologies (Baraldi et al., 2015), (Coldrick et al., 2015). Among others, the project will analyse requirements for physical and mathematical models (WP2) for the following physical phenomena:
    - Release and dispersion
    - Ignition and jet fire
    - Deflagration
    - Detonation.

  The project also aims to construct a publicly available database for validating models for these phenomena and to define benchmark cases for comparison of CFD analyses. According to Baraldi et al., a first version of the database contains data from some 30 experiments for hydrogen.

The EU Joint Research Centre organised a two-day workshop in 2012, where key experts from science and industry were asked to assess the state-of-the-art in safety assessment and to identify knowledge gaps. The results of this workshop have been reported in (Kotchourko, 2013) and (JRC, 2014). Another useful overview paper for hydrogen accidental release modelling and validation was provided by the International Atomic Energy Agency (IAEA, 1999), in particular Chapter 8.

Regarding the availability of models, several papers were found in which the computer models used were described. The modelling approached can be categorised as follows..

- The use of generic integral models for discharge, dispersion and fire phenomena. Integral models involve the solution of ordinary differential equations for a limited set of parameters (Batt, 2014). Integral models have the advantage that they can be derived from experiments relatively easy and that they require little calculation time. A downside is that they do not provide an opportunity for tailored assessment (taking into account specific local features). Generic integral models have been developed to assess process safety for a wide range of products and process conditions and different phenomena. Examples of generic integral models are SAFETI from DNVGL, Effects from TNO and FRED from Shell Global Solutions. SAFETI was used by Matthijsen and Kooi (Matthijsen and Kooi, 2006), Rosyid (Rosyid, 2006), Moonis, Wilday and Wardman (Moonis et al. 2010) and Li, Pan, Meng and Jianxin (Li et al., 2011). Hankinson and Lowesmith (Hankinson and Lowesmith, 2013) used Shell FRED. These integrated tools have the advantage that many different phenomena can be modelled, such as dispersion, pool evaporation, dispersion, jet fire, pool fire, fireball, BLEVE and vapour cloud explosion. These tools are not specifically designed for hydrogen release, so their validity must be demonstrated separately, and in the context of the application of the model.
- The use of integral models specifically developed for hydrogen. Few readily available tools were found in literature that were developed specifically for hydrogen. An exception is the HyRAM software toolkit developed by Sandia (Groth and Hecht, 2015). HyRAM integrates knowledge obtained in different international hydrogen projects, for example the HySafe project and work coordinated under the International Energy Association (IEA) Hydrogen Implementation Agreement (HIA). In the 2015 version of HyRAM (1.0 beta), three phenomena can be analysed: jet fire, vapour cloud fire with and vapour cloud fire with overpressure (deflagration or detonation). These are applicable for gas releases only. Though specifically designed for hydrogen systems, the models are quite generic in other aspects, for example in the correlations used to determine concentrations versus distance and flame lengths.
- The use of Computational Fluid Dynamics (CFD) models. CFD models are numerical models that use 3D partial differential equations to analyse flow. CFD models allow for complex analysis of flow and can take into account the influence of 3D objects. Downsides of the complexity are that setting up a CFD study is complex too and that running CFD models requires long calculation times. CFD tools were applied in several papers, in particular to assess overpressure effects for ignition of a hydrogen cloud in confined or congested areas, or to assess the influence of obstacles and structures on jet fires. Several references were found in literature to the use of CFD models, e.g. (Rigas and Sklavounis, 2005), (Venetsanos et al., 2010), (Molkov et al., 2007) and (Makarov and Molkov, 2013). CFD calculations are tailored to the application and the assumptions used need to be justified. The Susana project (Baraldi et al., 2015) aims to provide guidance for the justification of modelling assumptions.

- The use of shallow layer models. Shallow layers models are numerical models that use a system of 2D partial differential equations to analyse flow. Both complexity and calculation time are intermediate between integral models and CFD models (Batt, 2014). References to the use of shallow layer models were found in (Verfondern and Dienhart, 2007) and (Li et al., 2015).

Consequence models are used for quantitative consequence and risk assessment. Consequence and risk assessments come in different types, depending on the aim of the study. One type of application is to use a quantitative risk or consequence assessment for specific design questions, for example to determine a (sufficiently) safe distance between two specific pieces of equipment, e.g. (LaFleur et al., 2015). For this type of application, it is usefully sufficient to study one or two consequence phenomena for the pieces of equipment considered, and for a limited set of weather conditions and wind directions. Another application is to determine the total risk that the entire installation imposes to the surroundings (a 'full QRA'). For this application, several release and consequence events need to be considered for each equipment part in the installation, and for different weather conditions and wind directions. The type of application poses practical constraints on the models that can be used. While CFD analyses can be carried out to determine a safe distance between two parts of an installation, applying CFD for full QRAs is too demanding in terms of time and costs. As a result, full QRAs are almost exclusively carried out using integral models.

Selection of consequences to be modelled

In the previous section, the relevant critical events and dangerous phenomena for risk analysis were identified. The following physical phenomena models are required to assess the risks associated with these critical events and dangerous phenomena:

- Discharge and dispersion from compressed gaseous hydrogen equipment, due to rupture, breach or leak
- Vessel burst explosion
- Fireball and blast wave for rupture of a high-pressure gas tank
- Vented pipe explosion
- Discharge and dispersion from cryogenic equipment containing liquid hydrogen, due to rupture, breach or leak
- BLEVE (burst) and fireball following rupture of a cryogenic vessel or tanker
- Ignited releases from orifices (jet fires)
- Pool fire
- Vapour cloud explosion (deflagration and detonation)

The physical models have to take into account the properties of hydrogen where relevant. These specific properties were described in section 3.4. In addition, the emerging risk concerns hydrogen refuelling stations. For refuelling stations, it can be expected that release occur outside (in open air) but possibly in the vicinity of obstacles, roofs and semi-enclosures.

In the subsections below, the model requirements and presence of models and validation data are discussed. An important premise of the analysis is that it is assumed that all hydrogen systems at refuelling studies are located outdoors, and that infiltration of hydrogen in enclosures is prevented by design. Indoor releases and accumulation of hydrogen gas within enclosures are therefore not considered in the gap analysis below.

10.2.1 Discharge and dispersion for releases from compressed gaseous hydrogen containments, due to rupture, breach or leak

Discharge and dispersion are two phenomena that are closely linked. In particular for high-pressure releases, where the orifice pressure exceeds the ambient pressure, there is no clear-cut transition between discharge and dispersion. In hydrogen literature, the two phenomena are often discussed in combination. This approach is also adopted here.

Release scenarios for gaseous hydrogen include (i) catastrophic rupture of a pressurised tank or cylinder, and (ii) leak from a pipe or vessel, including rupture of a short pipe. Rupture or leak from a long-pipeline is not considered here, as all pipes on the refuelling station will be relatively short. For short pipes, discharge can be approximated with (quasi) steady state models.

The two release scenarios (catastrophic rupture and leak) require different physical models to calculate the source term. These source term models should be applicable for and validated for the high pressures typically used for gaseous hydrogen storage, e.g. pressures between 350 and 700 bar (35 to 70 MPa), or ultimately 1000 bar (100 MPa).

<u>Instantaneous release without ignition</u>

Catastrophic rupture of equipment containing pressurised gasses has received little attention in literature. For example, no models for this type of release are included in the Yellow Book (CPR14E, 1999). In addition, no experiments for this type of release were found in work package 4. Discharge and dispersion modelling for catastrophic rupture of compressed gaseous hydrogen (CGH2) containers is no exception. The dominant view appears to be that catastrophic rupture of hydrogen containers should be prevented rather than analysed. In addition, if rupture does occur, ignition and fireball are more likely than no ignition and gas dispersion.

Catastrophic rupture of CGH2 tanks was not discussed in overview documents such as (IAEA 1999), (HyFacts, 2013c) and (JRC, 2014). The only reference to catastrophic rupture discharge and dispersion modelling was found in publications in which consequences were calculated with SAFETI, e.g. (Rosyid, 2006). In these publications, catastrophic rupture and dispersion were modelled using the generic compressed gas instantaneous release model in SAFETI. None of these publications mention the availability of validation data.

Models to assess overpressure effects from tank failure will be discussed in the subsection dealing with tank explosions.

Summary:

- The model availability is scored RED. No specific models for hydrogen appear to exist. Models defined for other gasses are scarce and are likely to be inaccurate due to large differences in density/buoyance between hydrogen and other compressed gasses.
- The model validation is scored RED. No validation data were found.

<u>Leak from a pipe or vessel</u>

For leaks from pressurised hydrogen equipment (jet releases), a large amount of information is available in literature. A distinction can be made between releases directly from a vessel and releases from a pipe connected to a vessel. For the latter case, adiabatic expansion along the pipe needs to be considered. Time-dependence of the release rate, could be considered if the orifice size and/or the duration of interest is large. According to Chapter 2 of the Yellow Book (CPR14E, 1999), the physics of gas releases from pressurised systems are well-known. Many validated models exist to calculate discharge rates for leaks from pressurised equipment.

A distinction is often made between high-pressure momentum driven releases, low-pressure buoyancy driven releases and transient releases, e.g. (HyFacts, 2013c). For momentum driven releases, jet air entrainment is the dominant phenomenon for mixing hydrogen to concentrations below the Lower Flammability Limit, i.e. the lower concentration of interest. For low momentum releases, diffusion is relevant. Reduced momentum releases show transient behaviour.

During normal operation, the pressure at hydrogen refuelling stations is high, typically between 350 bar (35 MPa) and 700 bar (70 MPa). Undisturbed releases at high pressure will be momentum driven releases. At high pressure, the discharge flow will be chocked, with an orifice pressure above ambient pressure. Downstream of the orifice, the flow will contract until the smallest diameter is reached at the vena contracta, and expand to atmospheric pressure by means of shock waves. In hydrogen literature, high pressure releases with chocked flow are commonly referred to as “underexpanded” jets. Different models exist to calculate orifice conditions, expanded conditions and far field hydrogen concentrations for underexpanded jets. A common approach in the hydrogen community is to use the “notional nozzle concept” developed by Kalghatgi and Birch to obtain concentration versus distance correlations (Schefer et al., 2007), (Kotchourko, 2013).

For high pressure releases, non-ideal gas behaviour (or real gas behaviour) is relevant. As a result, an appropriate real gas Equation of State should be used (Markert et al., 2013). Models should also correctly calculate temperature changes during adiabatic expansion. Contrary to most other substances, hydrogen gas will heat rather than cool when expanding at room temperature. This effect is known as the reverse (or negative) Joule-Thomson effect.

Transient or buoyant releases can occur if the pressure is reduced, e.g. during maintenance or shut-down operations, or if the discharge is obstructed (e.g. for leaking flanges). For such releases diffusion must be considered. The air intake by diffusion can be derived from experiments (Houf and Schefer, 2008).

Several datasets are available for validating compressed hydrogen discharge and release models. More than 20 experiments for gaseous hydrogen and 14 experiments for helium were identified by the JRC in 2011 (JRC, 2011). The SUSANA project aims to put the outcomes of a number of relevant experimental tests in a publicly available database for validating purposes (Baraldi et al., 2015).

Refuelling stations are characterised by the presence of objects and structures in the vicinity of the fuel installations. As a result, releases will typically not be “free jets”, but rather along structures (attached jets) or towards structures (impinging jets). New experiments and models are required to analyse the precise effects of objects and structures (JRC, 2014). Another topic that is currently being researched is the effect of non-circular nozzles (Makarov and Molkov, 2013).

Summary:

- The model availability is scored GREEN. Different types of models are available for free jets. CFD can be used to study attached and impinging jets.
- The model validation is scored GREEN/ORANGE. A substantial amount of data is available for validating free jets. Added validation is desired for attached and impinging jets.

10.2.2 Vessel burst explosion

Catastrophic rupture of a high-pressure CGH2 tank has received little attention in hydrogen literature. According to Molkov and Kashkarov (Molkov and Kashkarov, 2015), “one group of experts assumes that the probability of a catastrophic temperature is so small that this scenario could be removed from the quantitative risk assessment at all” (Molkov and Kashkarov, 2015). Note: this position is not shared by Molkov and Kashkarov.

Catastrophic rupture of a vessel can occur for example as a result of material failure, due to overpressurisation while loading and due to overpressurisation caused by external heating. Typically, pressure relief devices are installed to prevent the pressure to increase to intolerable levels. As any device, a pressure relief device can fail. Therefore, catastrophic rupture of a high-pressure vessel is a possible scenario. Catastrophic rupture of a high-pressure vessel primarily produces a blast wave (vessel burst explosion) that is a result of the released energy. Direct ignition gives an additional fireball. In absence of ignition, an unignited puff disperses to the surroundings.

Generic vessel burst (blast) models for catastrophic rupture of compressed gas tanks are readily available and can be found for example in (CPR, 1999) and (CCPS, 2010). In most cases, dimensionless curves have been derived from experimental data. For the case considered, maximum explosion strength and explosion impulse can be deduced form these dimensionless curves by adding the appropriate dimension (e.g. static pressure prior to explosion). The validity of these models for rupture of CGH2 tanks is unknown. CGH2 tanks have a much higher pressure than ordinary compressed gas tanks and, for example, ideal gas approximations will give inaccurate outcomes. The amount of energy contributing to the explosion might depend on burning velocity and could be different between hydrogen and other substances.

One hydrogen blast wave model was developed by Molkov and Kashkarov (Molkov and Kashkarov, 2015).The model appears to be the only one dedicated to hydrogen. The authors used a generic vessel burst model developed by H.L. Brode as a starting point, and added non-ideal gas behaviour and chemical (combustion) energy. Model outcomes were compared to two bonfire tests for high-pressure vehicle tanks described by Zalosh (Zalosh, 2007).

Summary:

- The model availability is scored ORANGE. Generic vessel burst models exist but their validity still needs to be demonstrated.
- The model validation is scored RED. Only two tests were carried out. The quality of the data might be limited.

10.2.3 Fireball and blast wave for rupture of a high-pressure gas tank

If hydrogen released in a catastrophic rupture is ignited (directly), the resulting phenomenon is a fireball. Generic fireball models are readily available and descriptions of such models can be found for example in the Yellow Book (CPR, 1999) and in CCPS guidelines (CCPS, 2010). A distinction can be made between static models, in which the fireball radius, emissive power and height are fixed, and dynamic models, in which these parameters vary with time. In both cases, empirical correlations are used to determine fireball size, location and radiation.

The authors who included fireball scenarios in risk assessments for hydrogen applications, (Rosyid, 2006), (Moonis et al., 2010), (Li et al., 2011) and (Hankinson and Lowesmith, 2013), all made use of generic hydrocarbon fireball models. The accuracy of these models is probably limited, because hydrogen is different from other hydrocarbons. For example, the flammability range of hydrogen is large when compared to hydrocarbons and the burning velocity is high. In addition, no CO_2 or soot is produced in the combustion of hydrogen and radiative properties could therefore be very different.

Specific validated models for hydrogen fireballs are still lacking. According to Hankinson and Lowesmith “no validated hydrogen fireball models exists” and according to Molkov and Kashkarov “techniques to calculate separation distances from blast wave and fireball are absent”. The JRC has identified the simulation of fireballs as an important knowledge gap (JRC, 2014).

Summary:

- The model availability is scored ORANGE. Generic fireball models exist but their validity still needs to be demonstrated.
- The model validation is scored RED. No validation data is available.

10.2.4 Vented pipe explosion

Vented pipe explosions can occur due to inadequate purging of pipelines and due to inadequate dimensioning of vent systems. In a pipe, flames can accelerate, ultimately leading to a detonation. Such a detonation can cause considerable damage to nearby installations. The phenomenon is well-known and well-understood and was not further explored.

10.2.5 Discharge and dispersion from cryogenic equipment containing liquid hydrogen, due to rupture, breach or leak

For liquid releases, discharge, rainout, pool formation, pool evaporation and gas dispersion are closely linked phenomena that are often discussed in combination. This approach is also adopted here. Releases can either be instantaneous (rupture of a vessel or tanker) or continuous (leak).

Liquid hydrogen is usually stored or applied at temperatures just below its atmospheric boiling point (20 K or -253°C). Pressurised equipment is used in order to able to withstand small increases in temperature and pressure. Accidents can either occur at normal operating conditions or due to accidental heating and corresponding pressure increase. In the latter case, the hydrogen will be superheated.

For leaks from a vessel, incompressible flow can be assumed as flashing before the orifice will be negligible. For releases from (short) pipe, flashing in the pipe will be negligible if the temperature is below the atmospheric boiling point of hydrogen, but could be relevant if the product is superheated prior to release.

For leaks of hydrogen, hydrogen will partly evaporate prior to hitting the ground, while the remainder will form a liquid pool. The evaporation prior to rainout depends on the temperature and size of generated droplets, which in turn depend on exit pressure, exit temperature and orifice diameter. The evaporation prior to rainout could substantial in comparison with pool evaporation and shouldn't be ignored. Pool spreading is determined by the discharge rate and ground surface characteristics. Pool evaporation is determined by pool size and pool temperature, the latter being influenced by pool evaporation and by heat transfer from surrounding air, from the ground and from solar radiation. Initially, a vapour film could be created between the liquid hydrogen pool and the ground, that impedes heat transfer from the ground to the liquid pool (IAEA, 1999).

Vapour generated by the leak and the pool evaporation will initially be cold and denser than ambient air. As a result, the initial vapour cloud behaves as a dense cloud. Mixing with ambient air increases the temperature and reduces the cloud density to values below the density of ambient air. The cloud will subsequently behave as a buoyant cloud (IAEA, 1999). Further dilution with air will reduce the buoyance and make the dispersion neutral. The cloud density can also be affected by condensation of water vapour in air.

Many parameters and characteristics are thus needed to reliably model discharge, pool formation, pool spreading, pool evaporation and vapour dispersion, making the modelisation very complex. Different elements in the model chain can be studied with different (sub)models, as long as these (sub)models are coherently linked. Few software tools exists that have all these submodels integrated into a coherent model chain.

The quality of models for liquid hydrogen accidental releases, and the availability of validation data, have been discussed in various papers, most recently in (Bratt, 2014). The papers consistently show that insufficient data is available for modelling and validating liquid releases. For example, using the input of key experts from science and industry, Kotchourko et al. concluded that the quantity and the level of details of available experimental details for liquid hydrogen releases are limited and do not allow for accurate quantification and modelling of the phenomena and validation of the models (Kotchourko, 2013), (JRC, 2014). This is in line with observations of Pritchard and Rattigan that “the consequences of an accidental spillage or leak of liquid hydrogen are poorly understood (…)” and that “a better understanding of this initial phase together with more experimental data on the dispersion phase are required if reliable models for predicting the consequences are to be developed and validated” (Pritchard and Rattigan, 2010). Likewise, Lowesmith, Hankinson and Chynoweth observed that “a review of available experimental data on the hazards posed by releases of liquid hydrogen was undertaken, which identified that, generally, there is a dearth of data relevant to liquid hydrogen releases” (Lowesmith et al., 2013), while Bratt stated that “there remains a general lack of understanding that is necessary for accurate modelling” (Batt, 2014).

Descriptions of available experimental data can be found in (Verfondern and Dienhart, 2007), (Pritchard and Rattigan, 2010), (Venetsanos et al., 2010), (Lowesmith et al., 2013) and (Kotchourko et al. 2013). In total, around 10 experiments of different quality have been referred to. These experiments have been carried out by the US Bureau of Mines (Zabetakis and Burgess), AD Little Inc, NASA (Witcofski and Chirivella), BAM (Schmidtchen and Marinescu-Pasoi), the WE-NET project (Hijikata and Chitose), INERIS (Lacome, Dagba, Jamois and Perette), HSL (Royle and Willoughby). According to Batt (Batt, 2014) however, “to date, experiments on liquid hydrogen spills have only included quantitative observations, which are of limited use for validating models.” The outcomes of the NASA test, that involved a spill of 5,7 m^3 of liquid hydrogen, will be disclosed in a database for validation purposes via the SUSANA project (Baraldi et al., 2015).

Summary:

- The model availability is scored ORANGE. Generic models exist but their validity for hydrogen still needs to be demonstrated.
- The model validation is scored ORANGE. Validation data is available, but too limited given the complexity of the subject.

10.2.6 BLEVE (burst) and fireball following rupture of a cryogenic vessel or tanker

Boiling liquid expanding vapour explosion (BLEVE) is a physical explosion that can occur if a vessel containing saturated liquids ruptures instantaneously. For hydrogen, a BLEVE can occur if a cryogenic vessel containing liquid hydrogen is first superheated and then ruptures (Rigas and Sklavounis, 2005). In hydrogen literature, few references to the BLEVE phenomenon were found. An explanation could be that the general belief is that the likelihood of this event is too low. For example, it is believed that isolation in double-walled tanks is sufficiently limits heat transfer from an external fire and prevents overpressure generation and rupture. However, it cannot be warranted that all liquid hydrogen vessels are double-walled and adequately isolated. In addition, failure of cooling and/or pressure relief could result in superheated vessels during normal operation (Rigas and Amyotte, 2013). As such, the possibility of a BLEVE shouldn’t be ruled out a priori. The h2 tools lessons learned database contains one incident that was believed to have been a BLEVE, which occurred in 1974 (https://h2tools.org/lessons/liquid-hydrogen-tank-boiling-liquid-expanding-vapor-explosion-bleve-due-water-plugged-vent).

A BLEVE primarily results in a blast wave caused by the explosive evaporation and expansion of superheated liquid. For flammable materials, the released puff is often ignited directly, resulting in a fireball. The impact of the blast wave (overpressure) is different from that of a fireball (heat radiation) and normally both should be assessed. Generic BLEVE models are readily available to determine the strength of the explosion and descriptions of such models can be found for example in the Yellow Book (CPR, 1999) and in CCPS guidelines (CCPS, 2010). The validity of these models for superheated liquid hydrogen BLEVEs is unknown.

A publication by Hankinson and Lowesmith (Hankinson and Lowesmith, 2013, is the only reference found that specifically considered the possibility of a BLEVE. The overpressure effects were not calculated because “usually the fireball event dominates the size of the hazardous area”.

To summarise, there appears to be no validation data for hydrogen BLEVEs and no specific models. The validity of generic models is unknown.

Summary:

- The model availability is scored ORANGE. Generic models exist but their validity still needs to be demonstrated.
- The model validation is scored RED. No validation data were found.

10.2.7 Ignited releases from orifices (jet fires)

If a continuous release (a ‘leak’) of hydrogen ignites, flames will burn back to the orifice and subsequently produce a jet fire. Jet fires have been extensively studied for various flammable materials, most predominantly for natural gas (NG), liquefied petroleum gas (LPG) and various mixtures containing natural gas. Most studies focused on gaseous and two-phase releases. Liquid releases can give a jet fire if the product is very volatile. This liquid jet fire may be unstable, e.g. the flame length may fluctuate.

The flame shape of a jet fire depends on the momentum and density of the jet and on the release direction. If the momentum is high, the jet is not affected by gravity or buoyance effects, and the flame shape can be approximated by a cylinder. For low-momentum jets, gravity and density is important, and flame shapes can be curved (banana-shaped). In most cases, the flame shape is something in between, i.e. straight near the orifice and curved near the flame tip. Flame shape can also be affected by obstacles in or near the flame (attached or impinging jets).

Jet fire radiation depends on the substance involved, released mass, momentum and weather conditions. A summary of modelling options for jet fire flame shape and radiation was provided by Hankinson and Lowesmith (Hankinson and Lowesmith, 2012).

Several integral models have been developed that describe how the radiation at a distance can be calculated. In many cases, experimental correlations are used to derive the flame shape from conditions at the orifice or at a pseudo source near the orifice. The flame radiative power depends on the release rate, the released material, the momentum of the release (relevant for air ingress) and wind conditions. Most integral models have been validated for NG and LPG. Some models have been validated for other products.

Ignited gaseous hydrogen (CGH_2) releases from orifices

A relative large amount of work has been carried out to understand characteristics of ignited hydrogen gas releases (jet fires), in particular at small-scale. A recent overview of the state-of-the-art in jet fire modelling can be found in Chapter 7 of (JRC, 2014). Flame length modelling and validation have been described in detail by Molkov and Saffers (Molkov and Saffers, 2013). Ongoing research includes large-scale jet fires, jet fires along structures (attached jet fires) or towards structures (impinging jet fires) and the influence on non-circular orifices (JRC, 2014). In addition, for hydrogen jet fires, the influence of contaminations in the fuel, or from dust particles picked-up from the ground, and the influence of radiation reflection by the ground, are relevant (Hall et al., 2014), but not yet fully understood.

(JRC, 2011) contains references to a dozen recent (post 2005) experimental campaigns in which hydrogen gas jet fires were studied. The total list of available data would be substantially larger. Knowledge gaps for hydrogen gas jet fires identified in include the effects of wind, surface, release direction and obstacles on parameters of jet fires (JRC, 2011).

Sandia has developed an integral model for gaseous hydrogen jet fires, which was recently integrated in the HyRAM tool (Groth and Hecht, 2015) and updated for heat radiation experiments for large-scale hydrogen releases carried out by Ekoto (Ekoto et al., 2012). DNVGL use a generic jet fire model with a specific fraction of heat radiated set for hydrogen (Hankinson and Lowesmith, 2013). The outcomes were also validated against the experiments of Ekoto. Several other authors used the generic jet fire model in PHAST, e.g. (Matthijsen and Kooi, 2006), (Rosyid, 2006), (Moonis et al, 2010) and (Li et al., 2011).

Summary:

- The model availability is scored GREEN. Generic and specific models exist, in particular for free jet fires, both buoyant and momentum-driven, and to a lesser extent also for attached and impinging jet fires.
- The model validation is scored GREEN/ORANGE. Many gaseous hydrogen jet fire experiments have been carried out. Added validation is desired for effects of wind, surfaces and obstacles.

Ignited two-phase and liquid hydrogen from orifices

Contrary to hydrogen gas jet fires, experimental data for two-phase and liquid hydrogen jet fires is still limited. In (Veser et al., 2011) and (Friedrich et al., 2012), flame stability was investigated for liquid jets, using indoor laboratory scale experiments. These experiments confirmed that liquid hydrogen jets can ignite. Three different regimes were found; (i) stable burning with flames propagating upstream to the orifice (flash back to the orifice), stable burning without upstream flame propagation and (iii) unstable downstream propagation (flame quenching). For the stable liquid jet fires, flame length and flame radiation were analysed. Large scale liquid hydrogen releases in the open were recently carried out by HSL (Hall, 2014). The campaign focussed on flammability limits, flame speed and radiation produced by the flame. In the majority of these tests, ignition resulted in upstream flame propagation to the orifice (burn-back) (Hall et al., 2014). In one test, an explosion was observed just after the flashback to the orifice. The exact causes of this explosion remain unknown. Four out of fourteen tests either didn't ignite or did not produce a stable flame. No other references to liquid jet fire experiments were found in literature.

Modelling of two-phase and liquid hydrogen jet fires is shortly described in (Hankinson and Lowesmith, 2013). They argue that jet fire is a feasible phenomenon for liquid hydrogen releases because the amount of rainout is typically low. Subsequently, the consequences of a liquid jet fire are investigated with a generic jet fire model, assuming a fraction of heat radiated for hydrogen that is similar to that of LNG.

Summary:

- The model availability is scored ORANGE. No specific models for liquid hydrogen jet fires were found and only few models for generic liquid jet fires.
- The model validation is scored RED. Two sets of experiments were found. Both focussed on flammability limits and stability of the flame.

10.2.8 Pool fire

Ignition of a hydrogen liquid pool will result in a hydrogen pool fire. For releases of LPG, gasoline diesel and LNG, pool fire characteristics have been studied in detail. Several integral models have been developed that describe how the radiation at a distance can be calculated. In most models, the flame shape is approximated with a tilted cylinder. The height, tilt angle and radiative power of the flame are usually derived from substance characteristics, pool diameter and weather conditions. Many integral models have been validated for LPG, gasoline and diesel. Some models have been validated for other products (e.g. LNG).

Very little information is available in literature on the characteristics of hydrogen pool fires. According to Lowesmith, Hankinson and Chynoweth, only one experiment is available in which the properties of hydrogen pool fires were analysed (Lowesmith et al., 2013). The experiment, carried out by the US Bureau of Mines (Zabetakis and Burgess) in the late 1950s, was small scale (D = 0.33 m) and was carried out in a Dewar flask to eliminate heat flux from the ground surface. As a result, this experiment is not of much use for validating models.

It appears that no validated models for hydrogen pool fires exist. Hankinson and Lowesmith themselves used a pool fire model developed for LNG spills to calculate hydrogen pool fire effects. It is unknown if this model produces reliable outcomes for hydrogen. The burning properties of hydrogen are likely to be different from those of LNG. In addition, hydrogen combustion produces no CO_2 or soot. Therefore, the amount of heat radiated from a hydrogen pool fire could also be substantially different from that of an LNG pool fire.

Summary:

- The model availability is scored RED. No specific models for hydrogen appear to exist. Models defined for other gasses are scarce and are likely to be inaccurate due to differences in burning velocity and radiation production.
- The model validation is scored RED. No validation data were found.

10.2.9 Vapour cloud explosion (deflagration and detonation)

Vapour cloud explosion is one of the most destructive phenomena that can occur as a result of an accidental release from an installation with hazardous substances. As a result, the explosion behaviour of hydrogen-air mixtures has been studied quite extensively. A general description of vapour explosion is provided in (Lees, 1996). The fundamentals are described in (CCPS, 2010) and in (CPR, 1999), which also prove guidance for modelling vapour cloud explosions. In short, combustion of a flammable gas mixture will always produce some overpressure, but the amount of overpressure produces, varies substantially for different circumstances. Key parameters that determine the maximum overpressure are the fraction of the number of molecules prior and posterior to combustion, combustion energy, fuel concentration, fuel mass within flammable limits, ignition energy, flame speed, turbulence ahead of the flame front and level of confinement. Explosion behaviour can be very sensitive to both release conditions and geometry of the environment (congestion and confinement), and overall the assessment is very complex. If explosion effects are assessed by models, modelling assumptions and modelling constraints should be investigated with scrutiny.

When compared to other fuel-air mixtures, the propensity to explode is relatively large for hydrogen-air mixtures, due to their high burning velocity (see Table 9). As a consequence, explosive behaviour of hydrogen-air mixtures has been studied extensively and a vast amount of publications on the topic is available. The investigations include both experimental and numerical simulations. General information on parameters that are relevant for hydrogen vapour cloud explosions (deflagrations and detonations) can be found in (IAEA, 1999) and (JRC, 2011). A paper from Shirvill et al. specifically addressed explosions hazard for hydrogen refuelling stations (Shirvill et al., 2012).

The state-of-the-art in hydrogen explosion research was described in (JRC, 2014), using input from a two-day workshop in 2012, attended by key experts from science and industry and organised by the EU Joint Research Centre. The document shows that significant advancements have been made in understanding and modelling specific elements of vapour explosions. At the same time, explosion behaviour is so complex that many important knowledge gaps still remain, even for isolated (relatively simple) topics. Specific models have been developed for specific research questions, and in general, all models developed have limited scope of application. Integrating relevant model features into a single model to predict explosion behaviour will not be accomplished in the near future. Extrapolating outcomes from idealised geometries to real geometries will prove to be another challenge. A list of knowledge gaps is included in Chapter 6 of (JRC, 2014). It shows that a substantial amount of work is still required before explosion behaviour can be predicted reliably for real scenarios.

As stated before, the SUSANA project aims to develop a publicly available database for validating hydrogen safety models. According to (Baraldi et al., 2015), this database will contain outcomes of a number of tests (around 10) involving deflagrations and a few more related to deflagration to detonation transition (DDT) and immediate detonation. One of these tests, involves a realistic scale release into a simulated dispensing area carried out by HSL and described in (Shirvill et al,., 2012).

Outcomes of various experiments have been simulated with CFD models. For example, a benchmark exercise for the realistic scale release into a dispensing area between 6 different parties was carried out and reported in (Makarov et al., 2012).(Venetsanos, 2003) describes a CFD simulation for a heavy deflagration that occurred in the centre of Stockholm, in 1983.

In the full scale QRA studies encountered in literature, generic models are used for (quantitative) risk assessment. This is motivated by the fact that explosion behaviour is very sensitive to a large set of parameters, some of which are either difficult to control or difficult to predict, and that modelling all these effects of parameters is even more difficult. Rosyid (Rosyid, 2006) and Hankinson and Lowesmith (Hankinson and Lowesmith, 2013) used a TNT equivalence model, both acknowledging that this approach is not ideal. Moonis, Wilday and Wardman used the (generic) Multi-Energy model developed for hydrocarbons, also acknowledging that “it is uncertain how applicable they are for hydrogen” (Moonis et al., 2010).

Summary:

- The model availability is scored ORANGE. Generic integral models developed for hydrocarbons exist, but their validity for hydrogen has not yet been demonstrated. CFD models have been developed to analyse specific aspects of explosion behaviour, but integrated models that capture all relevant phenomena are still lacking.
- The model validation is scored ORANGE. Quite a few experiments have been carried out to study deflagration, detonations and deflagration to detonation transition (DDT). However, explosion behaviour is complex and sensitive to many parameters. Therefore, more experimental data are required to fully understand vapour cloud explosions of hydrogen-air mixtures and to validate models.

Table 29 - Results of the scenario gap analysis for hydrogen refuelling stations

Phenomenon	Model Availability	Model Validation
Gas releases: discharge and dispersion – instantaneous release	**RED** No models available for hydrogen. Generic models not accurate.	**RED** No validation available.
Gas releases: discharge and dispersion – continuous release	**GREEN** Models available.	**GREEN/ORANGE**

		Validation available for free jets. Limited data available for attached jets and impinging jets.
Pressurised gas tanks: vessel burst	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**RED** Two test carried out. Data quality might be limited.
Pressurised gas tanks: fireball	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**RED** Two test carried out. Data quality might be limited.
Vented pipe explosion	**GREEN** Phenomenon assumed to be well-known and well-understood.	GREEN Models assumed to be sufficiently validated for hydrogen.
Liquid releases: discharge, pool vaporisation and dispersion	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**ORANGE** Validation data available but too limited given the complexity of the topic.
Instantaneous superheated liquid releases: BLEVE and fireball	**ORANGE** No models available for hydrogen. Validity of generic models needs to be demonstrated.	**RED** No validation available.
Ignited gas releases from orifices (gaseous hydrogen jet fires)	**GREEN** Both generic and specific models exist	**GREEN/ORANGE** Many experiments carried out. More validation desired

		for the effects of wind, surfaces and obstacles.
Ignited liquid releases from orifices	**ORANGE** No specific models were found and just few generic models for liquid jet fires.	**RED** The two sets of experiments do not provide enough detail for validating models.
Pool fire	**RED** No models available for hydrogen. Generic models not accurate.	**RED** No validation available.
Vapour cloud explosion (deflagration and detonation)	**ORANGE** Generic models available but validity not demonstrated. Specific CFD models can capture specific aspects of explosion behaviour, but integrated models that capture all relevant aspects are still lacking.	**ORANGE** Quite a few tests have been carried out, but given the complexity, more tests are required to fully understand vapour cloud explosions of hydrogen-air mixtures and to validate models.

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