PhD in Industrial Engineering - Curriculum Chemical Engineering

Title of thesis: Development of a methodological framework for the integrated HSE assessment of

LNG supply and utilisation chain

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### **Extended Abstract**

# 1. Summary

The thesis discusses different approaches, which have been developed to support the Health, Safety, and Environment (HSE) assessment of the natural gas industry. In particular, the Liquefied Natural Gas (LNG) represents the focus of the PhD activity, as the most challenging section of the chain. Operational, technological, and safety issues related to the LNG come from the high flammability of the substance, the extremely low operative temperature (about -162 °C), as well as the potential to generate large amount of vapour in case of release (i.e. the volumetric expansion is of about 600 times from liquid to vapour phase). These hazardous issues are encountered during LNG storage and transport activities, which are often located in vulnerable areas. The activities analysed the LNG storage and transport systems through different approaches, with the aim of developing an integrated HSE assessment of the most relevant safety aspects. The work can be divided in three main parts, summarized in the following:

- Performance analysis of LNG storage systems through the physical modelling of relevant heat and mass transfer phenomena;
- Safety analysis of LNG storage systems through the probability modelling of accidental scenarios, escalation of effects, and analysis of the role of safety barriers;
- Safety analysis of LNG maritime transport systems through the development of a methodology for the semi-quantitative risk assessment.

Each activity is described in the following paragraphs, where the state of the art, the methodology, the possible applications, and the main results are reported.

## 2. Performance analysis of LNG storage systems

In the first part of the thesis, the operative hazards associated with LNG storage systems are discussed.

Problem addressed and State of the art: LNG storage tanks are constantly subject to heat exchange from the environment, due to the great difference between the temperature of the fluid stored in the tank (- 162 °C) and that of the ambient air outside the vessel. The extremely low working temperature, which induces significant heat transfer from the environment, leads to relevant design issues and operating problems for cryogenic storage tanks [2]. Figure 1 illustrates the heat transfer phenomena and consequent recirculating natural convective flow, which lead to a vertical temperature gradient in the tank lading [3,4]. Compared to the case of a homogeneous liquid bulk, the warmer liquid layer at the interface determines an increased pressurisation rate and the generation of a vapour (Boil-Off Gas). The performance and design of the insulation layer [3] and the chemical-physical properties of the stored substances drastically affect the pressurisation behaviour [5]. The mentioned phenomena were object of several literature studies dedicated to the evaluation of natural convention phenomena in cryogenic tanks, as summarized in Table 1.

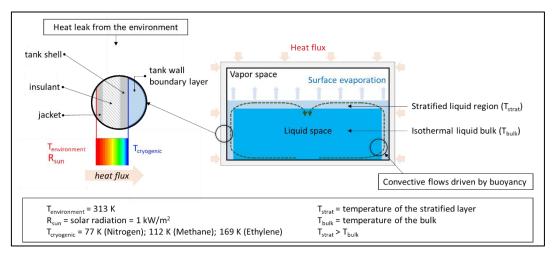


Figure 1. Physical phenomena involved in cryogenic vessel operations; b) visual simplification of the thermal stratification phenomenon.

Table 1. Summary of some recent numerical studies on the thermal stratification and pressurisation phenomena in cryogenic tanks. L=liquid, V=vapour.

Ref.	Year	Model	Phase	Substance	Tank scale (m <sup>3</sup> )	Investigation
[6]	2007	CFD	L+V	$LH_2$	0.8	aspect ratio
[7]	2008	CFD+lumped	L+V	$LOX,LN_2$	4·10 <sup>-4</sup>	stratification
[8]	2013	CFD	L	LNG	3.14	pressurisation
[9]	2014	CFD	L+V	$LH_2$	8·10 <sup>-4</sup>	insulation
[10,11]	2014,2015	CFD	L+V	$LH_2$	0.2	wall ribs, microgravity
[12]	2016	CFD	L+V	$LH_2$	5	interfacial turbulence
[13]	2016	CFD	L+V	LOX	12	pressurisation
[3]	2017	lumped	L+V	$LH_2$	88	insulation
[1]	2017	CFD	L+V	LN <sub>2</sub> ,LNG	3	filling, heat flux
[14]	2019	CFD	L+V	LOX	19	sloshing

**Key innovations:** Despite previous studies addressed cryogenic storage systems, they mainly focused on small-scale tanks. Moreover, the analysis of the effect of insulation performance and of stored fluid composition was not systematically addressed. In the present work, a 2D (2-dimensional) CFD (Computational Fluid Dynamics) model was developed to analyse the behaviour of cryogenic fluids in large-scale storage tank (100 m³). The boundary conditions were estimated from a 1-dimensional model to solve the heat transfer through the tank insulation layers, eventually taking into account accidental damages. The tank CFD model was preliminary validated against small-scale experimental data obtained for cryogenic nitrogen and then extended to the simulation of an industrial cylindrical tank, whose volume is 100 m³. The effect of filling level and possible insulation damage, on natural convection driving liquid stratification and ultimately tank pressurisation, was analysed. Specific performance indexes were proposed to efficiently compare the different scenarios.

**Applications:** The 2D CFD model was preliminary validated against experimental data obtained in [4], in which temperature and pressure of a small-scale tank (6.75 L) filled with LN<sub>2</sub> (liquefied nitrogen) were measured. The case is denoted as validation case (VC). The large-scale case (denoted as CS) reproduces a cryogenic LNG tank in use in a heavy trucks refuelling station located in Tuscany (Italy). Details on tank geometry, materials, and operating conditions are obtained through both field inspection and literature review of typical design of LNG storage tanks. The tank consists of an inner tank, which is in direct contact with the cryogenic fluid; an insulation layer under vacuum, and an outer external vessel. The tank is modelled both in normal operating conditions of the insulation system and in an accidental condition consisting in a partial loss-of-vacuum in the insulation. The effect of different filling levels is investigated as well. Table 2 summarizes all case-studies implemented in the analysis.

Table 2. Summary of industrial case studies implemented in the CFD model.

Parameter	VC	CS01	CS02	CS03
Working substance	N <sub>2</sub>	CH <sub>4</sub>	CH <sub>4</sub>	CH <sub>4</sub>
Liquid filling level (%)	50	90	90	40
Insulation state	See [4]	Intact	Damaged	Intact
Heat flux (W/m <sup>2</sup> )	3	4.3	23	4.3
Initial pressure (kPa)	99	690	690	690
Initial temperature (K)	See [4]	141.1	141.1	141.1

**Implementations:** For all the cases, a 2D domain was considered, due to the axial-symmetry of the tanks. Fully block-structured grids were generated with the software ANSYS Inc. ICEM. The grids were refined near the walls and at the liquid-vapour interface [15], resulting in 43,796 and 386,670 cells for VC and CSs, with minimum and maximum size of 0.1 mm-1.52 mm and 0.3 mm-25 mm, respectively. The VOF (Volume-Of-Fluid) method was employed due to the presence of an interfacial flow [16].

**Main Results:** The validation case results and the experimental data was in satisfactory agreement, with maximum error of about 0.8 % between experimental data and numerical predictions.

The industrial cases showed a pressurization of the tank limited to a rise in the range of 1.5 % - 6 %. The pressure build-up with a damaged insulation was about 5 times, compared to the intact insulation cases. The effects of insulation performance on the temperature may suggest a nearly linear correlation between the incoming heat flux and the temperature rise. The pressure rises 8 times faster with damaged insulation compared to the undamaged cases. Two performance indicators were defined to quickly assess the influence of the different variables on the relevant thermal phenomena: SI (safety indicator) and FI (flow indicator). SI compares the thermal energy accumulated in the liquid phase during the heat-up period against the theoretical thermal energy needed to reach a safety-critical condition. FI compares the natural convection occurring in the different case studies. Results showed that, even if the critical pressure conditions are still far at the end of simulations, SI is more than 6 times higher in the damaged insulation case, compared to the undamaged cases and shows a higher energy accumulation for lower than higher filling levels.

**Conclusions:** The main novelty of the analysis is that the model accounted for a large-scale geometry, which was rarely considered in previous studies on cryogenic storage tanks. Moreover, the implementation of a CFD model allowed to obtain accurate results on the velocity and temperature fields. The analysis may represent a useful tool supporting the management and the decision-making process of critical operations, such as those related to the cryogenic storage. Besides, the detailed results obtained in this work may support the development of lumped and integral models for the operability management field.

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#### 3. Safety analysis of LNG storage systems

Problem addressed: In the second part of the thesis, the focus moved on accidental scenarios induced by LNG releases. Large fires and explosions may occur following the accidental LNG release with potential impact other process units, leading cascading events (domino effects). The growing trend of interconnecting two or more facilities (i.e., forming a "chemical cluster" or "chemical industrial park" - CIP) represents a critical issue, since an accident can easily escalate from an industrial establishment to the nearby plants [6]. The PhD activity investigated the mechanism of LNG hazardous scenarios propagation in industrial assets (domino effect). Not only the failure procedure of a single installation (e.g., how temperature increases and how the tank wall is damaged etc.) is complex, but also the analysis of the domino propagation among the installations is difficult. To study the latter, the failure procedures of installations are usually performed through simplified and analytic approaches. In the literature, there is a lack of tools overcoming the issue of facilitate the modelling of cascading events while preserving the accuracy of results and the possibility to analyze different settings, such as complexity of layouts and the critical implementation of SBs.

State of the art: Common quantitative safety analyses often ignore cascading events in chemical clusters [7]. Nevertheless, several technical and scientific works were devoted to the development of methods for the quantitative assessment of domino effects, as documented by Necci et al. [4]. Relevant contributions addressed the implementation of domino effect in the "standard" QRA framework based on the combined estimation of frequency and consequences [1,12]. Multiple tools were developed and applied to carry out the evaluation of domino effect, such as: risk matrix screening [13,14], Monte Carlo simulation [15,16], event tree [17,18], graph theory [19], Bayesian networks [20-24], other tools interfaced with a geographical information system [25,26]. Safety barriers (SBs) implementation in domino effects analysis, is a critical element to derive sound information on the facility response given a primary event and to provide more accurate risk evaluations. Recent literature studies focused on the implementation, through simplified approaches, of SBs in the analysis of cascading events [41–43]. A two-parameters approach was proposed for the specific framework of domino effect prevention [45]. More generally, several tools were developed to undertake the quantitative assessment of mitigated domino scenarios following this approach, such as Bayesian networks [46], dynamic Bayesian network [23,24], and graph theory [18], performing also cost-benefit analyses [18,46]. However, these methodologies imply the definition of conditional probabilities, which are difficult to evaluate and likely not reliable for largescale industrial facilities and CIPs [22,28].

Key innovations: In the literature, there is a lack of tools overcoming the issue of facilitate the modelling of cascading events while preserving the accuracy of results and the possibility to analyse different settings, such as the implementation of SBs. Recently, domino effect assessment by agentbased modelling and simulation (DAMS) was proposed as an alternative tool to undertake the analysis of multiple scenarios [27,28]. The agent-based modelling and simulation (ABMS) relies on a bottom-up approach that describes a complex system through the interaction between its basic elements, i.e. "agents", including their features [29]. ABMS predicts the behaviour of the overall system by analysing the interactions of agents; thus, from the micro-scale perspective. The aim of the work was to further develop the DAMS tool by implementing the protection systems (SBs) and allowing to account for the interdependencies between different safety barriers and pieces of equipment to overcome the issues of common methodologies related to the complexity of the scenario evolution and the severe level of detail of the input data required for the analysis.

Applications and Implementations: The primary elements of a CIP are the storage and process units, which can be grouped in two main categories: atmospheric and pressurised equipment items. Therefore, the initial phase of the study consisted in equipment items schematization in terms of geometry and failure mode; considering both pressurized and atmospheric vessels. It is worth mentioning that the tool is applicable to any type of process equipment based on the availability of equipment vulnerability models, based on the detailed evaluation of the equipment failure mode. The second phase of the study aimed at SBs modelling, which represents the core of the work. Add-on safety barriers are characterized through the definition of quantitative performance parameters. In the third phase the numerical model was validated; a simplified test case was developed, and specific event tree analysis (ETA) was performed for the evaluation of final scenarios conditional probabilities. The analytical results were compared against the numerical results obtained from the tool. After verification, a large-scale case was implemented in the model and the effect of the different SBs in the mitigation of domino escalation was assessed. The schematic procedure for the implementation and application of the novel tool are shown in Figure 3.

A set of four simplified case studies was defined to verify the tool. In each case, the implementation of a single SB was considered, and the probability of each possible domino scenario was analytically evaluated trough ETA. It is worth mentioning that the same simplifying assumptions and probabilistic models, both for equipment involved in fires and safety barriers performance, were implemented in the ETA and in the tool. Hence, the verification was aimed at demonstrating the stability and soundness of the numerical tool in a simple application, with limited number of equipment, safety barriers and time steps. Then, the model was extended to the simulation of an industrial case study, considering a complex layout representative of a chemical cluster.

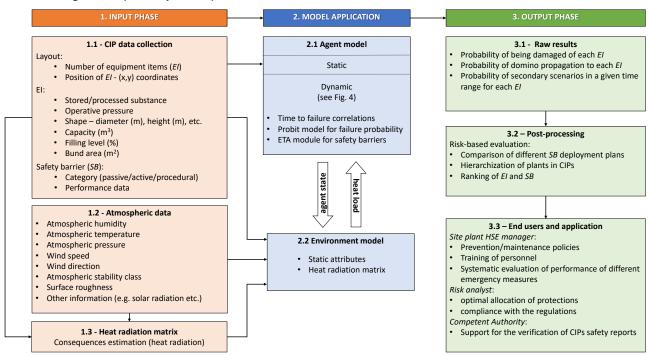


Figure 3. Schematic procedure for the implementation and application of DAMS-P.

**Results:** Validation: the tool showed a good agreement with analytical data for probabilities higher than 10<sup>-4</sup> and, however, for lower probabilities the tool provides reliable results considering the absolute value of scenarios. The tool was applied to several industrial case studies to demonstrate its capability in reproducing complex domino events, considering also synergistic effects, and accounting for the transient evolution of multiple scenarios in presence of safety barriers. This allowed for the identification of the critical barriers and the protection plans, according to their capability in the reduction of the escalation probability.

Conclusions: A tool for domino effect assessment, based on Agent-based modelling and simulation has been developed and the role of different categories of safety barriers has been addressed. The tool is suitable for the analysis of high complex layouts, being characterised by low computational costs and relying on simple, thus reliable, rules of accidents propagations. Results demonstrate the effective domino risk reduction achieved through the implementation of the protections. The capability of the approach adapts to a wide range of industrial sectors and critical infrastructures, in need of a simplified tool to describe the interactions and complex accident chains between a large number of industrial equipment. The results virtually provided by the tool may support the decision-making process on safety improvement of numerous and variegated chemical industrial parks (CIPs), through the identification of critical plants, equipment, components, and safety barriers.

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## 4. Safety assessment of LNG maritime transport systems

**Problem addressed:** The third part of the thesis focused on LNG transport systems, with reference to the maritime sector. LNG transport systems usually cross vulnerable zones, such as commercial or residential assets and industrial clusters, realistically increasing the risk level of the areas. Despite the effort made from the scientific community and the competent authorities, there is a lack of universally accepted methodologies for the safety assessment related to dangerous goods transport activities, in particular for the maritime transport systems. In fact, gas carriers approaching port areas do not undergo any risk assessment requirements.

State of the art: Limited studies dealt with methodologies to perform safety assessment of LNG maritime transport. The research in this field usually focused only on one aspect of the safety assessments or only on particular scenarios [100]. For example, the risk of LNG fuel storage tanks in LNG-fuelled ships was studied through a risk-based approach by combining dynamic process method with Monte Carlo simulation [178]. A quantitative risk assessment framework for determining the potential risk of leakage events in LNG-fuelled ships was also proposed [179]. Probabilistic risk assessment approach was applied to determine the safety exclusion zone for LNG bunkering stations on LNG-fuelled ships [180]. Hazards identification on LNG carriers was analysed, for example, by estimating the collision risk between an LNG tanker and a harbour tug during mooring operations [181]. A fuzzy set manipulation formula with multiple parameters such as consequence severity, failure consequence probability, and failure likelihood was used to assess the safety/risk levels of failure modes of LNG carrier systems [182]. The failure modes and consequences associated with cargo handling operation of LNG carrier were analysed by the means of a risk matrix method [183]. Same risk matrix based approach was applied for the development of method to identify and rank hazards associated with LNG carrier operations [184]. Consequence analysis of LNG releases was carried out for deep water port facilities through a CFD dispersion methodology [185]. The occurrence of fire and explosion from LNG ships was also evaluated, through fire and explosion hazard indexes [186]. A comprehensive methodology supporting the risk assessment for LNG carriers operation was developed based on societal risk acceptance criteria [187]. A recent review of publications dealing with risk analysis in the LNG sector revealed that the LNG carriers and LNG fuelled ships sector has received the most attention in the LNG sector accounting for the 34% of the total recorded publications. However, the percentage corresponds to 21 reported studies only [100]. The statistics highlight the need of further effort on the development of specific methods to perform safety assessment for LNG carriers.

Key innovations: In the study, two methods were developed for the safety assessment of LNG ships access to harbour areas. The first method relies on the application of a conventional tool, i.e. the risk matrix. The approach aimed at the development of a simplified procedure, based on common steps of safety assessment studies, specific for the risk assessment of LNG carriers in port area. The second method is based on the graph theory [199] and allows the analysis of complex situations, accounting also for possible domino scenarios. The graph theory is used to obtain graph indices that are representative of the risk. The approach is unconventional and needs a validation phase to assess whether it can be applied to perform safety assessments of HazMat transportation. The validation is performed implementing a simplified test case and comparing the risk indices obtained though the graph theory and the societal risk index, i.e. PLL. Then, the methodology is extended to the analysis of an industrial case.

## **Applications and Implementations:**

Method 1 - Risk Matrix Approach (RMA)

The methodology based on the Risk Matrix Approach (RMA) follows the fundamental steps of common safety assessments and evaluates the risk though a conventional method, i.e. the risk matrix. However, the proposed RMA is a case-specific procedure to perform risk assessment of HazMat ships access in vulnerable area. Since there is a lack of legislation and structured guidelines

on the topic, the Competent Authorities, that regulates this activity, require a technical support for the decision-making process. The basic concept of the RMA is to identify the possible accidental events and rank them according to their frequency and the severity. First, a quantitative analysis estimates quantitatively the frequency and severity of each scenario. Then, the results are ranked into a qualitative scale according to the risk matrix. Figure 4. shows the procedure of the risk assessment developed based on the RMA. The methodology covers all the steps of the procedure reported in the following figure. The RMA serves as a support tool for the risk-based decision-making process. Being a conventional method, risk acceptance criteria are also proposed. However, in the present analysis, the implementation of possible mitigation and prevention measures are only qualitatively assessed.

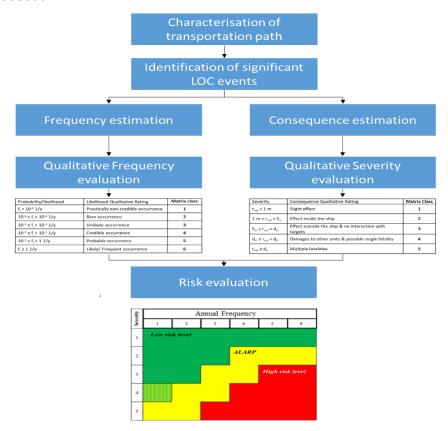


Figure 4. Schematization of the Risk Matrix Approach.

## Method 2 - Graph Theory (GT)

The Graph Theory (GT) application to perform safety assessment represents an emerging topic [205]. Hence, the development of such methodology aims mainly at the validation of the model based on GT and at providing evidences of its potentiality in the HazMat transportation field. The GT approach allows the analysis of complex systems and support benchmarking analysis between different configurations. GT describes a system through a set of vertices and a set of edges. A vertex can simply be represented as a node, and an edge can be drawn as a line, directed or undirected, connecting two vertices. In a weighted graph, a set of numerical values can also be assigned to either the vertices or edges of the graph. In a direct graph, a walk from the vertex "i" to the vertex "j" is a sequence of vertices and edges starting from "i" and ending in "j" where each intermediate vertex can be traversed several times. On the other hand, a path is a walk from the vertex "i" to the vertex "j" where the intermediate vertices "k" can be traversed only once. In the present study, the LNG carrier and the possible targets represent the vertices of the graph. The connections between vertices are associated to the consequences of a given accidental scenario. Therefore, the edges represent the physical effects due to a LOC, calculated through the consequence assessment. The edges are weighted by comparing the physical effect to the thresholds defined for the consequences' assessment.

### Results:

# Method 1 - Risk Matrix Approach (RMA)

A total number of 45 scenarios is obtained from hazard identification, including fire and explosions events, following the release of either liquid or vapor natural gas. A risk register was compiled including all the scenarios, providing an ID to each identified event, the description of the event and the risk-based classification; this includes frequency and consequence class evaluation, and finally, the risk level. The most critical scenarios evaluated were associated with major liquid releases, leading to pool spread and evaporation, with potential large fires and explosions. The consequences were represented through the use of buffer maps in order to trace the maximum extension of the scenarios. The outcomes of the analysis demonstrate that the LNG carrier access induce a relevant risk level for the industrial and civil installations close to the channel, thus the analysis may constitute a preliminary driver to enhance safety measures and procedures in the development of the LNG terminal with a dual purpose: i) reducing possible suboptimal interactions between the LNG carrier and the current port configuration; ii) reducing the risk level by lowering likelihood and / or vulnerability radius of the most critical events. Some prevention and mitigation actions are listed in the following in order to provide an example of utilization of the risk results obtained with the present methodology.

# Method 2 - Graph Theory (GT)

The graph metrics obtained for a simplified case are in good accordance with the behaviour of consolidated risk indices. The implementation of the graph theory to the LNG maritime transport shows the wide capabilities of the approach in providing information to perform benchmarking analysis of different configurations, such as different routing projects and different plans for protections implementation.

**Conclusions:** A specific risk-based analysis is developed to support the identification and evaluation of potential accidents associated with the transit of LNG carriers in harbour areas through a risk matrix approach. The most critical scenarios are identified, providing indications for risk control, in terms prevention and mitigation actions. The developed approach is a powerful tool since it is supported by scientific literature and at the same time it defines a set of simplified reference data avoiding rigorous procedures such as those required for the risk assessment for fixed plants. The presented method may support the planning of industrial harbour areas development in the perspective of a wider implementation of LNG bunkering and distribution terminals.

Besides, an unconventional approach base on graph theory is developed for the same purpose. The method evaluates the risk associated to the LNG carriers approaching harbour areas, taking into consideration possible secondary scenarios generated from the onshore installations. However, the model can be further improved though the implementation of a graphical-interface to facilitate the users in the implementation. For example, the Matlab code for the consequence assessment should be coupled with the I-Graph software in order to avoid external human actions.

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