Towards a regulatory framework for the use of liquid hydrogen as a fuel for ships: Critical analysis of the prescriptive requirements for bunkering operations

By Johanne Charlotte Jakobsen



Master of Science – Process Safety Technology

Department of Physics and Technology University of Bergen

June 2021

Acknowledgment

First, I would like to thank my main supervisor Dr Trygve Skjold for introducing me to the topic of this thesis. His time, expertise and feedback has been very helpful throughout the process. I would also express my gratitude to my co-supervisors Ivan Østvik, Kolbjørn Berge, Veronica Charlotte Andersen Haugan, Melodia Lucas Pérez, Bjørn J. Arntzen and Helene Hisken for meetings and advice during this period.

Furthermore, I would like to thank the people at Gexcon Fantoft that have been helping me with the FLACS software and making room for me at the office. Your help is taken with great gratitude.

Finally, I would like to thank my friends and family for their motivation and endless support during this period.

Summary

The global demand for energy increases rapidly with the growth in the population and a steady increase in the general standard of living. At the same time, the consumption of fossil fuels causes massive releases of greenhouse gases (GHG) that influence the global climate. Hence, the global energy mix needs a shift towards increasing use of renewable energy sources and sustainable use of conventional fuels. In this perspective, various energy forecasts and strategies outline a future where hydrogen and hydrogen-based fuels (including ammonia) will play an important role as an energy carrier in industry and society.

In various parts of the maritime sector, liquid hydrogen (LH2) can replace conventional fuels such as liquid natural gas (LNG) and marine fuel oils. Provided enough hydrogen can be produced from renewable sources, or from fossil fuels with carbon capture, it will be possible to reduce the GHG emissions from maritime transport significantly. However, a comparison of critical safety-related properties of different fuels shows that it is not straightforward to achieve the same level of safety for hydrogen systems, compared to conventional fuels.

Compared to LNG, LH2 has significantly lower storage temperature, much lower minimum ignition energy (MIE), significantly wider flammable range, and much higher reactivity. Of particular importance for safety distances related to fuel storage facilities and bunkering operations is the propensity of hydrogen-air mixtures to undergo deflagration-to-detonation-transition (DDT) under specific conditions. In summary, this implies a need for a different approach to safety engineering, including the methods used for estimating safety zones for bunkering operations. On the other hand, the low density and enthalpy of vaporisation of hydrogen imply that accidental releases in the open often will be dominated by buoyancy, which would be favourable from the point of view of safety.

Experimental data from large-scale releases of LH2 in the open are scarce. However, in 2019 the Norwegian Public Roads Administration (NPRA) and the Norwegian Defence Research Establishment (FFI) commissions a series of controlled release and dispersion experiments with LH2 from DNV GL. The experiments, performed at the large-scale test site at Spadeadam, included seven outdoor tests representative of accident scenarios during bunkering operations. The data from the tests document the size, shape and behaviour of the dispersed clouds generated for specific tank pressures, outflow rates, and weather conditions.

This thesis explores safety challenges for bunkering operations and other operations involving transfer of LH2 between or from cryogenic storage units. The aim is to provide science-based

recommendations for relevant regulations, codes and standards (RCS). The approach adopted entails numerical simulations of the DNV GL experiments, to build confidence in the predictive capabilities of the computational fluid dynamics (CFD) tool FLACS developed by Gexcon. The FLACS software is then used to simulate hypothetical accident scenarios involving LH2. The simulations focus on the formation and duration of flammable gas clouds near ground, without ignition. The analysis includes a sensitivity study to explore the relative effect of selected parameters on the size and shape of the dispersion clouds. Finally, the results from the simulations are used to evaluate prescriptive requirements for LH2 bunkering operations in the International Maritime Organisation (IMO) and other relevant RCS. Notably, the IGF Code only applies to the ship, including onboard bunkering stations, while standards such as Ships and marine technology – Specification for bunkering of liquefied natural gas fuelled vessels (ISO 20519) from the International Organization for Standardization (ISO) applies to onshore bunkering operations in ports and harbours.

The results from both experiments and simulations show that parameters such as wind velocity, release rate, release direction and outdoor temperature have significant impact on the dispersed cloud. However, for similar conditions, a release of LH2 extends further than a release of LNG, compared to earlier studies of LNG releases. Considering the ignition sensitivity and significantly higher reactivity, including the propensity for DDT, for hydrogen compared to methane, it is clear that releases of LH2 are more hazardous compared to releases of LNG. Hence, to achieve the same level of safety, assuming similar leak rates and leak frequencies, the safety distances, or safety zones, should be increased significantly in the case of LH2, compared with LNG.

Abbreviations

3D	Three-dimensional
AIT	Auto-ignition temperature
CCS	Carbon capture and storage
CNG	Compressed natural gas
DDT	Deflagration-to-detonation-transition
DNS	Direct numerical simulation
DSB	The Norwegian Directorate for Civil Protection
FFI	Norwegian Defence Research Establishment
GH2	Gaseous hydrogen, or compressed hydrogen
GHG	Greenhouse gases
HAZID	Hazard identification
HHV	Higher heating value
IMO	International Maritime Organization
ISO	International Organization for Standardization
LES	Large eddy simulation
LFF	Low flash point fuel
LFL	Lower flammability limit
LH2	Liquid hydrogen
LHV	Lower heating value
LNG	Liquid natural gas
LOHC	Liquid organic hydrogen carrier
LPG	Liquid petroleum gas
MESG	Maximum experimental safe gap
MIE	Minimum ignition energy
NMA	Norwegian Maritime Authority
NPRA	Norwegian Public Roads Administration
PPE	Personal protective equipment
QD	Quenching distance
QRA	Quantitative risk assessment
RANS	Reynolds-averaged Navier-Stokes
RCS	Regulations, codes and standards
SOLAS	Safety Of Life At Sea

Contents

Acknowle	edgment I
Summary	,
Abbreviat	tionsIV
1. Intro	oduction1
1.1	The role of hydrogen in maritime transport1
1.2 \$	Safe implementation of hydrogen for maritime systems
1.3	Approach5
1.4 0	Objectives5
1.5 0	Outline of thesis
2. Back	ground7
2.1	Why hydrogen?
2.1.1	Liquid hydrogen
2.1.2	Release of liquid hydrogen
2.2	Characteristics of hydrogen that cause safety challenges
2.2.1	Storing pressure
2.2.2	Boiling point
2.2.3	Flammable limits
2.2.4	Ignition sensitivity
2.2.3	Embrittlement 12
2.2.0	Emerging technologies and strength of knowledge
2.3	Characteristics of hydrogen that may be favourable
2.4	Basics aspects of risk assessments13
2.6	The IGF Code15
2.7	Bunkering and safety zones15
3. Liter	ature review17
3.1	Experimental findings of liquid hydrogen release in open rooms17
3.1.1	General description of experiment17
3.1.2	Dispersion mechanisms of the H ₂ flammable cloud
3.1.3	Conclusion of the NASA experiments
3.2	Ignited releases of liquid hydrogen20
3.2.1	Thermal of safety distances

3.3 L	iquid hydrogen releases show dense gas behaviour	
3.3.1	Background - Liquid release of hydrogen	21
3.3.2	Bunkering	
3.3.3	Vent mast releases	23
3.3.4	Conclusion of the work	25
4. Exper	iments involving outdoor releases	26
4.1 E	Background for the experiment	
4.2 D	Description of experiments	
4.2.1	Measurements of Ambient Conditions	
4.2.2	Dispersion Measurements	
4.2.3	Ignition Measurements	
4.3 R	Results summary from experiments	
4.3.1	Results Test 1	
4.3.2	Results Test 2	
4.3.3	Results Test 3	
4.3.4	Results Test 4	
4.3.5	Results Test 5	
4.3.6	Results test 6	
4.3.7	Results Test 7	35
11.5.7	home of the even extended accults	26
4.4 5	summary of the experimental results	
5. Metho	odology	
5. Metho 5.1 E	odology Background	37
5. Metho 5.1 E 5.1.1	odology Background The governing equations	
5. Metho 5.1 E 5.1.1 5.1.2	ackground The governing equations Turbulence models	37 37 38 39
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7	ackground The governing equations Turbulence models The model system	
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8	Background Background The governing equations Turbulence models The model system Validation	37 37 38 39 40 41
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2	Background Background The governing equations Turbulence models The model system Validation Model simplification and assumptions	37 37 38 39 40 41
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 M 5.3 S	Background Background The governing equations Turbulence models The model system Validation Model simplification and assumptions	37 37 38 39 40 41 41
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3 S	Background Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up	37 37 38 39 40 41 41 41
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.2 2	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry	37 37 38 39 40 41 41 41 41 41 41 42 42 42 42 43
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.2 2	Deckground Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid	37 37 38 39 40 41 41 41 42 42 42 43
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid Scenario	37 37 38 39 40 41 41 41 41 41 41 41 42 42 42 43 43 43 43
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.2 S	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid Scenario Monitor Points	37 37 38 39 40 41 41 41 41 41 42 42 42 42 42 43 43 43 43 43 43
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5	odology	37 37 38 39 40 41 41 41 41 41 41 41 41 42 42 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid Scenario Monitor Points Single field 3D output Simulation and output control	37 37 38 39 40 41 41 41 41 42 42 42 42 42 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45 45
 5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Geometry Grid Scenario Monitor Points Single field 3D output Simulation and output control Boundary conditions	37 37 38 39 40 41 41 41 42 42 43 44
 5. Method 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 	bodology	37 37 38 39 40 41 41 42 42 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 43 44
 5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 	Background Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid Scenario Monitor Points Single field 3D output Simulation and output control Boundary conditions Initial conditions Gas composition and volume	37 37 38 39 40 41 41 42 42 43 43 43 43 43 43 43 43 43 43 43 43 43 43 44 44
5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 5.3.10	Background Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Simulation set-up Geometry Grid Scenario Monitor Points Single field 3D output Simulation and output control Boundary conditions Initial conditions Gas monitor region	37 37 38 39 40 41 41 42 42 42 43 43 43 43 43 43 43 43 43 43 43 43 43 44 44 44
 5. Metho 5.1 E 5.1.1 5.1.2 5.1.7 5.1.8 5.2 N 5.3 S 5.3.1 5.3.2 5.3.3 5.3.4 5.3.5 5.3.6 5.3.7 5.3.8 5.3.9 5.3.10 5.3.11 	Background The governing equations Turbulence models The model system Validation Model simplification and assumptions Geometry Geometry Grid Scenario Monitor Points Single field 3D output Simulation and output control Boundary conditions Initial conditions Gas composition and volume Gas monitor region Leaks	37 37 38 39 40 41 41 42 42 43 43 43 43 43 43 44 44 44 44 44 44

	5.3.13	Ignition	
6.	Resul	ts and discussion	45
(6.1 V	Validation of FLACS-simulations compared to the experiments	45
	6.1.1	Test 1, Release without increasing tanker pressure	
	6.1.2	Test 2, Higher release rate and opposite wind direction	
	6.1.3	Test 3, Higher outflow rate	
	6.1.4	Test 4, Horizontal release	
	6.1.5	Test 5, First ignited test, vertical downward release	
	6.1.6	Test 6 Second ignited test, horizontal release	
	6.1.7	Test 7, Final release to empty tanker	
	6.1.8	Summary of the FLACS results	
(6.2 Т	The impact of changing essential parameters	
	6.2.1	Wind velocity	
	6.2.2	Pasquill classes	61
	6.2.3	Temperature	
	6.2.4	Grid	
	6.2.5	Change of release orientation	65
	6.2.6	Adding barriers	67
(6.3 A	Are safety distances for LNG suitable for LH2?	
7.	Concl	usions	
,	7.1 N	Aain conclusions	
,	7.2 S	buggestions for further work	
Bil	bliograp	hy	74
Ap	pendix	A: Coordinates for monitor points	
Ap	pendix	B – Results from experiments and simulations	

1. Introduction

1.1 The role of hydrogen in maritime transport

Energy technologies are important for everyday life. Consumption of energy has played a crucial role for humankind since early humans learned how to control fire, and energy will continue to play an essential role for the lives of our descendants. The demand for energy will increase with the rapid increase in the global population, combined with increasingly developed societies. The consumption of fossil fuels results in massive releases of greenhouse gases (GHG), in particular carbon dioxide (CO₂), that influence the environment and cause climate change. Hence, the energy system needs a shift towards sustainable use of conventional fuels and an increasing fraction of energy from renewable sources in the global energy mix. However, the inherent variation in the energy production from solar and wind implies a need for carbon-free energy carriers, such as hydrogen or hydrogen-based fuels (e.g., ammonia).

The International Energy Agency (IEA) reported that the global transport sector used 31 000 TWh in 2015, which constituted 14% of the global GHG emissions [1]. In April 2018, the International Maritime Organization (IMO) decided to reduce GHG emissions by at least 50% by 2050 [2], and the goal is to eventually reduce the emissions to zero. In addition to the global emissions, there are also strong incentives to reduce the local emissions of GHG and other pollutants. As an added measure to reduce the emission from maritime vessels, the Norwegian Parliament has decided that ships and ferries in the world heritage fjords need to implement zero-emission technology as soon as technical possible, and within 2026 [3].

Energy stored in batteries is a practical solution for ferries and other ships that travel relatively short distances. One example is the world's first electric car and passenger ferry MF "Ampere", trafficking European route E39 between Lavik and Oppedal. However, for long-distance freight the size and weight of large battery assemblies represent a significant challenge. For this segment, hydrogen technologies is a viable alternative to conventional fuels, such as marine fuel oils and liquid natural gas (LNG). Maritime vessels powered by hydrogen system can operate longer routs with lower vessel weight [4].

The maritime sector has several alternatives for sustainable replacement of conventional fuels, including methanol, ethanol, ammonia, compressed hydrogen (GH2), liquid hydrogen (LH2)

and liquid organic hydrogen carriers (LOHC). Figure 1 compares different fuels based on the gravimetric (specific) and volumetric energy densities. Hydrogen has significantly higher energy density per unit mass compared to other fuels, including ammonia and methanol. However, the volumetric energy density of hydrogen is low, even at high pressures or in liquid (cryogenic) state. The higher volumetric energy density of LH2, compared to GH2, is favourable for ships with high energy consumption [5].



Figure1: Energy densities for different fuels [6].

Hydrogen has both advantages and disadvantages as an energy carrier. The main advantage of hydrogen is that it is a zero-carbon energy carrier, which implies no direct emissions of carbon dioxide. The total GHG emissions will depend on how hydrogen is manufactured, and combustion of hydrogen can also result in local pollution from NOx [7]. Most of the hydrogen used today is manufactured by steam reforming of conventional fuels, such as coal, oil and natural gas, without carbon capture. However, it is foreseen that an increasing fraction of the hydrogen will be produces by electrolysis, using electricity generated from renewable energy sources [8]. The main challenges towards realising the hydrogen economy include technology development, implementation of infrastructure, costs, upscaling, availability and safety.

1.2 Safe implementation of hydrogen for maritime systems

This thesis evaluates safety challenges related to LH2 technologies for maritime applications, with particular focus on safety for operations in unconfined settings, such as bunkering of maritime vessels or transfer of LH2 from cryogenic tanks on deck to consumers such as fuel cells or turbines. The work progressed in parallel with another thesis that focused on LH2 operations in confined settings, such as fuel preparation rooms and fuel cell rooms.

Ships that are in operation today follow internationals regulations, codes and standards (RCS) and codes to achieve a certain level of safety. In response to the Titanic disaster on 15 April 1912, the first SOLAS (Safety Of Life At Sea) treaty was established in 1914. This and later treaties were established to increase the level of safety for ships by introducing minimum safety standards for constructions, equipment and operations on board [9]. The International Maritime Organization (IMO) was established in 1948. IMO issues international safety standard to promote maritime safety, including comprehensive international regulations [10].

The International Code of Safety for Ships using Gases or other Low-flashpoint Fuels (IGF Code) entered into force on 1 January 2017 [2]. This legislation was established to minimize the risk for ships, their crews and the environment, given the nature of gaseous fuels relative to conventional fuel oils [11]. The current version of the IGF Code provide mandatory provisions for all fuels with flash point below 60 °C (for the primary fuel), but specific requirements only for natural gas, including LNG (Part A-1 of the IGF Code). For all other fuels with low flash point, including hydrogen, the IGF Code and other documents from IMO prescribe functional requirements for an Alternative Design process that entails an extensive risk assessment. For instance, §3.2.1 of the IGF Code specifies [11]:

"The safety, reliability and dependability of the systems shall be equivalent to that achieved with new and comparable conventional oil-fuelled main and auxiliary machinery."

Since LH2 and LNG have some physical and combustion properties in common, including similar lower flammability limits (LFL), similar auto ignition temperatures (AIT), and low boiling points and flash points relative to ambient conditions, it could be tempting to apply similar functional requirements for both fuels. However, there are also significant differences between LH2 and LNG that might imply that more extensive safety measures will be required for hydrogen to achieve equivalent levels of safety. The minimum ignition energy (MIE) of hydrogen (≈ 0.017 mJ) is much lower than for methane (≈ 0.34 mJ), and hydrogen has a wider

range in flammable concentration (4-77 vol.%), compared to methane (5-15 vol.%) [12]. LH2 is stored at significantly lower temperatures (-253 °C) compared to LNG (-162 °C). Finally, stoichiometric or worst-case hydrogen-air mixtures are dramatically more reactive than methane-air mixtures. The maximum laminar burning velocity S_L for hydrogen is about 2.9 m/s, whereas the maximum laminar burning velocity of methane-air mixtures is about 0.36 m/s [12]. This has severe implications for the consequences of accidental explosions. Experiments in specific open congested geometries with stoichiometric fuel-air mixtures show that hydrogen produces significantly higher explosion pressures [13][14]. In summary, the safety-related properties of hydrogen differ significantly from conventional fuels, implying that the functional requirements in a prospective section for hydrogen in the IGF Code will have to differ significantly from those for natural gas to achieve a comparable level of safety.

Compliance with the Alternative Design route prescribed by IMO [15], is particularly challenging for the emerging hydrogen technologies, where the inherent lack of relevant experience implies significant uncertainty in any estimate of event frequencies. Furthermore, the results from a recent blind-prediction benchmark study for vented hydrogen deflagrations in 20-foot shipping containers demonstrate a severe lack of predictive capabilities for advanced consequence models [16]. The weak strength of knowledge in risk assessments for hydrogen systems implies that any quantitative assessment of risk will entail significant uncertainties [14]. This should be reflected in the way results from quantitative risk assessments (QRAs) are used to support decisions concerning the design and operation of hydrogen systems, including ships and bunkering systems in ports and harbours.

There is currently no standard or regulation that specify functional requirements for the use of hydrogen as fuel in the maritime transport sector. Hence, the main motivation for the work presented in thesis is to investigate specific challenges concerning the safe use of hydrogen as an energy carrier for ships. In particular, the thesis explores the relative level of safety for systems based on LH2 and LNG, with a view to propose recommendations for a prospective revision of the IGF Code and related standards that will include functional requirements for hydrogen, including LH2. The IGF Code applies to on-board bunkering station, while ISO 20519 [17] "Gas as a marine fuel – Controlled Zones during LNG bunkering" [18] and the guidelines from DNV GL "Recommended practise – Development and operation of liquefied natural gas bunkering facilities" [19] apply to bunkering operations on-shore. Finally, the present work in limited to open congested geometries, such as bunkering systems. The thesis

of another Master student focused on confined systems, such as fuel preparation rooms, fuel cell rooms and machinery spaces.

1.3 Approach

To gain more knowledge about the behaviour of liquid hydrogen (LH2) releases, DNV GL Spadeadam Research and Testing performed a series of large-scale release and dispersion tests commissioned by the Norwegian Defence Research Establishment (FFI) [20] on behalf of the Norwegian Public Roads Administration (NPRA) and the Norwegian Maritime Authority (NMA). The design of the experiments should replicate bunkering operations with large accidental releases of LH2. The test series included seven experiments with variations in storage pressure, release rate, release directions and weather conditions. As a part of the work for this master thesis, the experiments were simulated with the computational fluid dynamics (CFD) software FLACS to evaluate the predictive capabilities of the software. The same software with similar settings were then used to simulate hypothetical accident scenarios, for a range of parameters: release rates, temperatures, wind velocity etc. Finally, the results from the CFD simulations inform a critical analysis of the applicability of existing RCS for bunkering operations with LH2.

1.4 Objectives

The primary objective of this thesis is to determine whether and to what extent existing RCS for bunkering operations involving LNG are applicable for bunkering operations involving LH2. The secondary objectives are:

- To validate the CFD tool FLACS against large-scale release and dispersion experiments with LH2 in the open.
- To provide general recommendations for RCS concerning LH2 bunkering operations.

1.5 Outline of thesis

Chapter 2 presents background information of hydrogen as an energy carrier, including a review of safety-related properties of hydrogen and conventional fuels. Chapter 3 reviews previous work on LH2 releases in the open. Chapter 4 summarises the large-scale release and dispersion experiments with LH2 performed by DNV GL Spadeadam Research and Testing [20]. Chapter 5 describes the CFD simulations with FLACS, including simplifications and assumptions. Chapter 6 presents the results from the simulation and discusses the implications for RCS,

including the effect of critical parameters. Finally, Chapter 7 summarises the main conclusions and suggestions for further work.

2. Background

This chapter introduces hydrogen as an energy carrier and presents characteristic properties of hydrogen that may cause safety challenges for ships fuelled by hydrogen in the maritime transport sector.

2.1 Why hydrogen?

The maritime sector represents about 5% of the global oil demand today. Furthermore, it is responsible for 2.5% of global energy-related CO₂ emissions [21]. To reduce the emissions from the maritime transport sector, new technology is required. Norway has already introduced electric ferries as a means to reduce the emission of CO₂ and other GHG. The first fully electrical ferry, MF Ampere, was launched in 2015, and there are currently 34 electrical car ferries in operations in Norwegian fjords [22]. However, battery technologies are not suitable for all ships. For longer routes and larger ships, battery solutions are not viable solutions, partly because of the considerable size and weight, and partly due to the time required for charging the batteries. This is one of the motivating factors for considering hydrogen technologies as a viable alternative to conventional fuels such as LNG, diesel and marine fuels oils. According to Aarskog *et al.* [4]:

"A 250-350 bar hydrogen storage tank is about five times lighter than a maritime battery system. A hydrogen system can result in longer range or lower ship weight, which makes it an alternative for a wider range of applications"

Hydrogen is also a promising fuel for a sustainable future because of its low emission of GHG, especially CO₂.

Hydrogen is the first element in the periodic system, the lightest of all gases, and contains more chemical energy per unit mass (MJ/kg) than natural gas and gasoline. The high energy content combined with low CO₂ footprint makes hydrogen an attractive energy carrier in the transport sector. The low molecular weight implies that hydrogen has very low energy density (MJ/m³) at ambient temperature and pressure. In practical energy systems, this can to some extent be compensated by compressed storage at high pressures, typically 200-700 bar, or liquefaction. At -252.87 °C (20.28 K), hydrogen is a stable cryogenic liquid at atmospheric pressure. Alternative storage solutions include chemical compounds, such as ammonia or

liquid organic hydrogen carriers (LOHCs). The amount of pure hydrogen found in nature is very limited, and for energy applications hydrogen must be manufactured from energy sources. Hydrogen can for instance be produced from water (e.g., electrolysis), biomass (e.g., fermentation) and fossil fuels (e.g., steam methane reforming).

2.1.1 Liquid hydrogen

In the maritime sector liquid hydrogen seems to be the most advantageous way of storing hydrogen when it comes to bunkering process as well as the preferred solution for vessels with high power consumption [5]. When the hydrogen is stored as a liquid it has a higher volumetric energy density compared to compressed hydrogen. Storing hydrogen as a cryogenic liquid requires low temperatures (around 20-30 K) depending on the storage pressure (1-10 bar). In addition to the high volumetric density, hydrogen has a higher gravimetric density than diesel, gasoline, ammonia, methanol, and methane [6] and it is illustrated in Figure 1. This makes hydrogen more efficient for storing, transport and distribution. However, the low temperature requires a complex storing system and access of energy to achieve the low temperatures. Storing hydrogen at 20 K would require about 25-35% of the hydrogen energy if the hydrogen itself would supply the energy for cooling the storage system [21].

2.1.2 Release of liquid hydrogen

A release scenario of liquid hydrogen will depend on how it is stored and if the release scenario is impinging, confined or in the open. Hydrogen has a low boiling point (20 K at atmospheric pressure) and will rapidly evaporate when it is released in atmospheric conditions. Gaseous hydrogen is significantly lighter than air and will have a higher velocity upward in the atmosphere. The lower temperature for hydrogen causes a higher vaporizing compared with LNG, because the attraction between the molecules is weaker for LH2 than for LNG. This will be advantageous from a safety perspective if there was to be an accidental release of hydrogen. Due to the higher vaporizing ability hydrogen will remain at ground level for a shorter time, compared to a release of LNG.

2.2 Characteristics of hydrogen that cause safety challenges

Hydrogen has different characteristics than conventional fuels and might require different standards to achieve a comparable safety level to the conventional energy carriers. Ships that are in operation today and are fuelled with LNG follow standards from the IGF Code. In the

IGF Code part A – Alternative design (point 3.2.1) it says [11]: "*The safety, reliability and dependability of the systems shall be equivalent to that achieved with new and comparable conventional oil-fuelled main and auxiliary machinery*". This means that hydrogen needs to have a safety level that is comparable to the conventional fuels. Characteristics of hydrogen compared with conventional fuels are listed in Table 2.1. The critical properties of hydrogen when it comes to safety considerations will be discussed further.

Property	Hydrogen	Conventional fuels			
Higher heating value (HHV)	142 MJ kg ⁻¹	Methane: 55 MJ kg ⁻¹	Propane: 50 MJ kg ⁻¹	Diesel/jet fuel: 45-46 MJ kg ⁻¹	
Lower heating value (LHV)	120 MJ kg ⁻¹	Methane: 50 MJ kg ⁻¹	Propane: 46 MJ kg ⁻¹	Diesel/jet fuel: 43 MJ kg ⁻¹	
Storage and transport pressure	(GH2) 700 bar	CNG: 260 bar	LPG: 30 bar	Marine gas oil, heavy fuel oil, diesel and petrol are normally stored at atmospheric pressure	
Boiling point/ temp. for transport and storage	(LH2) -253 °C	LNG: -162°C	Propane: -42°C		
Flash point	(LH2) < -253 °C	LNG: -188 °C	LPG: - 104 °C	Marine fuel oil: > 60 °C	
Flammable limits (vol% fuel in air)	4-77	Methane: 5-15	Propane: 2.1 – 9.5		
Minimum ignition energy (MIE)	0.017 mJ	Methane: 0.28 mJ	Propane: 0.26 mJ		
Auto ignition temperature (AIT)	500 °C	Natural gas: 640 °C	Propane: 466 °C		
Maximum experimental safe gap (MESG)	0.29 mm	Methane: 1.12 mm	Propane: 0.92 mm		
Quenching distance (QD)	0.64 mm	2.03	1.75		
Maximum laminar burning velocity in air mixtures (S _L)	2.9 m s ⁻¹	Methane: 0.36 m s ⁻¹	Propane: 0.41 m s ⁻¹		
Enthalpy of vaporisation, <i>AH</i> _{vap}	0.92 kJ/mol	Methane: 8.17 kJ/mol	Propane: 15.7 kJ/mol		
The detonation cell size for stoich. fuel-air mixture	10 mm	Methane: 300 mm	Propane: 70 mm		

 Table 2.1 - Characteristic properties of hydrogen and conventional fuels [6], [12], [21], [23], [33]

2.2.1 Storing pressure

Gaseous hydrogen (GH2) is often stored and transported at significantly higher pressures, typically 350-700 bar, compared to other gaseous fuels. Compressed natural gas (CNG) and liquefied petroleum gas (LPG) are typically stored at 260 and 30 bar, respectively, and tanks for liquid fuels such as petrol, diesel and marine fuel oils will typically have atmospheric pressure in the tank space. The high storage pressure for GH2 imply significant challenges concerning the prevention of loss of containment, for instance cause by material or component failure, and releases from high-pressure reservoirs will often be dominated by momentum, not buoyancy.

2.2.2 Boiling point

Hydrogen has a very low boiling point (-253 °C), and LH2 is therefore stored at much lower temperatures than the conventional fuels, including LNG. Cryogenic storage and transport require special materials and complex system for cooling. Loss of containment, and hence insulation, of LH2 will result in flashing and further expansion as the temperature increases above the boiling point. A particular concern concerning accidental releases of LH2 is the possibility of condensing oxygen and nitrogen from the air. This can result in clogging of hydrogen lines, as well as the formation of an explosive condensate consisting of hydrogen, oxygen and nitrogen [23] [24].

2.2.3 Flammable limits

Whereas the lower flammability limit (LFL) of hydrogen (4.0 vol.% in air) is comparable to propane (2.1 vol.%) and methane (5.0 vol.%), the upper flammability limit (UFL) for hydrogen (75-77 vol.% in air) is much higher than for conventional fuels, including propane (9.5 vol.%) and methane (15 vol.%). The wide flammable range implies that it is more challenging to prevent the formation of explosive atmospheres [12].

2.2.4 Ignition sensitivity

Hydrogen has significantly lower minimum ignition energy (MIE ≈ 0.017 mJ), quenching distance (QD ≈ 0.64 mm) and maximum experimental safe gap (MESG ≈ 0.29 mm), compared to conventional energy carriers [12]. This implies that it is inherently difficult to prevent all ignition sources. This means that ignition sources that do not represent a hazard for conventional energy carriers, still can be a potential hazardous ignition source for hydrogen-air mixtures. Hydrogen is classified in Gas Group IIC, together with acetylene, which implies special requirements concerning electrical and non-electrical equipment. Finally, releases of

hydrogen from pressurised containers can under specific conditions result in spontaneous ignition.

2.2.5 Reactivity

Hydrogen has significantly higher maximum laminar burning velocity (2.9 m/s), compared to conventional fuels (Table 2.1). The laminar burning velocity S_L is a fundamental parameter of fuel-air mixtures. In principle, S_L is the propagation velocity of a planar (unstretched) flame front relative to the unburned mixture, for a specific pressure, temperature and fuel concentration [12]. The high laminar burning velocity of hydrogen is caused by fast chemical kinetics and high diffusivity.

A planar laminar flame is inherently difficult to realise in practice, partly due to flame stretch and partly due to various instability phenomena. In practice, most accidental explosions entail turbulent combustion, that under certain conditions can transition into detonations. A turbulent flame will always propagate at significantly higher velocity, the so-called turbulent burning velocity S_T , compared to the theoretical value of S_L for the same pressure, temperature and mixture composition. Expansion, especially in partly confined systems, and flame folding and generation of turbulence in the wakes of congestion, can result in flame acceleration and pressure build-up, and under certain conditions deflagration-to-detonation-transition (DDT) [12]. A deflagration is an explosion where the flame front propagates through turbulent heat and mass transfer, with a turbulent burning velocity that is lower velocity than the speed of sound in the unburnt mixture. In contrast, a detonation propagates as a shock front at supersonic speed. The detonation velocity for a stoichiometric hydrogen-air mixture is 1960 m/s [12].

Hydrogen has a high maximum laminar burning velocity (2.9 m/s) compared to conventional fuels. The laminar burning velocity is a measurement that describes how a plane flame front propagates through an unburned gas mixture, given the pressure, temperature and ratio of the mixture involved [12]. The high burning velocity is caused by fast chemical kinetics and high diffusivity. If there is an accidental release of hydrogen, the cloud will not be quiescent, but turbulent. If the cloud gets ignited there will not be a laminar burning of the hydrogen-air mixture, but a turbulent combustion. For a turbulent cloud the flame front is folded and form, which gives a wider effective surface area for the flame. This results in a considerably higher burning velocity compared to a laminar combustion [12]. A high burning velocity is more likely to cause an explosion and can develop a deflagration to detonation transition (DDT)

under specific conditions [25]. A deflagration is an explosion where the flame front propagates with a lower velocity than the velocity of sound in the unburnt mixture. The direction of the reaction product is opposite of the propagation of the reaction. For a detonation it is the shock front that accelerate through the quiescent, unburnt gas mixture with supersonic speed and the combustion zone follows immediately behind. Detonation velocity for hydrogen is 1960 m/s [12].

2.2.6 Embrittlement

Hydrogen can cause embrittlement in certain materials, including certain types of steel. Hydrogen embrittlement is a result of a process where hydrogen atoms dissolved in a solid material instigates changes to the mechanical properties through a series of complex micromechanisms. This can result in brittle behaviour, structural failure and loss of containment [26].

2.2.7 Emerging technologies and strength of knowledge

Hydrogen energy systems involve emerging technologies, and companies and personnel that perform risk assessments for hydrogen facilities may have limited competence on hydrogen safety. There are also significant shortcomings in existing regulations, codes and standards, and an inherent lack of relevant data from relevant systems that can support frequency assessments. A recent blind-prediction benchmark study revealed a severe lack of predictive capabilities for leading consequence models used for consequence assessments and design of risk-reducing measures [16]. The low strength of knowledge in risk assessments for hydrogen systems implies that the value of risk assessments as support for decisions can be limited, and in some situations the results from the risk assessment can give a false impression of the safety level for the stakeholders, including owners, operators and the public[14].

2.3 Characteristics of hydrogen that may be favourable

Hydrogen has some characteristic properties that may be beneficial from a safety point of view, compared to conventional fuels. The low specific density of hydrogen, i.e. the density relative to air (hydrogen is 14 times lighter than air at the same pressure and temperature), implies that loss of containment may result in buoyant plumes. This can prevent the formation of, or shorten the duration of, large flammable clouds near the ground, and hence reduce the consequences of accidental explosions. Hydrogen also has 4 times higher diffusion coefficient compared to methane, which implies that a flammable cloud will be diluted faster [8]. As such, open

geometries can be highly beneficial for preventing and mitigating hydrogen explosions. It should however be noted that buoyancy favours the formation of stratified, and potentially highly reactive, mixtures in confined systems [16].

A second safety-related property that is favourable for hydrogen is the absence of carbon, which implies no direct emission of CO_2 , but also no production of soot from a pure hydrogen flame, and hence less radiative heat transfer compared to hydrocarbons. Combustion of hydrogen with oxygen form water (Eq. 1), but combustion in air will also result in NO_x . In contrast, the combustion products from hydrocarbons are water and carbon dioxide (Eq. 2), as well as soot (especially for fuel-rich mixtures).

$$H_2 + O_2 \to H_2 O \tag{1}$$

$$C_x H_y + O_2 \to CO_2 + H_2 O$$
 (2)

Hydrogen has about 9.2 times lower enthalpy of vaporisation (kJ/mol) compared to LNG [20]. The low enthalpy of vaporisation of LH2 can be favourable from the point of view of safety, since rapid flashing and evaporation limit the contact time between LH2 and solid structures, and thereby prevent cryogenic failure of structural components.

Finally, the auto-ignition temperature (AIT) for hydrogen (500 °C) is similar to the AIT for conventional fuels, such as natural gas (640 °C) and propane (466 °C). Hence, considerations related to prevention of ignition by hot surfaces should be similar for hydrogen and other fuels.

2.4 Basics aspects of risk assessments

In broad terms, safety implies control over hazards that can result in losses, such as fatalities and injury to people, material damage, and deterioration of the environment. The purpose of a risk assessment is to increase the knowledge about a system, and support decisions that may entail difficult economic, ethical or political deliberations. A general definition of a hazard can be "a chemical or physical condition that has the potential for causing damage to people, property, or the environment" [27]. Risk, on the other hand, can be defined as "a measure of human injury, environmental damage or economic loss in terms of both the incident likelihood and the magnitude of the loss or injury" [27]. In simple terms, risk is often expressed as the product of event frequencies (derived from probability) and consequences.

A hazard is a physical condition of the system that can result in losses. For bunkering operations involving LH2, this can typically be the inventory of LH2, that, in the event of loss of containment, can result in the formation of an explosive atmosphere and possibly an explosion. Other hazards to consider include cryogenic spills, rapid phase transitions (RPTs), etc.

The first step of a risk assessment is to analyse the risk for the system, including system definition, hazard identification, frequency analysis and consequence analysis. The estimated frequencies and consequences can then be combined to a suitable measure of risk. The estimated risk is then compared with the appropriate acceptance criterion, and if the risk is not acceptable (or tolerable), it is necessary to implement risk-reducing measures and repeat the risk analysis. It follows that it is not straightforward to perform risk assessments for emerging technologies, where there is an inherent lack of relevant experience to support the various steps of the process.

Best practice in the area of process safety entails the use of a hierarchy of principles for risk reduction, starting with inherently safe (or robust/resilient) design, followed by preventive measures, mitigative measures and finally procedural safety. It is also essential to incorporate lessons learnt from past accidents and near misses in risk assessments and risk management.

2.5 Consequence modelling with FLACS

Simulations with the computational fluid dynamics (CFD) software FLACS is an essential part of the methodology used in this thesis. FLACS is an engineering model based on a specific family of CFD codes called porosity/distributed resistance (PDR) [28]. The PDR concept entails extensive use of sub-grid models, and, unlike most CFD tools, detailed geometry is represented by porosities and not resolved on the computational mesh. Other phenomena described by sub-grid models include turbulence generation in wakes behind obstacles, flame folding, and turbulent flame propagation. This implies that solutions to specific problems typically will not converge, and it is essential that users follow grid guidelines developed through validation of the software [29].

FLACS has been extensively modelled for scenarios involving release, dispersion and explosion of conventional fuels, including LNG, and also hydrogen. However, only limited work has been done on LH2 [30]. As such, it was of critical importance for the analysis in this

thesis to assess the predictive capabilities of FLACS through validation against the large-scale release and dispersion experiments performed by DNV GL at Spadeadam.

2.6 The IGF Code

The international code of safety for ships using gases or other low-flashpoint fuels (LFFs), also known as the IGF Code was established in 2015. The goal is to minimize the risk for the ships, the employees, and the surrounding environment under operation, installation, maintenance of the machinery, equipment and systems using low-flashpoint fuels [11].

The specific requirements and recommendations today apply to natural gas and liquid natural gas. For use of LH2, GH2 or hydrogen-based fuels the code needs to be reconstructive or design a new code to achieve a corresponding safety level to the conventional fuels. The maritime industry needs a goal-based regulatory framework for the use of hydrogen. The IGF Code is a comprehensive Code with numerous standards and regulations, including conversion, use, distribution, and storage of the fuel. Doing an analysis of all the parts of the Code will be very time consuming, and the thesis will further be focusing on part A-1, chapter 8, Bunkering. The goal of chapter 8 is "to provide for suitable systems on board the ship to ensure that bunkering can be conducted without causing danger to persons, the environment or the ship" [11].

2.7 Bunkering and safety zones

Bunkering is the supply and refilling of fuel for ships. The fuel can get transported from storage tanks to the vessel by pipeline bunkering, ship-to-ship (STS) bunkering or truck-to-ship bunkering [30]. The different bunkering methods are illustrated in Figure 2.2. The bunkering process is one of the procedures where there is a higher potential for a leak. Bunkering procedures for ships follow standards to achieve a reasonable safety level for the process. Ships fuelled by LNG follow the ISO20519 standard [17], and bunkering of liquid hydrogen is required to follow the same standard to achieve a comparable safety level [5]. In addition to the ISO20519 standard, regulations from "*Gas as a marine fuel - Controlled Zones during LNG bunkering*" [18] and "*Recommended practise- Development and operation of liquefied natural gas bunkering facilities*" [19] are also used for maritime vessels fuelled by LNG. The standards have two alternatives for documenting the associated risk. The first one is the "credible release approach", which will close areas for non-essential personnel during bunkering, to minimize the hazards for a potential release where the maximum LFL-distance will occur. This area is

estimated from HAZID (HAZard IDentification). The other alternative is doing a risk assessment for the bunkering site and estimate exclusion zones (inner, middle, and outer) for the hazardous areas. The safety area will cover the inner zone, while the monitoring and security area will cover the middle zone. For both alternatives it will be necessary to have all ignition sources under control in the safety areas while bunkering, i.e., all potential ignition sources must be turned off immediately, if there is an accidental release during bunkering operations.



Figure 2.2 - Common bunkering processes [30].

When the safety zones are being set up it will be necessary to estimate safety distances between the bunkering process and the staff working and passengers on board to minimize injuries and fatalities in case of an accident. The safety zone covers a small area around the bunkering facility and is only present during the bunkering. The purpose of the safety zone is to control leaks, avoid ignition, exclude non-essential staff, and protect the essential staff. The high outflow velocity for hydrogen and its wide flammability range makes the process for estimating a safety distance for bunkering hydrogen challenging.

3. Literature review

This section reviews previous work on loss of containment of liquid hydrogen in the open. Since only a limited number of large-scale experiments are described in the open literature, this chapter includes relevant findings concerning safety challenges for liquid hydrogen with focus on shipping, bunkering, and safety distances.

3.1 Experimental findings of liquid hydrogen release in open rooms.

This section summarises key findings from experiments performed by NASA, as outlined in the article "Experimental and analytical analyses of the mechanisms governing the dispersion of flammable clouds formed by liquid hydrogen spills" [32].

The NASA experiments were primary done to obtain knowledge of the physical phenomena of a release of liquid hydrogen. A leak may happen at large storge facilities and studying the dispersion of the flammable cloud will be a guide for further safety measures. The experiments resulted in further knowledge of hydrogen dispersion gained by data of temperatures, concentrations of hydrogen, turbulence levels and the effect of wind conditions. All these parameters influence the dispersion cloud and will be an important tool for estimating safety levels when it comes to transport, storing and use of liquid hydrogen. It is in general accepted that a spill of liquid hydrogen will evaporate rapidly and have a high buoyancy. Furthermore, will it diffuse in the ambient air with an increasing temperature. The buoyancy and diffusion will with time result in a cloud below the minimum flammability concentration of hydrogen in air mixtures (4 vol%), but how long time it takes from the spill starts to the concentration of the dispersion cloud is under 4 vol% hydrogen is unknown.

3.1.1 General description of experiment

The NASA experiment [32] setup consisted of two large storage tanks and a spill Dewar which released 5.3 m³ liquid hydrogen in the test. The liquid hydrogen was pressurized to 690 kPa and flowed through a 30 m long pipe. The release point (the end of the pipe) was placed in the centre of a spill pond with a diameter of 9.1 m that consisted of compacted sand. Furthermore, just below the release point, a steel plate was placed to avoid earth erosion.

Nine towers were placed in the spill pond in semicircles with three different radii, equipped with measuring instruments including cloud sampling bottles, H₂-sencors, and catalyst (hydrogen-air-mixtures below the lower flammability limit will react and release heat. The

correlation between the resistance imbalance between the arms at the catalyst was used to estimate ratio of the hydrogen and air), flame arrestors, thermocouples and UVW turbulence indicators.

Metrological data of temperatures, humidity, barometric pressure, and wind directions were measured before, during and after the experiments. For further details see reference [32].

3.1.2 Dispersion mechanisms of the H₂ flammable cloud

The strong correlation between the mixing temperature and hydrogen-air concentration was reflected in the experiments. When the hydrogen cloud has been lifted of the ground there is an adiabatic mixing of hydrogen and air (within 1 %). The adiabatic assumption was used in a model program to estimate hydrogen concentration of the dispersion cloud by data from the experiments. Two result of the mixing model is in Figure 3.1 and Figure 3.2.



from temperature data from towers 2, 5 and 8; Test 6, time = 20.94 s.



Fig. 8. Contours of constant hydrogen concentration deduced from temperature data from towers 2, 5 and 8; Test 6, time = 21.33 s.

Figure 3.1: Hydrogen release at 20.94 s [32]

Figure 3.2: Hydrogen release at 21.33 s [32]

The models give an illusion of the dispersion cloud and how rapidly it changes. It illustrates how the concentration of hydrogen changes both upwards and horizontal, after a short matter of time. There is only 0.4 s separating the two figures. The diffusion mechanism of hydrogen is strong and high concentration of hydrogen would rapidly decrease near the release point. Figure 3.3 shows pictures of the dispersion cloud taken under the experiments. The figure illustrates the effect that different wind speeds have on the releases. At lower wind rates the dispersion cloud raised mostly upwards, and higher wind rates gave a more horizontal moving

of the dispersion cloud. The metrological data had a significant impact on the release and should be considered when estimating safety levels for hydrogen system.



Figure 3.3: Photos of the wind effect on the dispersion cloud taken under the experiments [32].

3.1.3 Conclusion of the NASA experiments

A fast spill of liquid hydrogen will be characterized with a flammable dispersion cloud that detain at ground level of a short period of time. A leak with a high velocity will generate powerful turbulence caused by the momentum of the spill. Furthermore, the rapid phase change form liquid to vapor in combination with thermal instability will make hydrogen diffuse rapidly into the air, and the mixture of hydrogen and air will after a short period of time be lower than the minimum flammability limit. The dispersion cloud extends about 50-100 m at ground level with a cloud velocity at 0.5-1.0 m/s

Gentle spill over a longer period will be characterized with long term flammable cloud at ground level. A gentle spill has a lower turbulence and release rate, and reduced momentum of the spill. This characteristic of the dispersion cloud is assumed to be disadvantages and worsened the long-term cooling of the ground, which seems to be the most important heat transfer mechanism to estimate evaporation rate.

Another finding was the model program capability to estimate the ratio between hydrogen and air from the temperature measurements. This would be a useful tool for estimating concentrations of hydrogen in the dispersed cloud.

Storing facilities of LNG is normally recommended to include liquid containments dikes to prevent hazard form unfortunate spill/leaks [33]. The results of the experiments indicated that dikes around the hydrogen storage facilities would not be preferable. It would be more advantageous to promote the mechanism of spill and turbulence to let the hydrogen mix with the ambient air, than to collect dikes near the storage system.

3.2 Ignited releases of liquid hydrogen

The information below is from the article "Ignited releases of liquid hydrogen: Safety considerations of thermal and overpressure effects", for more further details see reference [34].

The purpose of the article was to figure out the hazard potential of a realistic ignited spill of LH2. The article had focus on flammability limits of a LH2 vapor cloud, flame speed through an LH2 vapor cloud and subsequent radiative heat levels after ignition. The experimental findings presented was split into three phenomena: jet-fires in high and low wind conditions, 'burn-back' of ignited clouds and secondary explosions post 'burn-back'. The purpose of the study was to gain information about safety distances that may be considered when setting up codes and standards for LH2.

3.2.1 Thermal of safety distances

Observations of the high-speed video in the experiment found that flame speed from 25 m/s up to 50 m/s occurred. For one occasion the hydrogen cloud got through three phases after it got ignited; burnt back to the release point, created a jet-fire and then a secondary explosion took place. For the jet-fire the criterion for "no-harm" were set to 1.6 kW/m2. The test was done for wind velocities at 2.15 m/s and 0.59 m/s (both with south westerly wind direction). The results from the two tests indicated a minimum separation distance from the hydrogen source where a person will feel "no pain". The minimum separation distance for 60 l/min based on radiative heat is 11.1 m for initial cloud deflagration, 11.3 m for secondary explosion, and between 12.6 m and 13.7 m for jet-fire, both high wind and low wind. The

pressure effect is not considered and may increase the distances. For more details see reference [34].

3.3 Liquid hydrogen releases show dense gas behaviour.

The information below is from the article "Liquid hydrogen releases show dense gas behavior", for more further details see reference [5].

The article by Olav Roald Hansen [5] is discussing some confusion about the behaviour of LH2 releases in the industries, whether a release into air will behave like a dense gas or a buoyant gas. The understanding of this aspect is critical to optimize design with regard to safety. This article explains the expected behaviour of LH2 releases and discuss expected hazard distances from LH2 releases compared to gaseous hydrogen releases and LNG and why a higher safety standard may be needed when designing hydrogen fuelled vessels than for existing LNG fuelled vessels.

3.3.1 Background - Liquid release of hydrogen

How the dynamics of a liquid hydrogen release will depend on how it is stored (temperature and pressure) and if the release scenario is impinging, confined or in the open. Normal temperature is 20-30 K at pressure between 1-10 bar for maritime applications as bunkering, storage, and transfer of hydrogen. When describing a liquid hydrogen release scenario, it can be separated into five stages: outflow phase, flashing, condensed air phase, "pool" and cold gas plume.

The outflow phase will have a high velocity (about 2.5 times higher than for LNG) because of its low liquid density. The velocity will be above 50 m/s at 1 bar overpressure and over 100 m/s at 4 bar overpressures. Liquid hydrogen has a boiling point at 20 K (-253 °C). An immediate evaporation (flashing) will occur if the temperature rises above the boiling point, which is most likely happen at a release of hydrogen, due to the low storage temperature. Around 2 % of the LH2 will flash per K which leads to a volume increase (expansion) around 120 % per K. If the storage temperature rises with 5 K over the boiling point 10 % of the LH2 will flash and the expansion will increase with a factor 7.

The low storage temperature for LH2 is much lower than boiling and freezing points for the components in the surrounding air. Oxygen has a boiling point at 90 K and freezing point at

54 K and nitrogen has a boiling point at 77 K and freezing point at 63 K. This can lead to hydrogen spray may exist along with oxygen and nitrogen solid or liquid particles in the near field when there is a release. If the hydrogen spray hits/impinges the near-field region before the multiphase of oxygen and hydrogen has been heated and evaporated, it is possible that particles of oxygen and nitrogen will react with LH2 and receive heat from the surrounding elements/objects. The dynamics between LH2 and solid air particles is complicated and may lead to an increasing oxygen concentration. This can further result to an increasing of gas reactivity. The very low temperature of LH2 makes it technically challenging to perform and to instrument meaningful experiments of good quality.

Hansen claims that bunkering studies do not recognizing that LH2-releases can be expected to show dense gas behaviour predicting buoyant plumes, may severely underestimate the bunkering safety zone. A too small bunkering safety zone may potentially expose bunkering staff and passengers for higher risks than considered acceptable. The higher reactivity, wider flammability range, higher release velocity and ignition probability of hydrogen compared to methane make it important to design LH2 fuelled vessels to higher safety standards than existing LNG vessels.

3.3.2 Bunkering

Today there is no safety standard for bunkering of LH2 and The Norwegian Directorate for Civil Protection (DSB) has requested that the standard for LNG is used for bunkering studies of LH2. Hansen performed a comparison assignment of LNG and LH2 where he studied a release at 5 barg through a D = 10 mm instrument connection using the tool FLACS. He simulated two scenarios from the rear of the road tanker with downwards release in 2 m/s wind and horizontal release in 2 m/s tailwind. The simulations are based on release on a cold winter day. The characteristics used in the simulation of the releases are shown in table 3.1

The results of the LNG-simulations gave a lower flammability limit (LFL)-distance at 36 m (downwards release) and 25 m (horizontal release). LFL-distance is how long the dispersed cloud extends and is above the lower flammability concentration. For hydrogen, this means concentrations above 4 vol%. The LFL-distance at horizontal release is almost 5 times longer for LH2 (122 m), and twice as long for the downward release (67 m). The illustrated flammable cloud is 12-38 times larger for LH2 and the explosive cloud is 1.5 - 2 larger.

Property	LH2	LNG	Ratio
Composition	100% H ₂	93%CH4, 5%C2H6, 2%C3H8	
Temperature	22 K	113K	
Density	68.9 kg/m^3	445 kg/m ³	1:6.5
Outflow velocity	120 m/s	47 m/s	2.6:1
Leak rate	404 g/s	1030 g/s	1:2.5
(Cd=0.62)			
Combustion heat	57 MJ/s	57 MJ/s	1:1
Energy density	0.51 MJ/m ³	2.0 MJ/m ³	1:4
LFL			

Table 3.1 - Comparison LH2 and LNG characteristics instrument release (5 barg and 10 mm) [5]

The LFL-distances for LNG make it manageable to estimate safety zones, but the significantly larger LFL-distances for LH2 will make it more challenging and unaffordable. Hydrogen has a LFL-concentration at 4 %, a concentration between 4 % and 8 % can be challenging to ignite due to its low reactivity. If the plume ignites at 8 % concentrations the temperature will be 370-700 °C, that will not cause a high risk for severe injury because of the short exposure time. A 8 % downwards LFL concentration for hydrogen will therefore be relevant for estimating a safety zone when bunkering. Hansen states that [5]:

"To justify a further reduction of the bunkering Safety Zone according to ISO20519 a quantitative risk assessment should be carried out estimating fatality risk contours. Such a study should consider release frequencies and rates for a larger variation of hole sizes, ignition probabilities, frequency of various wind conditions and directional dependencies to estimate location specific fatality risk from flashfires, jet-fires, and explosions. For bunkering sites with limited activity, the 10⁻⁵/year fatality risk contour can be significantly shorter than 52 m. With a high activity level larger safety zones might be required".

3.3.3 Vent mast releases

It may be necessary to use a vent mas release depending on vessel and design for some scenarios like bunkering and or for major releases into double piping between tank and vaporizer. The vent mast will have a similar temperature due to the ambient air. The temperature differences between the mast and LH2 will cause a major heat transfer so the hydrogen will vaporize. After some time, depending on the heat capacity, length, diameter, and thickness of the gas mast as well as the LH2 flow rate into the mast, the mast will be cooled down and the output of the mast will be denser than the surrounding air. The hydrogen may therefore fall on towards the deck/sea. This concern may be bigger for small vessels as fast passengers ferry because they

usually have la shorter vent mast than bigger vessels. Normally wind parameters and speed of the vessels will prevent the dense plume to be a safety concern for the passengers on board. In most cases such a release should be detected and stopped well before mast would be cooled sufficiently to release LH2. The main potential for such scenarios may be during bunkering and should be reflected when defining bunkering safety zones. Hansen's FLACS simulations, Figure 3.4 illustrates how different weather conditions will affect the dense plume out of the vent mast. Different wind rate, ambient temperatures and humidity effect the dispersion of the hydrogen release.



Figure 3.4: Illusion of how different wind and temperatures effect the dispersion of release [5]. The figure is a FLACS simulation of 500 g/s LH2 release from a 15 m tall gas mast. The left figures are simulated with outdoor temperature -10 °C while the right figures are simulated with outdoor temperature +15 °C. The white plume illustrates hydrogen concentrations above 15 vol%.

3.3.4 Conclusion of the work

Hansen concluded that the big safety knowledge gap is the people planning to build LH2 powered ships do not seem to acknowledge that LH2 release into air will show dense gas behaviour and not immediately rise upwards like release of hydrogen gas. This will be important information for explaining that LFL-distances for LH2 releases can be significantly longer than for comparable LNG-releases.

4. Experiments involving outdoor releases

The experiments are large-scale leakage of liquid hydrogen performed by the "State Highways Authority" and reported by the Norwegian Defence Research Establishment (FFI) [20]. The purpose for the experiments is to understand how LH2 will behave during a release and further use the data to provide safe use of LH2 as fuel in the maritime sector. The tests are divided into "outdoor leakage studies" and "closed room and ventilation mast studies". The experiments of the outdoor leakage studies will be further analysed while a parallel thesis is looking at the studies of closed room and ventilation mast.

4.1 Background for the experiment

The information below is from the FFI-report "Large scale leakage of liquid hydrogen (LH2)tests related to bunkering and maritime use of liquid hydrogen", for more details see reference [20].

The outdoor leakage studies are performed to evaluate the impact of hydrogen spill during bunkering operations and provide information about:

- Formation, including propagation and duration, of a liquid pool caused by leakage of LH2, and whether the liquid pool ceased to grow due to equilibrium between leakage and vaporization.
- Hydrogen concentration within the gas cloud, including propagation and duration of the hydrogen concentration in the dispersed cloud, caused by leakage of LH2.
- Condensation and freezing of components in air caused by leakage of LH2.
- Burning/deflagration/detonation of the gas cloud with H2 when ignited, and energy/pressure from any blast.

4.2 Description of experiments

Set-up for the experiments consisted of realistic dimensions of a bunkering operation, illustrated in Figure 4.1. A realistic release scenario will probably happen on the side of the ship while bunkering from a LH2 truck (up to 3,5 tonnes of LH2). The side of the ship was illustrated in the experiment by placing two ISO containers (H 2,570 mm x L12,180 mm x W 2,430 mm) at one side near the release point of liquid hydrogen. The experiments used the same dimensions of bunkering hose, flow rate, duration of release, and release point to achieve a realistic designing of the experiments. In addition to the ISO containers, an instrument box and a plastic

drum was placed in front of the release point to see if there was an impact on the release. Obstacles will cause more turbulence that can enhance flame acceleration if there is an ignition during a release.



Figure 4.1 - Inspiration image of bunkering and possible leakage of LH2 outdoors scenario [20].

The outdoor leakage study consisted of 7 experiments with different flow rate, wind rate, tanker pressure, atmospherically conditions and duration time for the release. Experiments 1-4 and 7 are done without ignition and experiment 5-6 were done with an ignition after 2 minutes. Overview of the experiments conditions is listed below.

Test	Time and	Release	Tanker	Nozzle	Outflow	Ignition	Run
	Date	orientation	pressure (barg)	size	rate (kg/min)		time (min)
1	12/11/19,	Vertical	2	1"	13,5	No	13
	5.11 pm	downwards					
2	12/12/19,	Vertical	6	1"	28,2	No	8
	2.57 pm	downwards					
3	12/13/19,	Vertical	10	1"	43,8	No	15
	11.05 am	downwards					
4	12/13/19,	Horizontal	10	1"	49,7	No	6
	12.37 pm						
5	12/13/19,	Vertical	10	1"	42,9	Yes	6
	2.37 pm	downwards					
6	12/13/19,	Horizontal	10	1"	49,9	Yes	3
	8.11 pm						
7	12/13/19,	Vertical	0.8	1"	9,7	No	8
	9.30 pm	downwards					

Table 4.1: Experimental data for the outdoor tests [20])]	[•
---	----	---	---

The liquid hydrogen was released through an orifice of 25.4 mm diameter placed 0.3 m above the ground in the middle of the test setup. The direction of the release was vertically downwards for Test 1- Test 3, Test 5 and Test 7, and horizontal for Test 4 and Test 6. The experimental set up is shown in Figure 4.2. The orange obstacles are placed on the test pad to estimate the prevalence of the emission and extent of any pool.



Figure 4.2: Experimental setup of outdoor leakage tests [20].

4.2.1 Measurements of Ambient Conditions

For all the tests weather conditions were measured. The measurements included wind speed, wind direction, ambient temperatures, and humidity. The wind speed and direction were measured by sensors placed 10 m and 5 m above the test pad, but only average measures of the sensor placed 10 m above the ground was used in the report.
4.2.2 Dispersion Measurements

Field temperature during the releases is measured by thermocouples placed near the release point. The temperature measures were done by 40 thermocouples (TT_49-TT_88) placed 30 m, 50 m, and 100 m away from the release point at four different heights for each location (0 m, 0.1 m, 1 m, and 1.8 m). 30 Oxygen sensors (OC_01-OC_30) was placed at the same location as for the thermocouples at three different heights (0.1 m, 1 m, and 1.8 m). By measuring the oxygen sensors, it is possible to use oxygen depletion to estimate hydrogen concentrations. When the concentration of hydrogen is estimated it is possible to see how long the lower flammability limits (4 vol%) for LH2 will extend. Location for thermocouples and oxygen sensor is shown in Figure 4.3 and Figure 4.4.



Figure 4.3: Location of sensor for measuring of dispersion cloud. Pink squares are thermocouples and oxygen sensors, red dots are radiometers and blue circles are pressure sensors. Blue cross is centre of test pad and release point [20].



Figure 4.4: Location for thermocouples and oxygen sensors in Test_02. Change of measurement points is done because the wind direction is from the east [20].

4.2.3 Ignition Measurements

Test 5 and Test 6 was ignited after 2 minutes. The test pad had used radiometers, calorimeters, and pressure sensors to measure thermal radiation, heat flux and field overpressure. The radiometers were placed 5 m, 10 m, 15 m, and 20 m from release point at 3 different height (0 m, 0.3 m (release height) and 1.2 m above the ground). The calorimeters were placed 0.2, 0.5, 1 and 5 m from the release point, 0.1 m height above ground level. The pressure sensors have the same location as the radiometers. Location of the sensors used is illustrated in Figure 4.3 and Figure 4.4 above.

4.3 **Results summary from experiments**

The data results are from the FFI-report, for more details see reference [20].

Weather conditions and results related to dispersion are described below. Test 5 and Test 6 also included an ignition after two minutes. The dispersion results apply to the highest hydrogen

concentration achieved during the test, and the lowest temperature measured. These are the critical parameters that describe how long the dispersion cloud stay at ground level. Concentration above 4 vol% is above the lowest flammable limit for hydrogen in air and constitute a potential danger.

4.3.1 Results Test 1

The release had an outflow rate of 13.5 kg/min and a duration of 13 minutes. The overpressure in LH2-tanker was 2 bar. Release orientation was vertically downwards.

Wind speed	$3.2 \pm 0.8 \text{ m/s}$
Wind direction	WSW (246±14 degrees)
Ambient temperature	1 °C
Weather	Overcast, rain prior to test

Table 4.2: Weather conditions – Test 1

Lowest field temperatures measured in Test 1 were between -2.9 °C and 1.6 °C. The lowest temperature was found on the thermocouples closest to release point (radius 30 m). The rest of the field temperature measurements were similar to the temperature of the ambient air. Very cold temperatures were not measured in this test.

The highest H_2 concentration in Test 1 was 1.8 vol%. This concentration was measured at sensor OC_05 with radius 30 m from release point and height 1.0 m above the ground. The highest H_2 concentration measured at radius of 50 m and 100 m from release point were 0.6 vol% and 0.5 vol%. Outflow rate in bunkering situations is expected to be up to 50 kg/min, and outflow rates in further tests were increased.

4.3.2 Results Test 2

Test 2 had a higher release rate than Test 1 and wind direction from east. The outflow rate was 28.2 kg/min and had a duration time of 8 minutes. The overpressure in the LH2 tank was increased from 2 bar to 6 bar to achieve a higher outflow rate. Measurement points were moved due to change in wind direction. Release orientation was the same as for test 1

Wind speed	$4.1 \pm 0.8 \text{ m/s}$
Wind direction	E (82±10 degrees)
Ambient temperature	1.5 °C
Weather	Overcast, rain prior to test

 Table 4.3: Weather conditions – Test 2

Field temperatures in Test 2 were between -7.6 °C and 2.1 °C. Lowest field temperature measured in test was -7.9 °C, found 30 m from release point with opposite direction of the release orientation.

Highest H₂ concentration in Test 2 was 4.2vol%. This concentration was measured at sensor OC_20 with radius 30 m from release point (opposite direction of release orientation) and height 1.0 m above the ground. The oxygen sensors in the same direction as release orientation measured no higher than 0.1 vol% hydrogen. The result from Test 1 illustrates the dependency the wind direction has on the dispersion cloud.

4.3.3 Results Test 3

Test 3 had almost 50% higher outflow rate than Test 2. Outflow rate was 43.8 kg/min and a duration of 15 minutes. The release orientation was the same as for Test 1 and Test 2. The overpressure in the LH2-tanker was increased to 10 bar to achieve a higher outflow rate.

Wind speed	5.8 ± 1.8 m/s
Wind direction	W (259±11 degrees)
Ambient temperature	2.9 °C
Weather	Overcast, rain prior to test

 Table 4.4: Weather conditions – Test 3

The wind direction was for Test 3 was similar to the wind measured Test 1. Measurement points was moved back to the same location as for Test 1. The lowest field temperature in Test 3 was between -8.0 °C and 3.1 °C. Lowest field temperatures measured in Test 3 was measured 30 m from release point in line with wind direction, 1.8 m above the ground.

The highest H₂ concentration in Test 3 was 8.6 vol%. This concentration was measured at sensor OC_07 with radius 30 m from release point and height 0.1 m above the ground. The hydrogen concentration decreased with increasing distance from release point. The highest hydrogen concentration measured by oxygen sensors with radius 50 m and 100 m was 3.3 vol%.

4.3.4 Results Test 4

Test 4 had an outflow rate just above the outflow rate for Test 3. The outflow rate was 49.7 kg/min and a duration time of 6 minutes. The release orientation was horizontal, same direction as the wind direction. The overpressure in LH2-tanker was 10 bar.

Wind speed	$6.7 \pm 1.6 \text{ m/s}$
Wind direction	W (264±10 degrees)
Ambient temperature	3.3 °C
Weather	Mainly cloudy, rain prior to test

 Table 4.5: Weather conditions – Test 4

The field temperatures measured in Test 4 were from -26.8 °C to 3.9 °C. The temperature -26.8 °C was found on the thermocouple closest to release point (30 m), in line with release direction and wind direction. The thermocouples placed 50 m in straight line from release point measured -10.9 °C, at the highest sensor (1.8 m above the ground). The other thermocouples placed 50 m and 100 m from release point measured temperatures similar to the ambient temperature.

The highest H₂-concentration in Test 4 was 17.2 vol%, measured at the oxygen sensors closest to release point (30 m), in line with release direction and wind direction. The oxygen sensors with 22.5° and a 45° angle showed significantly lower H₂-concentrations at 11.5 vol% and 3.4 vol%. This indicated a narrow area for flammable concentration for hydrogen. The highest concentration measured 50 m and 100 m from the release was 1.1 vol%.

4.3.5 Results Test 5

The release had an outflow rate at 42.9 kg/min and duration time of 2 minutes before the dispersion cloud got ignited. The ignition source was activated 18 m away from the release point. The release orientation was vertical downwards. Results related to H_2 concentration and

field temperature are results from the dispersion cloud before it got ignited. Results related to heat flux, radiation and overpressure are results after ignition and until the end of the release.

Wind speed	$5.2 \pm 1.9 \text{ m/s}$
Wind direction	W (257±12 degrees)
Ambient temperature	3.7 °C
Weather	Mainly cloudy, rain prior to test

Table 4.6: Weather conditions - Test 5

Before ignition

Lowest field temperature measured in Test 5 was between -8.5 °C and 4.1 °C. The lowest temperature was found on the thermocouples closest to release point (radius 30 m, 22.5° angel west). Rest of the field temperature was similar to the temperature of the ambient air expect from sensor 50 m in straight line from release point. These sensors had temperatures slightly under the ambient temperature around -0.4 °C and +2.0 °C.

The highest H_2 concentration that was measured in test 5 was between 6.2 vol% and 7.7 vol%. These concentrations were measured at the sensors closest to release point (radius 30 m) and at all heights (0.1 m, 1.0 m and 1.8 m).

After ignition

The highest thermal radiation was measured to 109.6 kW/m² at sensor Rad_02 10 m from the release point. The radiometer closest to the release point (5 m) did not work and would possibly get a higher thermal radiation at this point. Highest heat flux measured in Test 6 was 301.6 kW/m². Sensor Cal_7 was placed 0.5 m from release point.

4.3.6 Results test 6

The release had outflow rate at 49.9 kg/min and duration time of 2 min before the dispersion cloud got ignited. The ignition source was activated 30 m away from the release point. Release orientation was horizontal. Results related to H₂ concentration and field temperature are results from the dispersion cloud before it got ignited. Results related to heat flux, radiation and overpressure are results after ignition and until the end of the release.

Table 4.7: Weather conditions - Test 6

Wind speed	$2.7 \pm 0 \text{ m/s}$
Wind direction	WSW (245±15 degrees)
Ambient temperature	3.8 °C
Weather	Mainly cloudy, rain prior to test

Before ignition

The lowest field temperature measured in Test 6 was between -25.7 °C and 3.8 °C. The lowest temperature was found on the thermocouples closest to the release point (radius 30 m, 22.5° angle west). Rest of the field temperature was similar to the temperature of the ambient air. Highest H₂ concentration in Test 6 was between 18.6 and 21.0 vol%. These concentrations were measured at the sensors closest to release point (radius 30 m) and at all heights (0.1 m, 1.0 m and 1.8 m). The highest concentration was measured at 0.1 m above the ground. The sensors located 50 m and 100 m from the release point was lower than 1.8 vol %.

After ignition

The highest thermal radiation was measured to 75 kW/m² and the highest average thermal radiation was measured to 23 kW/m². The highest thermal radiation was measured at Rad_09 5 m from release point with angle 45° east. Highest heat flux measured in Test 6 was 35 kW/m². Sensor Cal_9 was placed 1 m form release point.

4.3.7 Results Test 7

Test 7 had outflow rate at 9.7 kg/min and a duration time of 8 minutes. Test 7 had the lowest outflow rate and the lowest overpressure in the LH2-tanker (0.8 bar). Release orientation was vertical downwards.

Wind speed	6.5 ± 1.4 m/s
Wind direction	W (266±11 degrees)
Ambient temperature	3.2 °C
Weather	Heavy rain prior to and during test

Table 4.8: Weather conditions – Test 7

The temperatures measured in Test 7 were from -0.2 °C and 3.3 °C. The lowest temperature in test 7 is significantly higher than for the other tests. The highest H₂-concentration measured was 2.7 vol%, found at the oxygen sensors closest to the release point. H₂-concentration measured 50 m and 100 m from release point were lower than 1.0 vol%. All the concentrations measured in Test 7 were lower than the flammable concentration limits for hydrogen (4 vol%).

4.4 Summary of the experimental results

The results regarding the H₂-concentration in the dispersed clouds showed no concentrations higher than the LFL 50 m from the release point for vertically releases. For the horizontal releases there were measured H₂-concentrations above the LFL 50 m from the release point, but not 100 m away from the release point. As expected, the H₂-concentrations and the field temperatures were almost linear correlated. Near the release point the H₂-concentrations were high and the field temperatures were low. The measurements of the temperatures and the H₂-concentrations confirmed the high natural buoyancy for hydrogen. The findings from the experiments will be useful knowledge to take into account when establishing standards for safety zones during bunkering operations.

5. Methodology

The simulation program FLACS (FLame ACceleration Simulator) is used to run dispersion simulations of liquid hydrogen release. FLACS is a Computational Fluid Dynamics (CFD) software established to preform modelling of dispersion, explosion and fire in the process industries. The FLACS simulations in this thesis are used to examine how dispersion clouds of big releases of liquid hydrogen behave.

This chapter introduces the program and method that is being used to simulate the large-scale experiments of dispersion of liquid hydrogen. The CFD-tool FLACS is an advanced software based on complex equations and turbulence models, that will be explained further below. The software is primarily used for gases, and since this is a study of liquid hydrogen, some assumptions have been made. These assumptions and the set-up in FLACS presented in the following. Furthermore, a validation study of FLACS as a tool for simulating dispersion of liquid hydrogen is presented.

The simulations are a re-creation of experiments of large-scale leakage of liquid hydrogen reported by the Norwegian Defence Research Establishment (FFI) [20]. If the approach is sufficient, the simulations can be a guiding tool to establish safety standards for bunkering operation using liquid hydrogen and discuss measures to increase the safety for use, storage, and distributions of hydrogen as a fuel for ships.

5.1 Background

FLACS is a Computational Fluid Dynamics (CFD) software established to model dispersion of flammable or toxic gases, gas and dust explosions, pool and jet fires and propagation of blast and shock waves in the process industries. FLACS is a tool for safety applications (preventing and improving of safety level). The program uses numerical methods and algorithms to analyse fluids flow, with or without chemical reactions [35]. To analyse the fluid flows, CFD is based on the fundamental governing equations of fluid dynamics. This is the equations of continuity, momentum, and energy [36]. The equations from "Unit Operations of Chemical Engineering"[37] and are described below.

5.1.1 The governing equations

The continuity equation

The continuity equation describes conservation of mass for a continuous system. In words the equation can be written as:

$$Rate of mass accumulated = Rate of mass flow in - Rate of mass flow out$$
(1.1)

The momentum equation

The momentum equation is based on the physical principle in Newton's second law, F=ma. In words the equation can be written as:

Rate of momentum accumulation = Rate of momentum entering

$$-Rate of momentum leaving + Sum of forces acting on the system$$
 (1.2)

The energy equation

The energy equation is based on the physical principle in the thermodynamics first law, energy can neither be created or destroyed in an isolated system. In words the equation can be written as:

Rate of change of energy inside fluid element = Net flux of heat into element + Rate of work done on element due to body and surface forces (1.3)

For viscous flow the equations above make up the Navier-Stokes equations. For viscous flow the transport phenomena of friction, thermal conduction and mass diffusion is included [33]. The Navier-Stokes equation describes the movements for viscous liquids and gases. The For inviscid flows the equations above make up the Euler equations. For inviscid flows, flows where the viscosity of the fluid is zero, the transport phenomena of viscosity, mass diffusion, and thermal conductivity is neglected [36].

In addition to the equations above the mixture fraction is an important parameter to define. The mixture fraction describes the local fuel-air ratio in non-premixed combustion [38]. The mixture fraction of the fuel can be written as:

$$Z = \frac{m_1}{m_1 + m_2} \tag{1.4}$$

Where m_1 is the quantity of the fuel and m_2 is the quantity of the oxidizer.

5.1.2 Turbulence models

To analyse the fluid flow, if it is dispersion or combustion, it is necessary to analyse the energy caused by turbulence. Turbulence flows have continuous fluctuations of velocity, caused by vortices generated by shear within the flow [38]. The fluctuations of velocity can lead to fluctuations in temperature, density, and mixture of the flow. The flow swirl with the reverse current created when the flow is in a turbulent regime. The swirling is called eddies. Figure 5.1 illustrated how the turbulent flow from a nozzle makes eddies. At first there are small eddies, and the small eddies develop into larger eddies in the downstream.



Figure 5.1: Illustration of the growth of a turbulence jet [39].

It possible to analyse the turbulence without a turbulence model, but by solving the governing equations directly. This approach is called, direct numerical simulations (DNS). DNS include simulation of alle the eddies, it gives a high amount of data, but this is a very time-consuming method and can only be used for idealised system and is mostly used in academia and research of simple flows.

CFD-programs uses turbulence models to solve the governing equations. LES-models resolve eddies above a given size by solving the Navier-Stokes equations, like the k- ϵ model, based on the assumption that the smallest eddies can be solved by an isotropic model. Another method is using Reynold Averaged Navier-Stokes (RANS)equations. RANS are time-averaged equations of motions of the fluid flow, interested in the mean values of the turbulent flow [36]. This is the method used in FLACS. The equations are Favre-averaged, also called density-weighted average. This means that the flow is separated into an average and a fluctuation component, where the fluctuation in the flow is the turbulence [36]. The turbulence model is a necessary tool for estimating the impact of the smallest eddies.

5.1.7 The model system

FLACS is based on a 3-dimensional (3D) CFD-tool solving the Favre-average transport equations for mass, momentum, enthalpy, turbulent kinetic energy, rate of dissipation of turbulent kinetic energy, mass fraction of fuel and mixture-fraction on a structured Cartesian grid using a finite volume method. The biggest difference that separate FLACS form other CFD-tool is the use of the distributed porosity concept to represent geometry [35]. This concept represents large objects on-grid and small objects is represented sub-grid. The simulations of the local congestion and confinement is represented by the porosity field. The sub-grid objects can then allow to contribute with flow resistance (drag), turbulence generation and flame folding in the simulations [35].

The FLACS-software is primarily used for simulations of flammable and toxic gases that is well known in the process industry, but the program is not limited to a particular marked or industry. According the FLACS user's manual [35]: "The basic conservation laws apply equally well to safe design and optimisation of new technology, including the emerging field of renewable energy". The first step in this thesis is to validate the software respond to simulate dispersion of liquid hydrogen.

This thesis will discuss the approach of the outdoor experiments in the FFI-report by using the simulation tool FLACS.

5.1.8 Validation

Previously simulations of large-scale liquid hydrogen are limited. First, there a limited number of physical experiments done. Some validation of experiments including hydrogen jets has been performed. The assessment of these simulations is that FLACS simulations can give a sufficient approach of simulating hydrogen. Validation of liquid hydrogen is even more rarely, then for gaseous hydrogen. A lot of validation has been done for scenarios involving gaseous hydrogen. The simulation tool is complex and requires sound knowledge of the physics and the software to achieve a good approach. In this thesis there is done an approach that is inspired by the one used by Hansen in his paper "Liquid hydrogen releases show dense gas behavior" [5] described in chapter 3. The approach is to simulate a steady state leakage of cold gaseous hydrogen instead of simulating the hydrogen directly as a liquid.

5.2 Model simplification and assumptions

The software FLACS is primarily a simulation tool for flammable and toxic gases. This is one of the main challenges for using FLACS to simulate dispersion of LH2. To do this approach of the experiments, several assumptions are made.

Liquid hydrogen has a boiling point at -253 °C. The storing temperature for LH2 is so low, that for a release with these temperatures, the ambient air may cool down below its freezing point. This can cause solidifying of the O_2 and N_2 particles in the air around the release point. Currently it is not practical to simulate phase changes (flashing) from liquid to gas directly with the CFD code since the code is primarily for gas dispersion. Therefore, it is assumed that the dispersion of LH2 will evaporate from liquid into gas phase immediately after the release. The LH2 will rapidly be in cold gas phase and diffuse into the ambient air.

Hydrogen in gas phase is therefore used in the simulations of the release scenarios.

The path from the LH2 tanker to the release point is not included in the simulation. Simulating LH2-flow inside geometries is more complex and is disregarded in these simulations. Parameters regarding the LH2 flow inside the pipe from the LH2 to the release point will not be taken into account of the dispersion. Parameters like for example heat transfer from the pipe to the LH2 flow may be disregarded because of this.

Estimating the pool parameters in the FFI experiments is challenging due to the liquid phase of

the hydrogen and the formation of a pool of liquid hydrogen. However, this scenario is not relevant for the bunkering operation and the results from pool array will not be further discussed. Based on the assumptions done and limited simulation experience the simulation results must be considered with some uncertainties.

5.3 Simulation set-up

All the steps of the set-up for the dispersion simulation are shown below. The geometry is a simple construction of the experiments where the focus is the behaviour of the dispersion cloud.

5.3.1 Geometry

The first step was to set up a geometry file. The geometry was made in CASD, under the geometry tab. The test set-up for the experiments was a simple construction, only consisting of a release point, and two ISO-containers and some small barriers. The geometry file consisted of one box illustrating the ground and one box illustrating the containers on one side of the release point. These containers are illustrating the side of a ship, getting fuelled by LH2. The figure of the experimental set up is shown in chapter 4. The ground was 200 m x 90 m x 0.15 m, and the container was 13 m x 2.5 m x 5.2 m (same dimension as two ISO- containers stacked on top of each other).



Figure 5.1: Geometry set-up consisting of ground and two ISO-containers on the of the release point.

5.3.2 Grid

The core domain, covering the area close to the release point was set to a cell size 0.300 m, resulting in a total cell number of 95 676 cells for this domain. The stretch domain covers a longer area. Some of the measurement points are located 100 meters away from the release point. If the core domain with a uniform grid cell size covers all the area with cell sizes, it will result in very time-consuming simulations. Therefore, the stretch domain function is used here. The stretch domain has a max factor 1.200, and the largest cell size calculated by FLACS to 26.508 m. The total number of cells in the grid are 387 748.

5.3.3 Scenario

The scenario is defined in the CASD function. The scenario setting was set to simulation type "Dispersion and ventilation".

5.3.4 Monitor Points

The monitor points reflected the measuring point for the experiments. The monitor point had the same coordinates as the measuring points, and the variables set for all the seven tests were:

- Fuel mole fraction, FMOLE
- Temperature, T
- Velocity vector, UVW
- Equivalence ratio, ER

5.3.5 Single field 3D output

The same variables that are listed under monitor point, were set up in the single field 3D output. The result is then possible to view as in a two-dimensional (2D) cut plane and as a threedimensional (3D) plot.

5.3.6 Simulation and output control

The solver mode was set to transient. Maximum time was set to 120 seconds for all simulations, except for the simulation with ignition (Test 5 and Test 6). The experiments had a duration time from 3 minutes up to 15 minutes. Some test simulations were done over the actual duration time of the experiment. These tests gave the same values that were achieved during the two first minutes of the simulation. Simulating scenarios for several of minutes is very time consuming, and since no significant changes in the results by increasing the duration time were observed, the maximum time was set to 120 seconds. The other variables were left unchanged.

The value of CFLC was set to 10 and CFLV was set to 1, that is a general recommendation for "dispersion and ventilation" scenarios in the user manual [35].

5.3.7 Boundary conditions

By setting the values of wind direction and wind velocity in the "Wind Wizard", the boundary condition was set automatically to nozzle and wind. The nozzle formation is recommended as boundary condition for wind and dispersion simulations.

5.3.8 Initial conditions

The temperature was set to the outside temperature for each test, with variations from 1 $^{\circ}$ C to 3.8 $^{\circ}$ C. The ground roughness was set to 0.03 which is recommended for open flat terrain. The other variables were left as the default value.

5.3.9 Gas composition and volume

Volume fractions was set to 100 % for hydrogen, and the equivalence ratio was set to "1e+30".

5.3.10 Gas monitor region

The size of the gas monitor region was 20 m x 30 m x 30 m, with coordinates (-30, -15, 0) placed behind the release point.

5.3.11 Leaks

The leak had open side -Z (vertical downwards) for Test 1, Test 2, Test 3, Test 5 and Test 7. The leak open side for Test 4 and Test 6 was +X (horizontal). The outflow rate for each test was set in the "Leak Wizard" and was varying from 0.162 kg/s up to 0.833 kg/s. The outlet was from a 1" pipe. Data of the outflow rate for each test is described in chapter 4.

5.3.12 Wind

Parameters related to wind velocities and wind direction was set in "Wind Wizard". These variables were different for each test. The variables for wind are presented in chapter 4.

5.3.13 Ignition

Time of ignition was set to 999999 seconds for all test, except from Test 5 and Test 6. Here the time of ignition was set to 120 seconds.

6. Results and discussion

The results from the FLACS simulations are presented below, where the measurements from each test is compared to the simulation. In addition to the tests there is done some variation of parameters that may have a significant effect on the dispersion cloud. Further, to see if this will cause hazardous scenarios of an accidental release during bunkering operations. Based on the experiments and the simulations done, the main safety concerns for using liquid hydrogen as fuel for ships will be discussed. Furthermore, discuss if it is needed to develop new safety codes and standards to achieve a comparable safety level for ships using liquid hydrogen with the ships in operation today using LNG.

6.1 Validation of FLACS-simulations compared to the experiments

The results from the outdoor leakage tests are compared to the simulation results by FLACS. The comparison is done to validate the recreation of the dispersion cloud of liquid hydrogen by using the FLACS program. Some of the critical parameters that separate liquid hydrogen from other conventional fuel is the low storing temperature (-253 °C) and a lower flammable limit (4 vol% in air). These parameters will be compared for each test. The data values of temperatures and concentrations are shown in Appendix B.

Due to limited time, the ignition in Test 5 and Test 6 is excluded from the thesis. The simulation results from tests, will only include data regarding the release before it got ignited.

6.1.1 Test 1, Release without increasing tanker pressure

This simulation had an outflow rate of 0.228 kg/s with leak direction -Z, and the reservoir had pressure 2 barg. The wind velocity was set to 3.2 m/s with direction 246 degrees (WSW). The outdoor temperature was 1 °C.



Figure 6.1: Comparison of simulation results and measurements of highest H2-concentration for Test 1

The concentration results from FLACS compares well with the measurements from Test 1 for the higher oxygen sensors. The highest H2-concentration at the sensor 0.1 m above the ground has a more significant deviation. The FLACS results give a higher concentration compared with the test. This deviation may be caused by the simplification and assumption explained in chapter 5.2.



Figure 6.2: Comparison of simulation results and measurements of lowest temperatures for Test 1

The temperature results at the sensor closes to the release point show a lower temperature in the simulation results compared with the measurement in Test 1. The simulation has not included heat transfer from ground in the calculations, which may be a part of the reason the FLACS results give a lower temperature. However, the sensor with longer distance from the release point show a smaller deviation. Both the simulation result and the measurement have a temperature close to the ambient temperature, which illustrate that the hydrogen already have gained buoyancy and most of the dispersion cloud has diffused into the air at this point.

6.1.2 Test 2, Higher release rate and opposite wind direction

In the simulation of Test 2, the outflow rate was increased to 0.473 kg/s and the release direction was still -Z. The overpressure in the reservoir was set to 6 bar. The wind velocity was set to 4.1 m/s with direction 82 degrees (E). The outdoor temperature was 1.5 °C.



Figure 6.3: Comparison of simulation results and measurements of highest H2-concentration for Test 2

In this test the wind direction changed and there was no hydrogen concentration at the monitor point or measurement point east of the release point. The dispersion cloud had the opposite direction compared to Test 1. The concentration west from release point showed a higher concentration in the FLACS result compared with measurements in Test 2. The concentration predicted by FLACS results is more than twice as high as the measured value.



Figure 6.4: Comparison of simulation results and measurements of lowest temperatures for Test 2

The same tendencies are shown in the temperature results. The FLACS results illustrate a lower temperature compared with the measurements in Test 2. A higher concentration and a lower temperature correspond because more hydrogen present in a dispersion cloud gives lower temperature. When the temperature increases the hydrogen will diffuse more rapidly in the ambient air. The reason why FLACS gives a higher concentration and lower temperature may be caused by the neglect of heat transfer from the ground and the pipe.

6.1.3 Test 3, Higher outflow rate

Test 3 simulation increased the outflow rate to 0.730 kg/s with release direction -Z. The overpressure in the reservoir is increased to 10 bar. The wind velocity was set to 5.8 m/s with direction 259 degrees (W). The outdoor temperature was 2.9 °C.



Figure 6.5: Comparison of simulation results and measurements of highest H2-concentration for Test 3

The simulation of H2-concentration in Test 3 agrees more closely with the experiments than for Test 1 and Test 2. The biggest deviation is still at the lowest sensors, but the deviation is considerably lower than for Test 2. This test has a higher wind velocity that may help the hydrogen concentration to be lifted from ground level in FLACS. Figure 6.5 shows that the deviation reduces with higher placed oxygen sensors. A difference from this test is that the FLACS results give a lower concentration for the sensors 1.0 m and 1.8 m above the ground. The buoyancy effect may be higher in the FLACS set up that in the experimental tests.



Figure 6.6: Comparison of simulation results and measurements of lowest temperatures for Test 3

The predicted temperatures deviate less from the corresponding measurements with increased distance from the release point. The deviation increases when the distance from the release point decreases. This is repeated for all tests.

6.1.4 Test 4, Horizontal release

In the simulation of Test 4, the outflow rate was increased to 0.828 kg/s with release direction +X. The overpressure in the reservoir was 10 bar. The wind velocity was set to 6.7 m/s with direction 264 degrees (W). The outdoor temperature was $3.3 \text{ }^{\circ}\text{C}$.



Figure 6.7: Comparison of simulation results and measurements of highest H2-concentration for Test 4

The FLACS result of Test 4 show a significantly lower concentration of hydrogen compared to the measurements in the test. This simulation has a higher outflow rate, but the biggest difference from the earlier tests is the leak direction. The leak direction is now oriented along the ground and not towards the ground. The simulation of Test 4 show a significantly higher deviation from the concentration measured in the experiment. The deviation is big for all the height for the oxygen sensors. At the sensor 0.1 m above the ground det deviation is 9 vol%, at the sensor 1 m above the ground the deviation is 10.4 vol% and at the sensor 1.8 m above the deviation is 7.2 vol%.



Figure 6.8: Comparison of simulation results and measurements of lowest temperatures for Test 4

The temperature shows the opposite trend compared to the other tests. There is a significant deviation for the temperature results closest to the release point, but the simulation now predicts a much higher temperature than measured in the test. The predicted and measured temperatures further away still correspond well like in the earlier tests.

6.1.5 Test 5, First ignited test, vertical downward release

The simulation set up for Test 5 had a slightly lower outflow rate at 0.740 kg/s than Test 4 and the release direction was changed back to -Z. The overpressure in the reservoir was 10 bar. The wind velocity was set to 5.2 m/s with direction 257 degrees (W). The outdoor temperature was $3.7 \,^{\circ}$ C.



Figure 6.9: Comparison of simulation results and measurements of highest H2-concentration for Test 5 (before ignition)

The concentration results have the same trend as for Test 1. The FLACS results agree well with the measurements from the test at oxygen sensors 1.0 and 1.8 m above the ground. The biggest deviation is at the sensors near ground level, where FLACS predicts a higher concentration of hydrogen.



Figure 6.10: Comparison of simulation results and measurements of lowest temperatures for Test 5 (before ignition)

The FLACS results of the temperature show the same trend like for most of the experiments. There is a much lower temperature in the simulation results at the sensors closest to the release point.

6.1.6 Test 6 Second ignited test, horizontal release

The simulation set up for Test 6 had an outflow rate at 0.833 kg/s and the release direction was changed to +X. The overpressure in the reservoir was 10 bar and the wind velocity was set to 2.7 m/s with direction 245 degrees (WSW). The outdoor temperature was 3.8 °C.



Figure 6.11: Comparison simulation results and measurements of highest H2-concentration for Test 6 (before ignition)

The results show a big difference between the simulation results and the measurements from the test. It is the same trend as for Test 4, which also had a release orientation +X. The simulation shows a lower concentration and has a significant deviation for oxygen sensors at all heights.



Figure 6.12: Comparison simulation results and measurements of lowest temperatures for Test 6 (before ignition)

The results regarding the temperature again show the same trend as for Test 4. There is a big difference of the temperatures between the simulations and the measurements 30 m away from the release point. The simulation results predict a considerably higher temperature compared with the measurements. The simulation result with longer distance get a temperature near the temperature in the test.

6.1.7 Test 7, Final release to empty tanker

Simulation of Test 7 had outflow rate 0.162 kg/s and release direction -Z. The overpressure on the reservoir was decreased to 0.8 bar. Wind velocity was set to 6.5 m/s with direction 266 degrees (W). The outdoor temperature was 3.2 °C.



Figure 6.13: Comparison simulation results and measurements of highest H2-concentration for Test 7

The simulation result of this test has the same concentration (2.5 vol%) as the measurements in Test 7 at the oxygen sensors closest to the release point. For the other sensors there is a deviation around 1 vol%.



Figure 6.14: Comparison simulation results and measurements of lowest temperatures for Test 7

The simulation results give a lower temperature then the measurements in Test 6. In Figure 6.14 the deviation looks big, but the temperature was only 2.4 C° lower at the sensor 30 m form release point and 2.5 C° lower at the sensor 50 m from release point. The approach is not that bad. A lower temperature in FLACS may be caused by the neglected heat transfer.

6.1.8 Summary of the FLACS results

The simulation results of the seven tests can be summarized as:

- FLACS predicts a higher concentration compared to the measurements closest to the ground (0.1 m) for the tests with vertical downwards release direction (-Z). The discrepancy between the predicted and the measured concentration decreases when increasing the distance from the release point.
- FLACS predicts a lower concentration compared to the measurements for the tests with horizontal release direction (+X). The deviation for these tests is not decreasing when the distance from release point increases, like for the vertical downwards releases. The deviation is similar for all height of the oxygen sensors. The concentration does not reflect the concentration measured in these tests. The deviation is big, and the simulation result should be considered with some uncertainties.

- As additional to the concentration results the temperatures from the simulations give a lower temperature at the sensors 30 m from release point. The high concentration and low temperature are consistent with each other. The horizontal releases have the opposite trend where the simulations give a higher temperature, corresponding to the lower concentration for these tests.
- The simulation results of temperatures 50 m away from the release point agreed cooperating well with the measurement from the tests. Both the tests, and simulations gave temperatures similar to the ambient temperature. This confirms the buoyancy effect for hydrogen.

The tests are done with different outflow rates and wind parameters. The 2D-plots below illustrate the concentration profiles for the tests.



Figure 6.15: Test 1, concentration profiles



. Figure 6.16: Test 2, concentration profiles



Figure 6.17: Test 3, concentration profiles



Figure 6.18: Test 4, concentration profiles



Figure 6.19: Test 5, concentration profiles



^{Run: 000000} Var: MoleFractionFuel_3D Figure 6.20: Test 6, concentration profiles



Figure 6.21: Test 7, concentration profiles

The darkest blue colour illustrate area with 2 vol% hydrogen. The second darkest blue colour illustrate where there is 4 vol% of hydrogen in the cloud. For this area the concentration above the flammable limit for hydrogen in air. The test with longest range of this concentration is Test 4 where the concentration profile extends almost 80 meters from the release point. Test 4 had a horizontal release and the highest outflow rate of the seven tests. For Test 3 and Test 5 the concentration profile of 4 vol% hydrogen extended around 60 meters from release point. These

tests also had a high outflow rate, but the release was orientated vertical downwards. These results show a corresponding trend for high outflow rate and long distances with concentrations over flammable limit in the dispersion cloud.

6.2 The impact of changing essential parameters

The dispersion of LH2 depends on a numerous of variables. The impact of some variables may be crucial, and it is necessary to define its impact on a potential leak to achieve a sufficient safety level. In this subchapter variables that effects the dispersion cloud of LH2 will be analysed. Furthermore, see if any of the variables have some limitation to achieve a comparable safety level for bunkering of LNG with bunkering of liquid hydrogen.

6.2.1 Wind velocity

Wind velocity has a significant impact of the leakage and it is a variable that is not possible to control. This makes it important to the analyse of the wind velocity. A bunkering operation needs to assure that it is prepared for leakage scenario for a wide range of wind velocity. In this analyse the wind velocity is varying form 0.5 m/s to 30 m/s. The lowest temperature and highest concentration of hydrogen for the different velocities are illustrated in Figure 6.22 and Figure 6.23 below.



Figure 6.22: Simulation results of lowest temperature when varying wind velocities

The simulation results show a significant lower temperature and a higher H2-concentration for wind velocity between 0.5 m/s and 10 m/s. For wind velocities between 15 m/s and 30 m/s the

temperature rise to around the ambient temperature and the highest H2-concentration is well below the flammable limit for hydrogen in air.



Figure 6.23: Simulation results of highest H2-Concentration when varying wind velocities

The results illustrate that a wind velocity higher than 15 m/s makes the dispersion cloud diffuse into the ambient air quickly. The hazardous time near ground level will decrease compared to the wind velocity from the test scenario. However, a low wind velocity will result in a longer time where there is a potential hazard scenario. This is because limited wind will increase the time that the dispersion cloud is at ground level. The concentration of the dispersion cloud after 120 s at ground level with different wind velocities is illustrated in Figure 6.24 and Figure 6.25.

The figures illustrate that a higher wind speed gives a small thin dispersion plume, and the concentration decreases quickly. The dispersion cloud with limited wind speed shows a wider area with higher concentrations and the dispersion cloud extend in all directions. The low wind velocity increases the time for the buoyancy forces to work [5], and the cloud will remain at ground level for a longer period compared to the simulations with a higher wind speed. These results show that a higher wind velocity will be favourable to increase the buoyancy of the dispersion cloud. But more wind will generate more turbulence and increase the risk if the cloud was to ignite. The turbulence will increase the propagation for a potential flame.

Wind velocity and wind direction have a significant impact on the dispersion cloud and is a parameter that is necessary to have under control during bunkering operations.



Figure 6.24: Concentration profiles in dispersion cloud varying the wind velocity from 0.5 m/s to 10

m/s



Figure 6.25: Concentration profiles in dispersion cloud varying the wind velocity from 15 m/s to 30 m/s

6.2.2 Pasquill classes

The stability of atmospheric can be separated into Pasquill classes [35]. The Pasquill class categorise the amount of atmospheric turbulence present. There is six level of stability, and the classes are defined in Table 6.1 below. The data used in this test is the same data as in Test 5. The only parameter that is changed is the Pasquill class. Results are shown in Figure 6.26 and Figure 6.27 below. The FLACS user's manual [35] do not recommend using class A-C, because they are unstable and can cause stability problems. However, since this is just a test scenario all the Pasquill classes are simulated to see the impact of different stability classes.

Pasquill Class	Definition
Α	Very unstable
В	Unstable
С	Slightly unstable
D	Neutral
Е	Slightly stable

Stable

F

Table 6.1: Pasquill stability classes

The results in Figure 6.26 illustrates that higher level of turbulence present increases the H2concentration in the dispersion cloud.



Figure 6.26: Simulation results of highest H2-Concentration when varying Pasquill Class



Figure 6.27: Simulation results of lowest temperature when varying Pasquill Classes

The results in Figure 6.27 illustrate that higher stability increases the temperature of the dispersion cloud. The most unstable Pasquill classes decrease the temperature and have a higher concentration of hydrogen. The most favourable situation is a low level of turbulence present, therefore Pasquill class F, stable. A high turbulence level in the dispersion cloud can result in a higher level of danger if there is an accidental release. More turbulence can increase the flame propagation [36]. The Pasquill classes are estimated based on the wind speed, incoming solar radiation, and sky cover. Together these parameters are used to confirm the atmospheric diffusion. Furthermore, to describe the wind spread impact on a downwind plume of an emitted source, or a release of liquid hydrogen in this case [38].

6.2.3 Temperature

The experimental test was done in a short period of time, which result in a limited variation of outdoor temperatures. Since a bunkering operation will be done at all seasons, the outdoor temperatures will have a wider range of differences then there is in the experimental tests. It is done a sensitivity test of different outdoor temperatures varying from -20 °C (a cold winter day) to +30 °C (a hot summer day). The results are plotted below in Figure 6.28 and Figure 6.29 to see how the outdoor temperature effects the concentration of hydrogen and the temperature in the dispersion cloud. (IT= initial temperature, also known as outdoor temperature)



Figure 6.28: Simulation results of highest H2-Concentration when varying outdoor temperatures

The plot does not illustrate a proportional correlation between the initial temperature and the H2-concentration in the dispersion cloud. When the outdoor temperature is -20 °C, it would be expected a higher concentration of hydrogen, than for outdoor temperatures at -15 °C. A lower difference between the cold gas phase and the ambient temperature is expected to increase the time of the dispersion cloud to diffuse with the ambient air. Furthermore, obtain a higher H2-concentration near ground level [23]. The deviation from the expected correlation between a lower outdoor temperature and an increased diffusion time of the dispersed cloud may be caused by the approach to simulate cold gaseous hydrogen, instead of liquid hydrogen directly in FLACS.



Figure 6.29: Simulation results of lowest temperatures when varying outdoor temperatures

However, the outdoor temperature has a perceptible impact on the temperature near the release point. The outdoor temperature and the field temperature seem to increase proportionally. A release on a cold winter day will have a significant lower field temperature near leakage point compared to a hot summer day. When developing safety zones, it is important to make sure the safety measures is suited for a wide range of outdoor temperatures.

6.2.4 Grid

When the simulation scenario is set, it is time to define a suitable grid for the simulation. The grid must cover alle the parts that is going to be monitoring and be small enough to catch up the variables that is going to be analysed. Small grid size cells give a more precise simulation result, but also require a considerably longer running time for the simulation. To find the balance between grid cell size and desired simulation result is demanding. A sensitivity test of grid cell sizes was done near the size used in the simulations in chapter 6.1 (0.30 m). The data used in this sensitivity test is from Test 4.



Figure 6.30: Simulation results of highest H2-Concentration when varying grid cell size in FLACS

A comparison of the concentration results when varying grid cell size, give a significant change for some of the sizes. The grid cell size at 0.30 m, 0.25 m and 0.20 m give a correspondingly equal result. When the size increases from 0.30 m to 0.35 m the concentration jumps from 8 vol% to 28 vol% for the concentration 0.1 m above the ground. But when the size increases to 0.40 m the concentration falls down to 13.9 vol% and has the value closest to the measurements from the test. However, the comparison of these grid cell sizes actually implies that 0.40 m will
give a concentration closer to the measurements from the test compared with a grid cell size of 0.30 m.



Figure 6.31: Simulation results of lowest temperatures when varying grid cell size in FLACS

A comparison of the temperature results when varying grid cell size applies the same trend for grid cell size 0.30 m, 0.25 m and 0.20 m. These sizes give a similar result. For grid cell size 0.35 m there is a big deviation for the temperature 30 m from release, but when the cell size increase to 0.40 m the deviation is limited. For the temperature 50 m from release point the 0.40 m cell size has the biggest deviation compared to the other grid cell sizes.

6.2.5 Change of release orientation

The release orientation in the tests were either horizontal or vertical. The horizontal releases were along the x-axis, in direction along the ISO-container, representing the side of the ship. None of the experiments had horizontal releases with direction against the container. Therefore, it is done a simulation of Test 3 with release orientation against the container to compare releases along and against the container. The simulation result is illustrated in Figure 6.32 and Figure 6.33.



Figure 6.32: Simulation result of highest H2-concentration with release orientation against and along the ISO-container in Test 3.

The release against the container shows a lower H2-concentration at the oxygen sensor near the ground and a higher H2-concentration at the highest oxygen sensors. The experimental tests have barriers with limited effect on the release, due to its orientation. When the release is oriented against the container, the concentration in the dispersion cloud shows an opposite behaviour compared to the release along the container. A higher concentration at the highest oxygen sensor can be caused by more turbulence present in the dispersion cloud as an effect of the container.



Figure 6.33: Simulation result of lowest temperature with release orientation against and along the ISO-container in Test 3.

The results of lowest temperatures show a higher temperature when the release is orientated against the container.

6.2.6 Adding barriers

There are done some added simulations to see the effect of adding barriers in front of the release. In one simulation it is added three tall obstacles to illustrate three pallet stackers, which is a common sight to be found at a harbour. For the other simulation it is added containers. There is done one simulation with one container and one simulation with two containers on top of each other. The simulations are done to see if barriers like this are necessary to consider when establishing safety distances for bunkering of liquid hydrogen. Figure 6.34, 6.35 and 6.36 are 2D-plots that illustrate the barriers and the dispersed cloud.



Figure 6.34: Concentration profile of dispersion cloud with 3 high barriers in front of the release point.



Run: 500000

Figure 6.35: Concentration profile of dispersion cloud with 1 ISO-container in front of the release point.



Figure 6.36: Concentration profile of dispersion cloud with 2 ISO-containers on top of each other, in front of the release point.

Further, the results from all the different simulations are plotted together in Figure 6.37 and Figure 6.38 to compare the effect of the barriers in front of the release.



Figure 6.37: Simulation results of highest H2-concentration with release orientation against different barriers.

The concentration results 0.1 m above the ground show a higher concentration for the simulation without barriers, this simulation has a linear decreasing of hydrogen concentration with increasing the height for monitor points of concentration. For the simulation with the three tall barriers the concentration increases unlike the other simulations. This may be caused by an increased level of turbulence generated from multiple of barriers compared to one big barrier. The simulations with one and two containers have a decreasing concentration, but a considerably lower decline. The temperature results are illustrated in Figure 6.38 under. The simulation with no barriers has the lowest temperature 30 m from release point and the simulation with two containers on top of each other has the lowest temperature 50 m from release point. The temperatures in all the simulations at 50 m are near the ambient temperature.



Figure 6.38: Simulation results of lowest temperature with release orientation against different barriers.

6.3 Are safety distances for LNG suitable for LH2?

LH2 and LNG have many similar characteristics when it comes to physical and combustion properties. But are the safety standards that are being used today for LNG sufficient for liquid hydrogen? Do the results from the FLACS simulations and the experiments from the FFI-report indicate need for new safety standards for bunkering LH2?

In the safety standard ISO 20519:2017 [17] for bunkering LNG, there is required to do a risk assessment of the bunkering location to determinate if it is acceptable for the bunkering operation to be conducted. This will be important for bunkering of LH2 as well. The risk assessment shall define if the following parameters are acceptable [17]:

- The controlled of area/zone (safety, hazard, etc.) required.
- Acceptable range of sea states, tidal change, currents and weather conditions under which bunkering can take place safely.
- Any requirements applicable to the proposed bunkering location imposed by a competent authority that has jurisdiction over where the bunkering take place.

The purpose of the safety zone is to have control over leaks and spills, ignition sources, that non-essential personal is excluded from this zone and introduction of PPE (personal protective equipment) for essential personal. Estimating safety zones are often based on a quantitative risk analysis (QRA) [40]. To perform a sufficient QRA for a technology with low maturity brings several of challenges. Limited data exist to leak frequencies, and consequences of an accidental leak can be challenging to predict. When discussing the need for a new code for bunkering LH2, the assumptions is based on the physical properties of LH2.

The safety zone is an area that can be exposed for flammable gas in case of accidental release during bunkering operation. Since the MIE for hydrogen is only 0.017 mJ while for methane 0.28 mJ, it will demand more to have the ignition sources under control. The low MIE together with the wide flammability range (4-77 vol%), results in a recommendation to have larger safety zone for LH2 compared to LNG during bunkering operations. The experiments simulated above illustrate concentration profiles for the dispersion clouds. For vertical release with equivalent wind direction together with a high outflow rate, illustrate the concentration profile over the flammable limit to extend up to 80 m from release point. In DNV GL guideline for LNG bunkering facilities [19] it states that: *"Whatever approach is used and whatever result is*

obtained, the safety zone shall extend not less than 10 m around any point of the connected bunker system."

The simulation results from FLACS indicate a need to increase this minimum safety zone for LH2 bunkering to achieve a comparable safety level. The comparison study by Hansen [5] of LH2 and LNG hazard distances when bunkering confirms the need to increase the safety zone for LH2. Due to the LFL-distances for LH2 extend 5 times longer compared to LNG. This implies a need for new standards regarding safety zones during bunkering of liquid hydrogen to obtain the goal of chapter 8 in the IGF code "to provide for suitable systems on board the ship to ensure that bunkering can be conducted without causing danger to persons, the environment or the ship" [11].

Based on the assumptions done for the FLACS simulations, the results should be considered with some uncertainties. Especially, the results near the release point due to the higher amount of deviation. This might be caused by the assumption that the hydrogen is in a cold gas phase right away after the release. The experiments had some measurements that indicated an amount of liquid hydrogen for a small period of time. Due to this, it is not fully possible to confirm all the parameters involved in a release of liquid hydrogen in the FLACS simulations in this thesis. The FLACS results have some limitation due to the simplifications and the disregarded effects of the impact of the pool, flashing inside the pipe, solidify of O₂ and N₂ particles in the surrounding air and the disregarded heat transfer from the surroundings.

7. Conclusions

This thesis investigated whether and to what extent existing regulations, codes and standards (RCS) for bunkering operations involving liquid natural gas (LNG) are applicable for bunkering operations involving LH2.

7.1 Main conclusions

The following conclusions follow from the results and discussion in Chapter 6:

- It is important that new or updated regulations, codes and standards (RCS) for the safe layout, design and operation of bunkering facilities for liquid hydrogen (LH2) account for the specific properties of hydrogen.
- The validation of the CFD tool FLACS against large-scale release and dispersion experiments with LH2 in the open shows sufficiently predictive capabilities of the software to support the investigation of safety distances for LH2 facilities.
- Various parameters influence the simulations, and there is significant uncertainty associated with the simplifying assumptions and the spatial resolution on the computational grid. In particular, wind velocity and direction have strong influence on the extent and duration of the dispersed cloud, and both parameters should be considered during bunkering operations.
- Existing RCS for bunkering operations involving LNG are not directly applicable for bunkering operations involving LH2. The reactivity of hydrogen-air mixtures implies that new or improved RCS for bunkering operations with LH2 should account for the possibility of deflagration-to-detonation-transition (DDT) in the dispersed fuel-air clouds.
- Overall, the safety-related properties of hydrogen and hydrogen systems imply more comprehensive safety measures compared to conventional fuels, including LNG. This includes larger safety zones, where the largest zones correspond to scenarios with a high outflow rate and low wind velocity.

7.2 Suggestions for further work

Various experimental and numerical investigations can be conducted to verify, validate and extend the results from the present study:

- None of the large-scale release and dispersion experiments performed by DNV GL entailed releases with leak and/or wind direction towards the container that represented a

ship, and the experimental setup involved limited congestion or confinement. Hence, further studies should explore more realistic conditions for bunkering operations, including conditions that may result in significant flame acceleration and DDT. Relevant geometrical configurations that could be represented in such studies include the elongated, semi-confined, and often congested space between the ship and the quay (as well as under the quay), gangway and bunkering systems, cable trenches, light poles and instrumentation boxes, forklift trucks and stacks of pallets, containers (especially the space underneath or between containers), etc. It is crucial to eliminate the possibility of localised DDT events that can trigger a detonation in the flammable cloud.

- It is also relevant to explore the effect of heat transfer from LH2 to the surroundings, including the condensation of the ambient air, to improve the understanding of the safety challenges associated with this phenomenon.

It is of vital importance to complete thorough and critical analyses of the RCS for LH2 bunkering operations, including the IGF code and recommended practices from classification societies such as DNV and Lloyds Register. Science-based recommendations for RCS must account for realistic operating conditions, and it is imperative to incorporate lessons learnt from recent accidents [26].

Bibliography

- 1. IEA (2017). World Energy Outlook 2017. International Energy Agency (IEA), Paris.
- International Maritime Organization, Annex 11, Resolution MEPC.304(72), Initial IMO strategy on reduction of GHG emissions from ships, http://www.imo.org/en/OurWork/Environment/PollutionPrevention/AirPollution/Documents/ Resolution%20MEPC.304(72)_E.pdf [accessed 14 November 2018].
- NCE Maritime Cleantech. Norwegian parliament adopts zero-emission regulations in the fjords.
 2018. [Accessed 15 November 2018]. [Internet] [cited 2020-10-26].
- F.G. Aarskog, O.R. Hansen, T. Strømgren, Ø. Ulleberg. Concept risk assessment of a hydrogen driven high speed passenger ferry. Int J Hydrogen Energy. 2020; 45: 1359-1372. DOI: https://doi.org/10.1016/j.ijhydene.2019.05.128
- O.R. Hansen. Liquid hydrogen releases show dense gas behavior. Int J Hydrogen Energy. 2020;45: 1343-1358. DOI: https://doi.org/10.1016/j.ijhydene.2019.09.060
- Lloyd's Register for Ocean Hyway Clustre. Hydrogen and Ammonia Infrastructure. Safety and Risk Information and Guidance, May 2020. Report no: PRJ11100256122r1
- A. Gruber, M.R. Bothienc, A. Ciani, K. Aditya, J.H. Chen, F.A. Williams. Direct Numerical Simulation of hydrogen combustion at auto-ignitive conditions: Ignition, stability and turbulent reaction-front velocity. Combustion and Flame, 2021. DOI: https://doi.org/10.1016/j.combustflame.2021.02.031
- Blue Move Mulighetsstudie for hydrogen produksjon, industri, lagring og distribusjon. Jan 2017. Version 1, [Internet] [cited 2020-11-15]. http://www.nordichydrogenpartnership.com/wp-content/uploads/2017/03/Rapport-KL-2017-01-BM-V1.pdf
- 9. IMO, International Maritime Organisation. [Internet]. 2019 [cited 2020-05-01]. <u>https://www.imo.org/en/About/Conventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-(SOLAS),-1974.aspx</u>
- 10. IMO, International Maritime Organisation. [Internet]. 2019 [cited 2020-05-01]. https://www.imo.org/en/About/HistoryOfIMO/Pages/Default.aspx
- IGF Code (2016). International Code of Safety for Ships using Gases or other Low-flashpoint Fuels (IGF Code). Adopted on 11 June 2015.
- Eckhoff, R.K. Explosion Hazards in The Process Industries. 2nd ed. Amsterdam: Elsevier; 2016.
 559 p.

- 13. A.A. Konnova, A. Mohammad, V.R. Kishore, N.I. Kim, C. Prathap , S. Kumar. A comprehensive review of measurements and data analysis of laminar burning velocities for various fuel+air mixtures. Progress in Energy and Combustion Science. 2018. DOI: https://doi.org/10.1016/j.pecs.2018.05.003
- 14. T. Skjold. On the strength of knowledge in risk assessments for hydrogen systems. 2020. 13th International Symposium on Hazards, Prevention, and Mitigation of Industrial Explosions Braunschweig, GERMANY.
- IMO (2013). Guidelines for the approval of alternatives and equivalents as provided for in various IMO instruments. MSC.1/Circ.1455, IMO, London.
- 16. T. Skjold, H. Hisken et al., Blind-prediction: Estimating the consequences of vented hydrogen deflagrations for inhomogeneous mixtures in 20-foot ISO containers. Journal of Loss Prevention in the Process Industries. 2019. DOI: <u>https://doi.org/10.1016/j.jlp.2019.06.013</u>
- ISO 20519:2017. Ships and marine technology Specification for bunkering of liquefied natural gas fuelled vessels. The International Standards Organization; February 2017.
- Gas a marine fuel recommendations of controlled zones during LNG bunkering. Version 1.0, Society for Gas as a Marine Fuel, May 2018.
- 19. DNV GL. 2014b. Recommended practice DNVGL-RP0006:2014-01: development and operation of liquefied natural gas bunkering facilities. Oslo: DNV.
- 20. J. Aaneby, T. Gjesdal, Ø.Voie. Large scale leakage of liquid hydrogen (LH2) tests related to bunkering and maritime use of liquid hydrogen. Norwegian Defence Research Establishment (FFI), Jan 2021.
- IEA (2019). The future of hydrogen seizing today's opportunities. International Energy Agency (IEA), June 2019.
- 22. Energi og klima. Elektriske bilferger i Norge. . [Internet]. 2021 [cited 2020-05-18]. https://energiogklima.no/elektriske-bilferger-i-norge/
- 23. L.E. Klebanoff, J.W. Pratt, C.B. LaFleur. Comparison of the safety-related physical and combustion properties of liquid hydrogen and liquid natural gas in the context of the SF-BREEZE high-speed fuel-cell ferry. Int J Hydrogen Energy. 2017; 42: 757-774. DOI: http://dx.doi.org/10.1016/j.ijhydene.2016.11.024
- 24. D.K Pritchard, W.M Rattigan. HSE. Hazards of Liquid Hydrogen. RR796-research Report.
- 25. E.S. Oran, G. Chamberlain, A. Pekalski. Mechanisms and occurrence of detonations in vapor cloud explosions. Process in Energy and Combustion Science. 2019. DOI: <u>https://doi.org/10.1016/j.pecs.2019.100804</u>

- 26. Store Norske Leksikon (SNL). Hydrogensprøhet [Internet]. 2018 Jan [cited 2020-11-09]. https://snl.no/hydrogenspr%C3%B8het
- 27. D.A. Crowl, Y.-D. Jo. The hazards and risks of hydrogen. (2017) Journal of Loss Prevention in the Process Industries, 20: 158-164. DOI: https://doi.org/10.1016/j.jlp.2007.02.002
- 28. Skjold, T., Pedersen, H.H., Narasimhamurthy, V.D., Lakshmipathy, S., Pesch, L., Atanga, G.F., Folusiak, M., Bernard, L., Siccama, D. & Storvik, I.E. (2014). Pragmatic modelling of industrial explosions in complex geometries: review of the state-of-the-art and prospects for the future. Zel'dovich Memorial: Accomplishments in the combustion Science in the last decade, Volume 1: 70-74. Edited by A.A. Borisov & S.M. Frolov. ISBN 978-5-94588-156-3. Torus Press, Moscow.
- 29. Skjold, T., Pedersen, H.H., Bernard, L., Middha, P., Narasimhamurthy, V.D., Landvik, T., Lea, T & Pesch, L. (2013). A matter of life and death: validating, qualifying and documenting models for simulating flow-related accident scenarios in the process industry. Fourteenth International Symposium on Loss Prevention and Safety Promotion in the Process Industries, Florence, 12-15 May 2013, published in Chemical Engineering Transactions, 31: 187-192. ISBN 978-88-95608-22-8, DOI: <u>http://dx.doi.org/10.3303/CET1331032</u>
- Middha, P.; Ichard, M.; Arntzen, B. J. (2011) Validation of CFD modelling of LH2 spread and evaporation against large-scale spill experiments, International Journal of Hydrogen Energy 36(3), pp. 2620-2627. DOI: <u>http://dx.doi.org/10.1016/j.ijhydene.2010.03.122</u>
- 31. Safety manual on LNG bunkering procedures for the Port of Helsinki. SSPA Sweden AB, Jun 2017. Report no: RE20167730-01-00-D. [Internet] [cited 2020-11-11]. https://www.portofhelsinki.fi/sites/default/files/attachments/Port%20of%20Helsinki_%20Safet y%20manual%20on%20LNG%20bunkering.pdf
- 32. R.D. Witcofski, J.E. Chirivella (NASA). Experimental and analytical analyses of the mechanisms governing the dispersion of flammable clouds formed by liquid hydrogen spills. 1984; 9(5):425-435.
- 33. U.S. Department of energy. An Approach To Liquefied Natural Gas (LNG) Safety And Environmental Control Research. 1978. DOE/EV-0002.[Internet] [cited 2020-11-23].
- 34. J.E. Hall, P. Hooker, D. Willough. Ignited releases of liquid hydrogen: Safety considerations of thermal and overpressure effects. Int J Hydrogen Energy. 2014; 39: 20547-20553. DOI: http://dx.doi.org/10.1016/j.ijhydene.2014.05.141
- 35. Gexcon AS. FLACS v20.1 User's Manual. Gexcon AS, 2020.

- 36. J.D. Anderson. Computational fluid dynamics: The basics with applications. McGraw-Hill series in mechanical engineering. McGraw-Hill, New York;1995. 547 p.
- 37. W.L McCabe. Unit operations of chemical engineering. 7th edition. Boston: McGrave-Hill education; 2005. 1140 p.
- J. Warnatz. Combustion: Physical and Chemical, fundamentals, Modeling and Simulation, Experiments, Pollutant Formation. 4th edition. Berlin: Springer; 2006. 378 p.
- 39. P.Leung, C.H Gibson. Turbulence and Fossil Turbulence in Oceans and Lakes. Chinese Journal of Oceanology and Limnology. (2004)
- 40. S. Lees' Loss Prevention in the Process Industries: Hazard Identification, Assessment and Control. Elsevier Science, Oxford, United States, 4th edition, 2012.

Appendix A: Coordinates for monitor points

Oxygen sensor	Thermocouple	X (m)	Y (m)	Z (m)
-	TT49	21.213	21.213	0
OC_01	TT50	21.213	21.213	0.100
OC_02	TT51	21.213	21.213	1.000
OC_03	TT52	21.213	21.213	1.800
-	TT53	27.716	11.481	0
OC_04	TT54	27.716	11.481	0.100
OC_05	TT55	27.716	11.481	1.000
OC_06	TT56	27.716	11.481	1.800
-	TT57	30.000	0	0
OC_07	TT58	30.000	0	0.100
OC_08	TT59	30.000	0	1.000
OC_09	TT60	30.000	0	1.800
-	TT61	27.716	-11.481	0
OC_10	TT62	27.716	-11.481	0.100
OC_11	TT63	27.716	-11.481	1.000
OC_12	TT64	27.716	-11.481	1.800
-	TT65	21.213	-21.213	0
OC_13	TT66	21.213	-21.213	0.100
OC_14	TT67	21.213	-21.213	1.000
OC_15	TT68	21.213	-21.213	1.800
-	TT69	46.194	19.134	0
OC_16	TT70	46.194	19.134	0.100
OC_17	TT71	46.194	19.134	1.000
OC_18	TT72	46.194	19.134	1.800
-	TT73	50.000	0	0
OC_19	TT74	50.000	0	0.100
OC_20	TT75	50.000	0	1.000
OC_21	TT76	50.000	0	1.800
-	TT77	46.194	-19.134	0
OC_22	TT78	46.194	-19.134	0.100
OC_23	TT79	46.194	-19.134	1.000
OC_24	TT80	46.194	-19.134	1.800
-	TT81	98.481	17.365	0
OC_25	TT82	98.481	17.365	0.100
OC_26	TT83	98.481	17.365	1.000
OC_27	TT84	98.481	17.365	1.800
-	TT85	98.481	-17.365	0
OC_28	TT86	98.481	-17.365	0.100
OC_29	TT87	98.481	-17.365	1.000
OC_30	TT88	98.481	-17.365	1.800

Table A.1: Coordinates for monitor points, relative to the release point for tests 1, 3 and 7.

Oxygen sensor	Thermocouple	X (m)	Y (m)	Z (m)
	TT49	21.213	21.213	0
OC_01	TT50	21.213	21.213	0.100
OC_02	TT51	21.213	21.213	1.000
OC_03	TT52	21.213	21.213	1800
	TT53	27.716	11.481	0
OC_04	TT54	27.716	11.481	0.100
OC_05	TT55	27.716	11.481	1.000
OC_06	TT56	27.716	11.481	1.800
	TT57	30.000	0	0
OC_07	TT58	30.000	0	0.100
OC_08	TT59	30.000	0	1.000
OC_09	TT60	30.000	0	1.800
	TT61	27.716	-11.481	0
OC_10	TT62	27.716	-11.481	0.100
OC_11	TT63	27.716	-11.481	1.000
OC_12	TT64	27.716	-11.481	1.800
	TT65	21.213	-21.213	0
OC_13	TT66	21.213	-21.213	0.100
OC_14	TT67	21.213	-21.213	1.000
OC_15	TT68	21.213	-21.213	1.800
	TT74	-27.716	11.481	0
OC_16	TT75	-27.716	11.481	0.100
OC_17	TT76	-27.716	11.481	1.000
OC_18	TT77	-27.716	11.481	1.800
	TT78	-30.000	0	0
OC_19	TT79	-30.000	0	0.100
OC_20	TT80	-30.000	0	1.000
OC_21	TT81	-30.000	0	1.800
	TT82	-27.716	-11.481	0
OC_22	TT83	-27.716	-11.481	0.100
OC_23	TT84	-27.716	-11.481	1.000
OC_24	TT85	-27.716	-11.481	1.800
	TT86	0.800		0
OC_25	TT87	0.800		0.100
OC_26	TT88	0.800		1.000
OC_27	TT89	0.800		1.800
	TT89	6.700	9.000	0
OC_28	TT90	6.700	9.000	0.100
OC_29	TT91	6.700	9.000	1.000
OC_30	TT92	6.700	9.000	1.800

Table A.2: Coordinates for monitor points, relative to the release point for Test 2.

Appendix B – Results from experiments and simulations

	Lowest Temperature, Radius 30 m	Lowest Temperature, Radius 50 m and 100 m	Highest H2- Concentration, 0.1 m high Oxygen Sensor	Highest H2- Concentration, 1.0 m high Oxygen Sensor	Highest H2- Concentration, 1.8 m high Oxygen Sensor
Test 1					
Experiment	-2.9 °C	-0.5 °C	0.9 vol%	1.8 vol%	1.5 vol%
FLACS	-7 °C	-1.2 °C	3.4 vol%	2.2 vol%	1.8 vol %
Test 3					
Experiment	-8 °C	-0.4 °C	6.4 vol%	8.6 vol%	5.8 vol%
FLACS	-17.2 °C	-2 °C	8.7 vol%	6.9 vol%	4.9 vol %
Test 4					
Experiment	-26.8 °C	-10.9 °C	17.2 vol%	16.8 vol%	11.9 vol%
FLACS	-15 °C	-10.4 °C	8.2 vol%	6.4 vol%	4.7 vol%
Test 5					
Experiment	-8.5 °C	-1.5 °C	6.2 vol%	7.7 vol%	7.6 vol%
FLACS	-17.3 °C	-4.8 °C	8.8 vol%	7.5 vol%	7.2 vol%
Test 6					
Experiment	-25.7 °C	-2 °C	22 vol%	31 vol%	22 vol%
FLACS	-16 °C	-2.7 °C	8 vol%	8 vol%	6.6 vol%
Test 7					
Experiment	-0.2 °C	1.5 °C	2.5 vol%	2.7 vol%	2.2 vol%
FLACS	-2.6 °C	-1.0 °C	2.5 vol%	1.7 vol%	1.1 vol%

Table B.1: *Comparison of temperatures and H2-Concentrations measured in Test 1, Test 3 - Test7 with data from simulations.*

Table B.2: Comparison of temperatures	and H2-Concentrations	measured in	Test 2 with data
from simulations.			

	Lowest Temp., Radius 30 m (West)	Lowest Temp., Radius 30 m (East)	Lowest Temp., Front of ISO container	Highest H2- Concentration , Radius 30m (west)	Highest H2- Concentration , Radius 30m (East)	Highest H2- Concentration , Front of ISO container
Experiment	-7.6 °C	1 °C	1 °C	4.2 vol%	0 vol%	0 vol%
FLACS	-20 °C	1.2 °C	1.4 °C	9.4 vol%	0 vol%	0 vol%

Table B.3: Simulation results from varying Pasquill classes.

Pasquill Class	Α	В	С	D	Е	F
Highest H ₂ -concentration	17.7 vol%	14 vol%	14.1 vol%	11.3 vol%	10.2 vol%	8.8 vol%
Lowest temperature	-37.3 °C	-28.5 °C	-28.8 °C	-22.4 °C	-19.8 °C	-17.3 °C

Wind Velocity	0.5 m/s	1 m/s	5 m/s	10 m/s	15 m/s	20 m/s	25	30
							m/s	m/s
Highest	7.9	9	11	10	0.84	0.7	0.6	0.5
H ₂ -concentration	vol%	vol%	vol%	vol%	vol%	vol%	vol%	vol%
Lowest temperature	-15.5 °C	-17.9 °C	-22.6 °C	-20.3 °C	0.97 °C	1.3 °C	1.5 °C	1.7 °C

 Table B.4: Simulation results from varying different wind velocities

 Table B.5: Simulation results from varying grid cell size

	Lowest Temperature,	Lowest Temperature, Radius 50 m	Highest H2- Concentration, 0.1 m high	Highest H2- Concentration, 1.0 m high	Highest H2- Concentration, 1.8 m high
Using data form Test 4	Radius 30 m	and 100 m	Oxygen Sensor	Oxygen Sensor	Oxygen Sensor
Experiment	-26.8 °C	-10.9 °C	17.2 vol%	16.8 vol%	11.9 vol%
FLACS					
Grid Cell Size					
0.30 m	-15 °C	-10.4 °C	8.2 vol%	6.4 vol%	4.7 vol%
0.20 m	-15.5 °C	-10.0 °C	8.1 vol%	6.4 vol%	4.6 vol%
0.25 m	-16.7 °C	-8.9 °C	8.6 vol%	6.9 vol%	5.0 vol%
0.35 m	-63.3 °C	-2.5 °C	28.7 vol%	25.5 vol%	10.8 vol%
0.40 m	-29.0 °C	-1.5 °C	13.9 vol%	11.5 vol%	7.4 vol%

 Table B.6: Simulation results from varying initial/outdoor temperature

Using data form Test 4	Lowest Temperature, Radius 30 m	Lowest Temperature, Radius 50 m and 100 m	Highest H2- Concentration, 0.1 m high Oxygen sensor	Highest H2- Concentration, 1.0 m high Oxygen sensor	Highest H2- Concentration, 1.8 m high Oxygen sensor
Experiment	-26.8 °C	-10.9 °C	17.2 vol%	16.8 vol%	11.9 vol%
FLACS, Initial temperature					
3.3 °C	-15 °C	-10.4 °C	8.2 vol%	6.4 vol%	4.7 vol%
10 °C	-11.6 °C	-4.5 °C	9 vol%	7.5 vol%	5.7 vol%
20 °C	-3.3 °C	4.48 °C	9.38 vol%	7.8 vol%	5.8 vol%
30 °C	6.7 °C	13.78 °C	9.03 vol%	7.15 vol%	5.17 vol%
-5 °C	-25.3 °C	17 °C	9.06vol%	7.5 vol%	5.5 vol%
-10 °C	-30.2 °C	-21.78 °C	9.20 vol%	7.5vol%	5.5 vol%
-15 °C	-36 °C	-24.9 °C	9.77 vol%	7.9 vol%	5.64 vol%
-20 °C	-39.1 °C	-29.2 °C	9.11 vol%	7.2 vol%	5.1 vol%