

State of the Art of Hydrogen Storage and Utilization for Marine Applications

Matteo Passalacqua (matteo.passalacqua@edu.unige.it)

Alberto Traverso

Idrogeno e Tecnologie per la Generazione Energetica e la Propulsione nei Trasporti Green

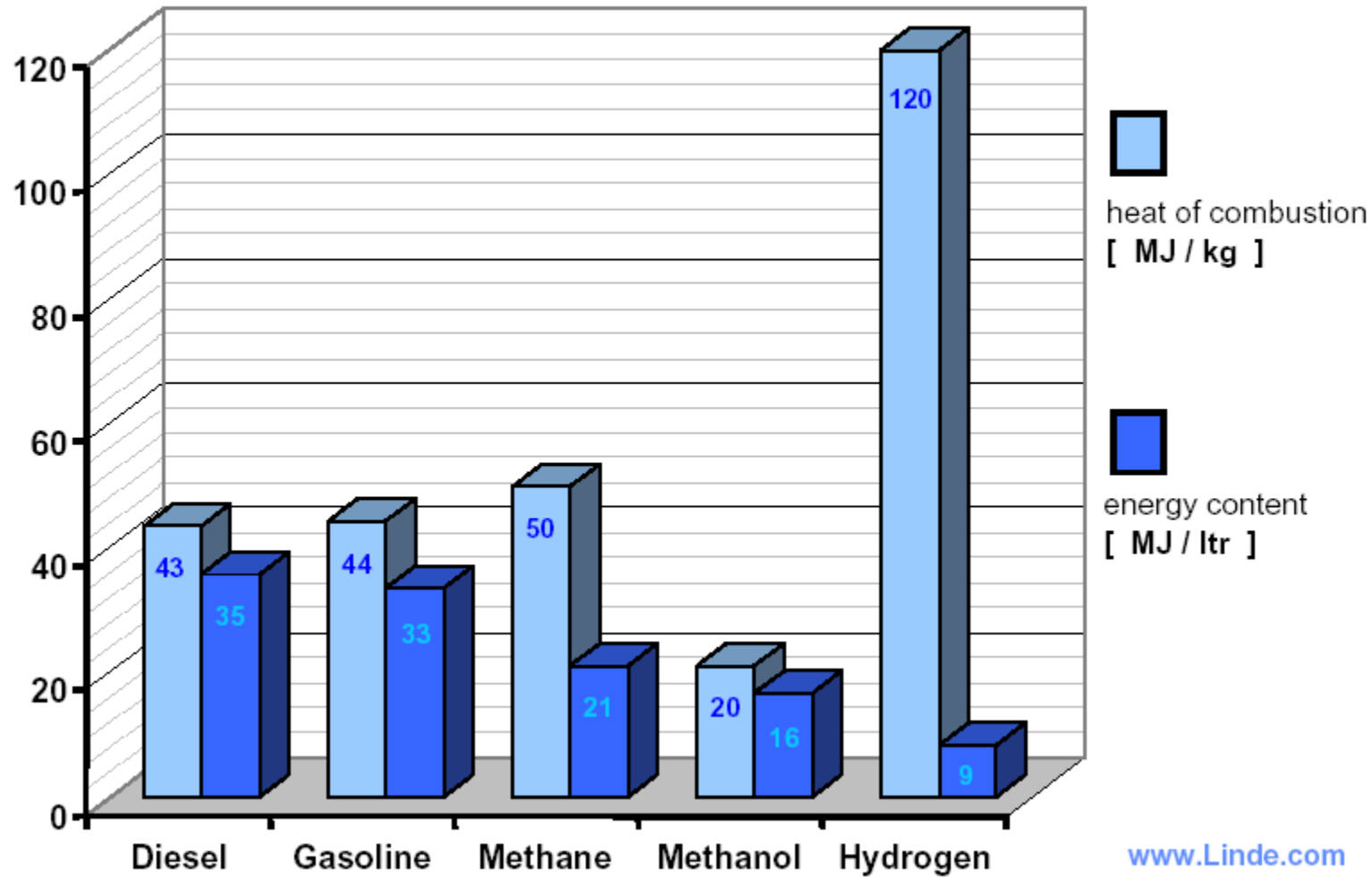
Genova, 25/01/2024

Table of contents

- Comparison of alternative marine fuel
- Hydrogen storage in marine environment
- Liquid hydrogen (LH₂) as marine fuel
- The problem of boil-off gas (BOG) and its treatment

Hydrogen as Alternative Fuel

comparison of fuels - heat of combustion / energy content -



Linde Gas AG
© 2001 LINDE

wolf, sde, 1760, Fach 60
...pres\fundus\fundus_enppt

	NH ₃ (-33°C)	LH ₂ (-253°C)	MDO	LNG (-162°C)	LPG	MeOH	Biofuels (HVO)
Storage Density [kg/m³]	682	71	850	470	537	790	850 - 900
Lower Heating Value [MJ/kg]	18,8	120	44	48,6	45,5	19,8	37,8
Autoignition Temperature [°C]	630 - 650	580	225	537	410 - 580	470	204
Toxicity	Toxic	Not Toxic	Not Toxic	Not Toxic	Not Toxic	Toxic	Not Toxic
Net Volumetric Energy Density [MJ/m³]	12822	8540	35700	21840	24433	15641	34020
Gross Volumetric Energy Density [MJ/m³]	≈ 10500	≈ 6400	-	≈ 13000	≈ 18500	≈ 14000	-
Flammability Limit [%vol]	15 - 28	4 - 75	1,8 - 8,2	4 - 15	1,8 - 10	6,7 - 36	0,6 - 7,5
Converters (TRL ≥ 5)	- ICE - FC - GT	- ICE - FC - GT	- ICE - GT	- ICE - FC - GT	- ICE - GT	- ICE - FC	- ICE

Compared to current standard (MDO)		NH ₃ (-33°C)	LH ₂ (-253°C)	LNG (-162°C)	LPG	MeOH	Biofuels (HVO)
	Net	≈ 36%	≈ 24%	≈ 64%	≈ 68%	≈ 44%	≈ 95%
	Gross	≈ 28%	≈ 18%	≈ 36%	≈ 52%	≈ 39%	-

Table of contents

- Comparison of alternative marine fuel
- **Hydrogen storage in marine environment**
- Liquid hydrogen (LH₂) as marine fuel
- The problem of boil-off gas (BOG) and its treatment

Overview

Table 4. Storage methods overview.

Method	Gravimetric Energy Density (wt %)	Volumetric Energy Density (MJ/L)	Temperature (K)	Pressure (barg)	Remarks
Compressed	5.7	4.9	293	700	Current industry standard
Liquid	7.5	6.4	20	0	Boil-off constitutes major disadvantage
Cold/cryo compressed	5.4	4.0	40–80	300	Boil-off constitutes major disadvantage
MOF	4.5	7.2	78	20–100	Attractive densities only at very low temperatures.
Carbon nanostructures	2.0	5.0	298	100	Volumetric density based on powder density of 2.1 g/mL and 2.0 wt % storage capacity.
Metal hydrides	7.6	13.2	260–425	20	Requires thermal management system.
Metal borohydrides	14.9–18.5	9.8–17.6	130	105	Low temperature, high pressure thermal management required
Kubas-type	10.5	23.6	293	120	
LOHC	8.5	7	293	0	Highly endo/exothermal requires processing plant and catalyst. Not suitable for mobility
Chemical	15.5	11.5	298	10	Requires SOFC fuel cell.

Rivard , Trudeau, Zaghib, «Hydrogen storage for mobility: A review», Materials, 2019

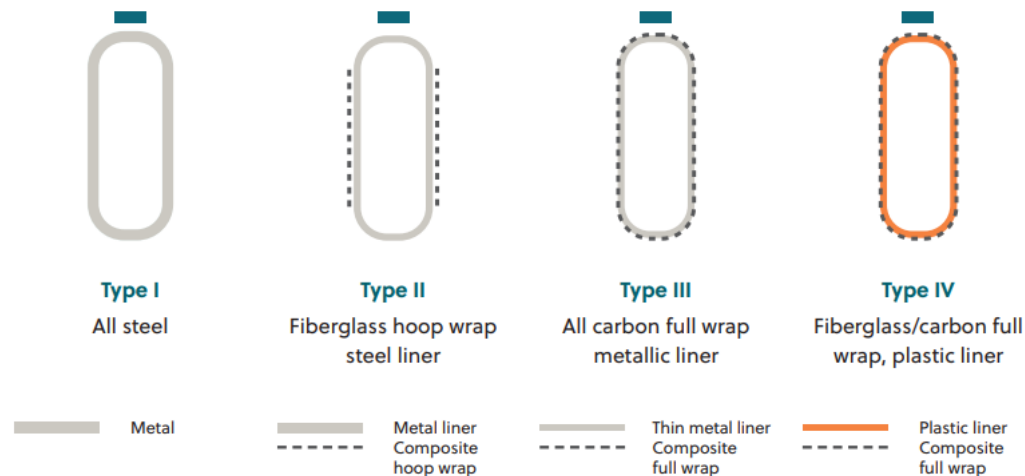
CGH₂ as marine fuel

- Zero-carbon emission fuel
- High mass-LHV compared to any other fuel
- H₂ may be exploited in different converters with high efficiencies

Drawbacks:

- Low storage energy density w.r.t. liquefied hydrogen
- Stricter safety concerns

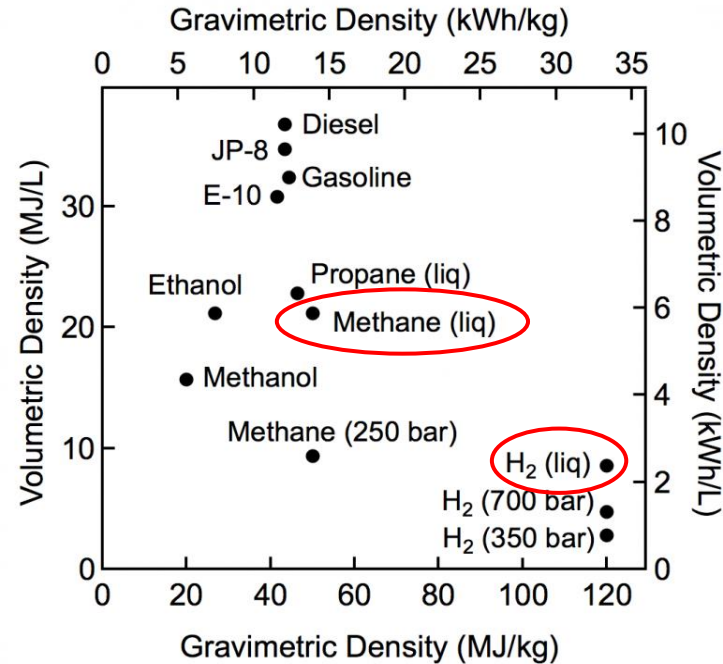
Types of high-pressure cylinders



Fuel	Stored density [kg/m ³]	Energy density [MJ/m ³]
MDO	830	35000
CGH ₂ (350 bar)	23,7	2844
CGH ₂ (700 bar)	39,7	4768
LH ₂	71	8540
LNG	430	21400

LH₂ as marine fuel

Liquid storage guarantees the highest energy density for physical based H₂ storage



- Major challenges:
 - Efficient cryogenic storage
 - Regasification and feeding system to the prime mover
 - Stricter safety concerns



First Liquid Hydrogen tanker, KHI *Suiso Frontier*, operative



First Liquid Hydrogen powered ferry, *Norled Hydra MF*, operative

Towards LH₂ through LNG experience

Property	LH ₂ VS LNG	Comment
Reactivity with materials	LNG	Higher reactivity. H ₂ requires high quality materials
Heat capacity	LH ₂	LH ₂ has higher heat capacity, advantageous in liquid storage
Heat flux from surroundings	LNG	Consequence of lower temperatures (provided that insulation is equal)
Flammability range in air	LNG	Flammable conditions are more easily formed with hydrogen
Ignition energy	LNG	<u>Hydrogen clouds are more easily ignited than NG clouds</u>
Ignition temperature	LNG/O	Natural gas has slightly higher ignition temperature
Liquid phase ΔT in range 1-10 bar	LNG	13 °C vs. 30 °C. Requires more efficient control of heat leakage
Laminar flame speed in air	LNG	<u>Higher for hydrogen, i.e., greater risk of spreading fire</u>
Dense phase behaviour of leakages	LH ₂ /O	Similar behaviour. Both have density higher than air at near condensation temperature, but hydrogen tends to escape faster

Nerheim, Aesøy and Holmeset, "Hydrogen as maritime fuel – can experiences with LNG be transferred to hydrogen systems?", Journal of Maritime Science and Engineering, 2021

Table of contents

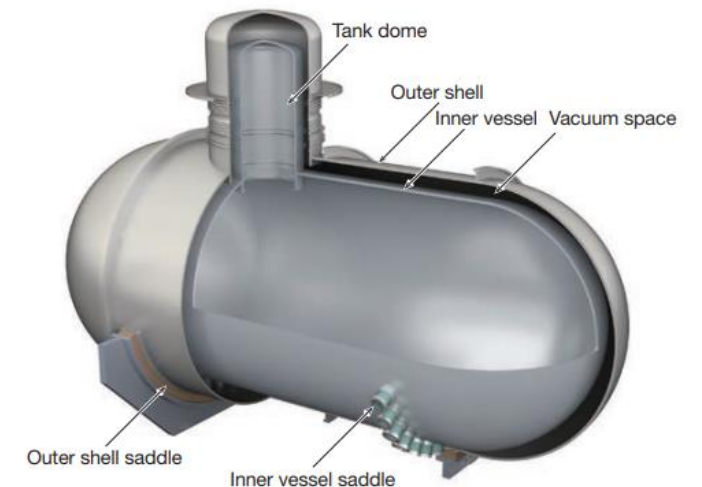
- Comparison of alternative marine fuel
- Hydrogen storage in marine environment
- **Liquid hydrogen (LH₂) as marine fuel**
- The problem of boil-off gas (BOG) and its treatment

The Suiso Frontier and the HySTRA project

The *Suiso Frontier*, carries 1250 m³ (~90 tons) LH₂ between Kobe (JAP) and Hastings (AUS) as part of the HySTRA International Project

The cryo vessel and the loading/unloading terminals are located in the airport island (8 km away from the commercial port)

In December, A delegation of TPG visited the storage site at Kobe port



The Norled Hydra

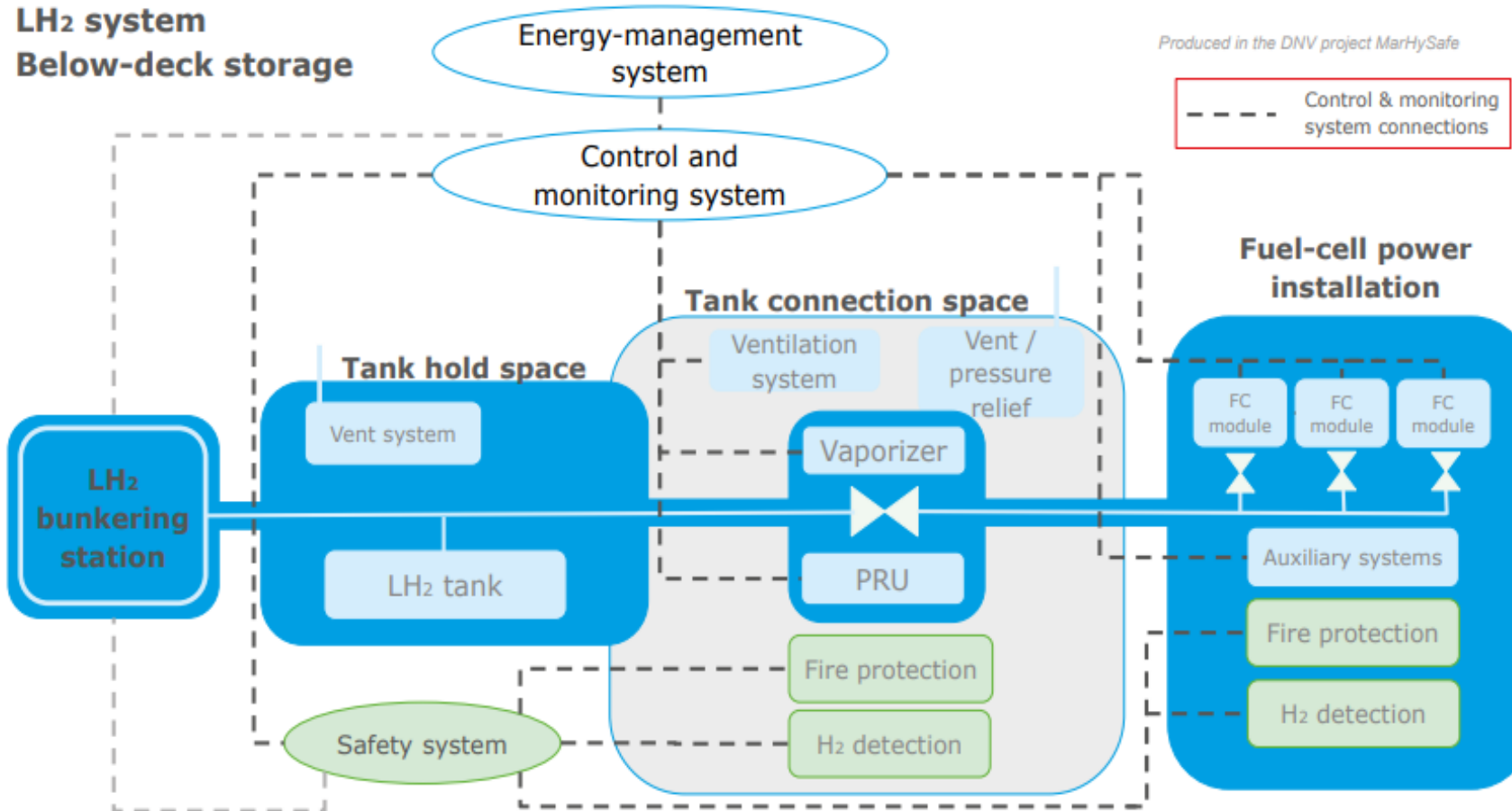
The first (and up to the present only) LH₂ powered ship is a short-sea ferry in service among the norwegian southern fjords



Liquid hydrogen is stored in a cylindrical tank located on the open deck for safety reasons

The fuel is supplied via insulated truck trailer

Handling systems layout - 1



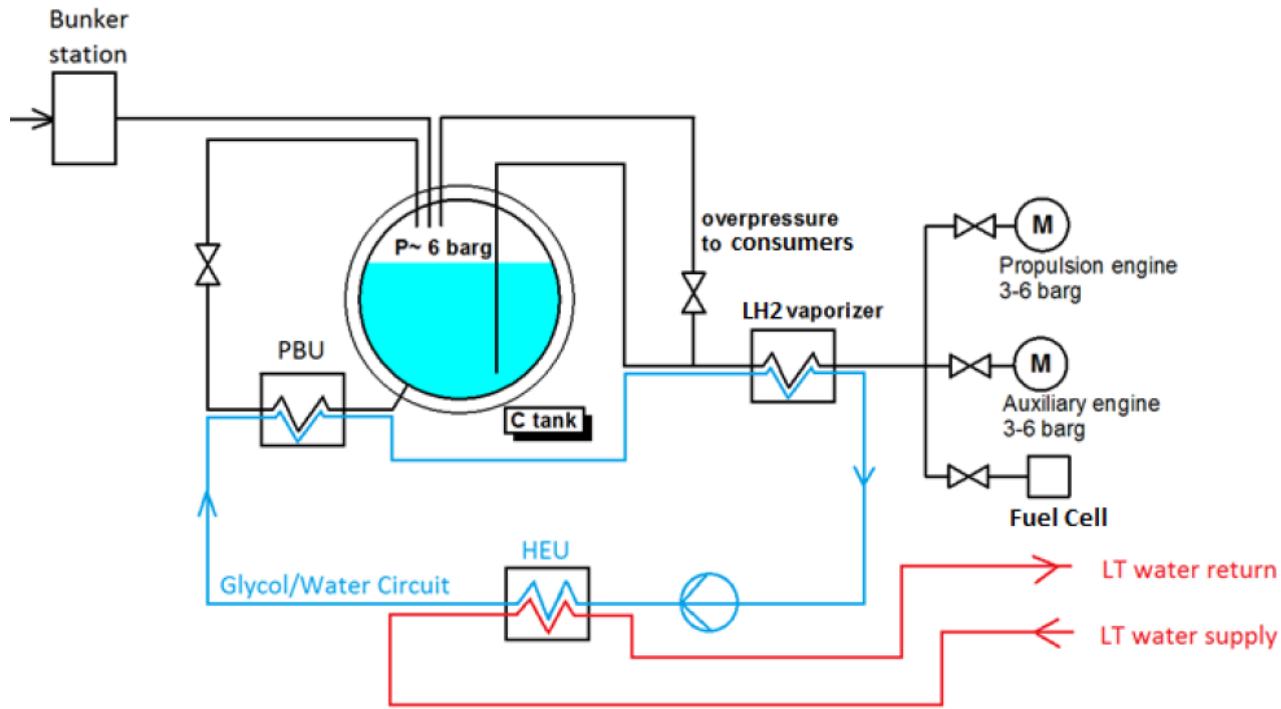
Current safety recommendations discourage below-deck storage of hydrogen

However, DNV has formulated a conceptual LH₂ sub-deck handling system layout in the scope of MarHySafe project

This should enhance LH₂ uptake as alternative fuel

DNV, "Handbook for Hydrogen-fuelled Vessels", Deliverable, MarHySafe project, 2021

Handling systems layout - 2



Scarce insight is available on the topic due to the lack of market-ready solutions. A couple of them are reported hereby:

- MAN Energy Solutions has a marine-ready LH₂ engine feed system (figure)
- Linde has a product for automotive refueling stations (from LH₂ to high pressure hydrogen)
- Wartsila has developed an onboard LNG reforming system to produce hydrogen and separate CO₂

Besides, several research-scale solutions or prototypes exist

MAN Energy Solutions/MAN Cryo, "LH₂ Marine Power Pack – Hydrogen Power Pack for Passenger Vessels", 2021

Table of contents

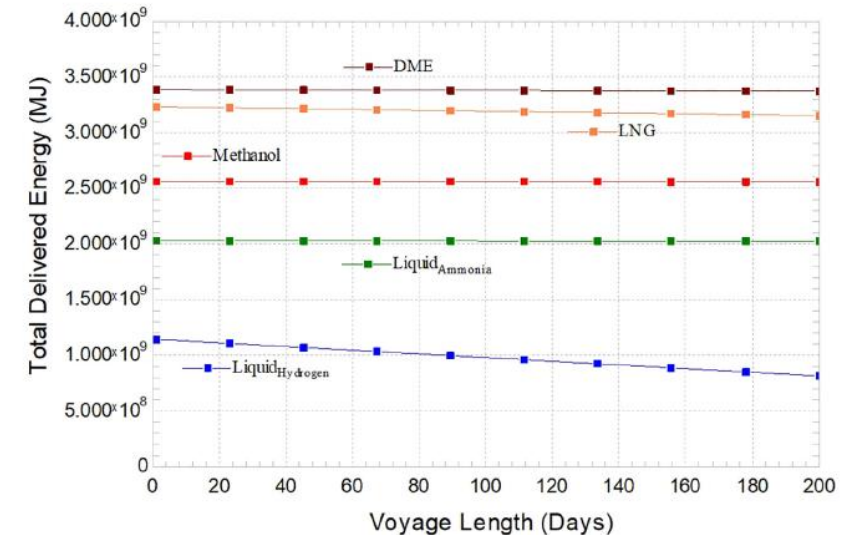
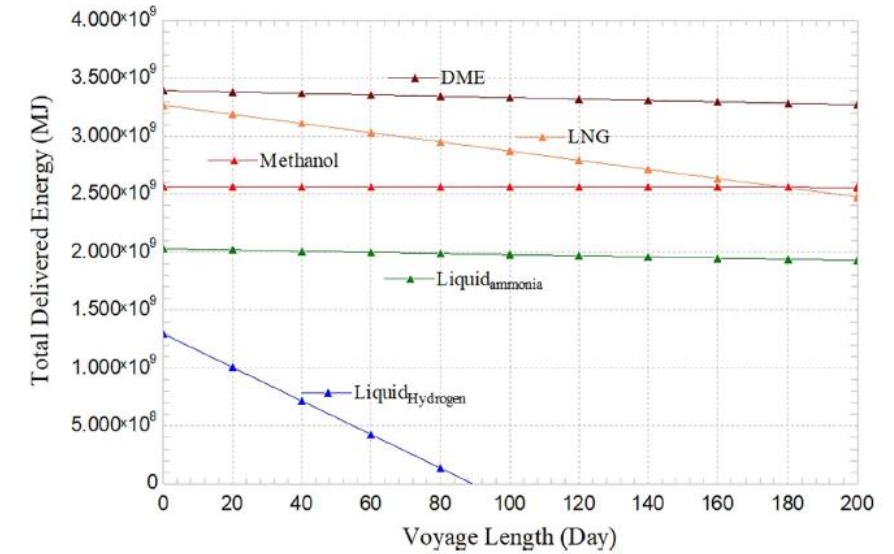
- Comparison of alternative marine fuel
- Hydrogen storage in marine environment
- Liquid hydrogen (LH₂) as marine fuel
- The problem of boil-off gas (BOG) and its treatment

The problem of boil-off gas (BOG) - 1

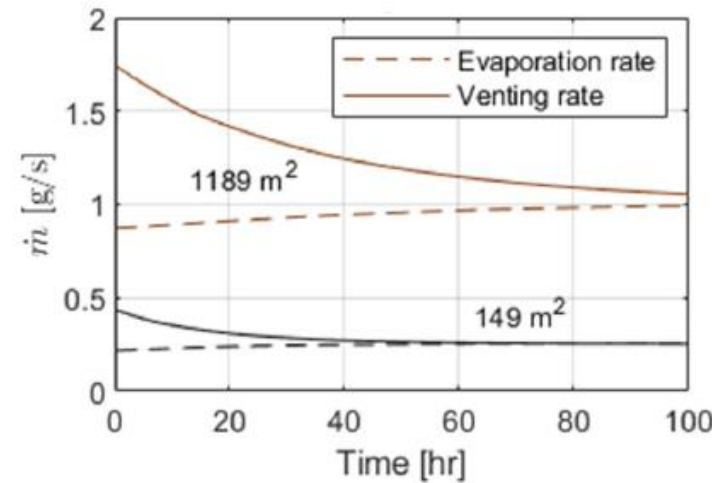
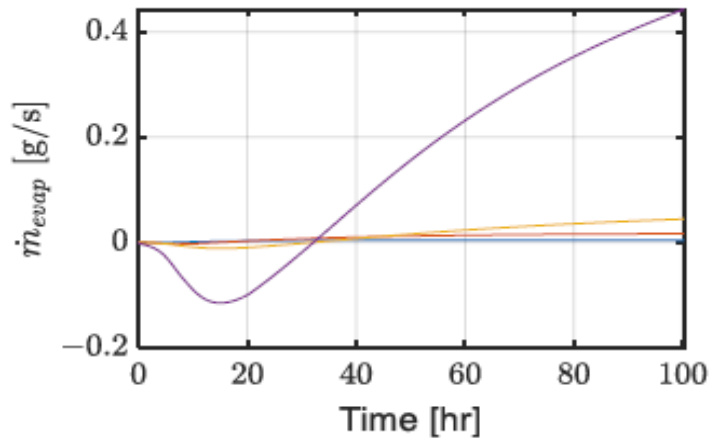
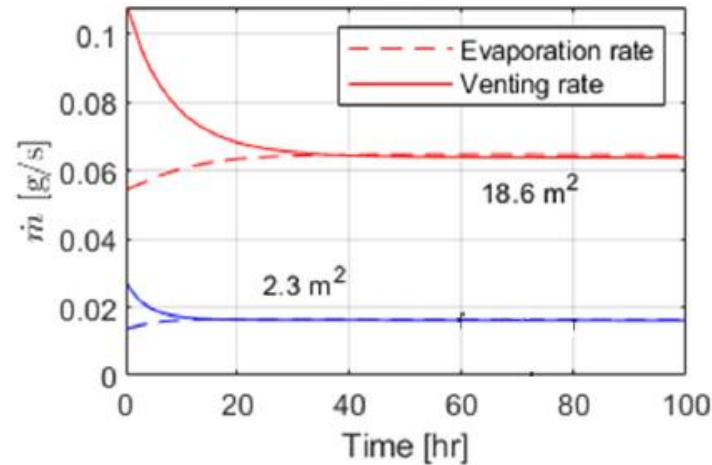
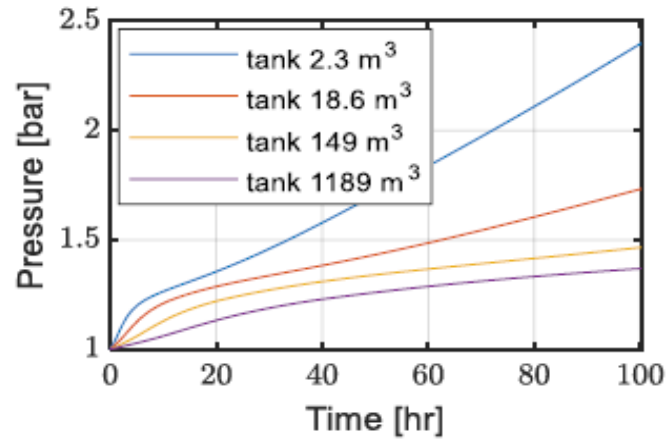
The total energy decreases due to the boil off: hence the cruciality of handling the evaporated BOG.

As shown, saturation temperature (and consequently the main parameter that drives the BOG rate) cannot be significantly increased by pressurizing the tank

Hydrogen		Natural Gas	
Pressure [bar]	Temperature [°C]	Pressure [bar]	Temperature [°C]
1	-252,8	1	-161,6
6	-244,9	6	-134,4
10	-241,7	10	-124
12	-240,5	12	-119,9
		20	-107,3
		30	-95,8
		40	-87



The problem of boil-off gas (BOG) - 2



As expected, the size of the tank is the most influential parameter

On such parameter depend:

- Exchange surface extension
- System's thermal capacity
- System's dynamics

Matveev and Leachmann, "The effect of liquid hydrogen tank size on self-pressurization and constant-pressure venting", Hydrogen, 2023

Future steps for marine green cryo-fuel

*Development
of a solid
hydrogen
market*

Social/economic

*Development of
maritime safety
regulations*

*Technological
transfer from
LNG knowlege*

Technologic

*Technology
transfer from
aerospace
sector*

Bibliography

SEA_LNG-DNV-GL, *Comparison-of-alternative-Marine-Fuels*. Website accessed 12-2023

Linde Gas AG, 2021

Piccardo S., *"Liquid hydrogen as fuel"*, SUPEHR-19 Conference, Savona - IT

MAN Cryo, *"LH₂ Marine Power Pack – Hydrogen Power Pack for Passenger Vessels"*, 2021

A. Valera-Medina, H Xiao, M Owen-Jones c, W.I.F. David, P.J. Bowen, *"Ammonia for power"*, Progress in Energy and Combustion Science, 2018

Piccardo S., *"Liquid hydrogen as fuel"*, SUPEHR-19 Conference, Savona, 2019

Rivard , Trudeau, Zaghbi, *"Hydrogen storage for mobility: A review"*, Materials, 2019

Song, Tinoco et al, *"A comparative study on energy efficiency of the maritime supply chains for liquefied hydrogen, ammonia, methanol and natural gas"*, Carbon Capture Science and Technology, 2022

Duang, Xue, Gong, Tang, *"A thermal non-equilibrium model for predicting LNG boil-off in storage tanks incorporating natural convection effect"*, Energy, 2021

Kochunni, Chowdhuri, *"Concept and evaluation of energy-efficient boil-off gas reliquefiers in LNG carrier ships propelled by dual-fuel engines"*, Energy Conversion and Management, 2021

Chang, *"Thermodynamic design of hydrogen liquefaction systems with helium or neon reverse Brayton refrigerator"*, Cryogenics, 2018

Kwak, Heo et al., *"Energy-efficient design and optimization of boil-off gas (BOG) re-liquefaction process for liquefied natural gas (LNG)-fuelled ship"*, Energy, 2018

Zhang, Lior, *"A novel near-zero CO₂ emission thermal cycle with LNG cryogenic exergy utilization"*, Energy, 2007

UniGe



State of the Art of Hydrogen Storage and Utilization for Marine Applications

Matteo Passalacqua