Exploring the potential of LOHC for powering ships

Van Bogaert Elian

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Promotor: Guido Delvaux
Copromotor: Patrice Perreault

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Foreword

This thesis deals with LOHC (Liquid Organic Hydrogen Carriers) and the surrounding infrastructure required to power ships and establish a supply chain.
I chose this topic after writing the bachelor scription “Ammonia as a carrier of hydrogen on board of ships”. A lot more was left to explore in the interesting field of alternative fuels. A search for an industrial partner eventually led me to Prof. Patrice Perreault, who introduced me to the concept of LOHC and Hydrogenious LOHC Technologies. The company showed their interest in a thesis on liquid organic hydrogen carriers from a maritime perspective.

I want to thank my promotor Guido Delvaux for his time, and shared interest in this topic. His perspective, knowledge and comments helped me to produce this work.
I also want to thank Patrice Perreault for his time, effort, opinions, and perspective to realise -this thesis.

Abstract

The energy transition is a very hot topic. This can create an information overload.
For this reason, the first chapters create an overview and compare different energy carriers/ fuels.

This thesis explores the requirements to supply hydrogen via *LOHC (*Liquid Organic Hydrogen Carriers). One of the few hydrogen storage and transport systems where the carrier can be reused.
The goal is to study the needs for developing a hydrogen supply chain to power ships while remaining objective. Tunnel vision is avoided.

The liquid organic hydrogen carriers first need to be hydrogenated. This means 'loading' hydrogen into the carrier molecule. Afterwards it can be released by a reactor and the carrier can be reused.
The carrier should be relocated again to the hydrogenation plant.

Mainly operations are influenced while infrastructure needs minor adaptations.
Conventional bunkering only has one direction of flow while with an LOHC system there are two. This translates to the entire supply chain.

Smaller projects illustrate that this technology is still in its early stages. But at the same time investments and fundings reflect overall interest.

Samenvatting

De energietransitie is een zeer actueel onderwerp. Dit kan leiden tot een overdaad aan informatie.
Daarom wordt in de eerste hoofdstukken een overzicht gegeven en worden verschillende energiedragers/brandstoffen vergeleken.

Deze thesis onderzoekt de vereisten om waterstof te leveren via LOHC (Liquid Organic Hydrogen Carriers). Dit is een van de weinige waterstofopslag- en transportsystemen waarbij de drager kan worden hergebruikt.
Het doel is om de behoeften te bestuderen om schepen van hernieuwbare energie te voorzien. Tunnelvisie wordt vermeden.

De liquid organic hydrogen carriers moeten eerst gehydrogeneerd worden. Dit betekent dat er waterstof in het dragermolecuul moet worden 'geladen'. Daarna kan de waterstof worden vrijgegeven door een reactor, en kan de drager worden hergebruikt.
De drager moet opnieuw naar de hydrogenatie installatie worden verplaatst.

Vooral operaties worden beïnvloed, terwijl de infrastructuur kleine aanpassingen nodig heeft. Conventioneel bunkeren heeft maar één stroomrichting, terwijl er met een LOHC-systeem twee zijn. Dit vertaalt zich naar de hele supply chain.

Kleinere projecten illustreren dat deze technologie nog in de kinderschoenen staat. Maar tegelijkertijd geven investeringen en financieringen de algemene interesse en kansen weer.

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List of abbreviations

GHG: Greenhouse Gasses

EEXI: Energy Efficiency Existing Ship Index

CII: Carbon Intensity Indicator

SEEMP: Ship Energy Efficiency Management Plan

MEPC: Marine Environment Protection Committee

FTS: Fisher Tropsch Synthesis

HFO: Heavy Fuel Oil

MGO: Marine Gas Oil

LNG: Liquefied Natural Gas

BOG: Boil-Off Gas

DAC: Direct Air Capture

DMFC: Direct Methanol Fuel Cell

HTPEM: High-Temperature Proton Exchange Membranes

LOHC: Liquid Organic Hydrogen Carriers

HVO: Hydrotreated Vegetable Oil

FAME: Fatty Acid Methyl Esters

LBG: Liquefied Biogas

HEFA: hydro Processed Esters & Eatty acids

RED: Renewable Energy Directive

LFP: Lithium Iron Phosphate

NMC: Nickel Manganese Cobalt

PM: Particulate Matter

SOx: Sulphur Oxides

NOx: Nitrogen Oxides

FC: Fuel Cell

DMFC: Direct Methanol Fuel Cell

DAFC: Direct Ammonia Fuel Cell

SOFC: Solide Oxide Fuel Cell

BOG: Boil-off gas

BOR: Boil off rate

PEMFC: Proton Exchange Membrane Fuel Cell

HTPEMFC: High Temperature Proton Exchange Membrane Fuel Cell

AFC: Alkaline Fuel Cell

PAFC: Phosphoric Acid Fuel Cell

MCFC: Molten Carbonate Fuel Cell

SOFC: Solid Oxide Fuel Cell

OECD: Organisation for Economic Co-operation and Development

LOHC: Liquid Organic Hydrogen Carrier

MCH: methylcyclohexane

NEC: N-ethyl carbazole

DBT: Dibenzyltoluene

BT: Benzyltoluene

CINEA: Climate Infrastructure and Environment Executive Agency

wt%: Weight percentage

LHV: Lower Heating Value

CL: Common Line

MSDS: Material Safety Data Sheet

PPE: Personal Protective Equipment

SOPEP: Ship Oil Pollution Emergency Plan

HICE: Hydrogen Internal Combustion Engines

Glossary

Drop-in fuels: Fuels that can use existing engines & infrastructure without modifications.

Hydrogenation: A chemical reaction where hydrogen reacts with another compound.

Dehydrogenation: A chemical reaction where hydrogen is extracted from a molecule.

rate determining step: The slowest reaction of a chemical reaction, determining the overall reaction speed

well to wake emissions: Complete life-cycle emissions of a fuel; from production to delivering thrust.

1 Introduction

Global efforts are seen trying to reduce human impact on the environment. The energy sector gets a lot of attention. People are becoming more aware of how urgent change is needed. Reduction plans are made. Targets are set. Regulations become more stringent.

The most obvious steps are clearly visible with electrification of cars and transport. However, for high energy demanding sectors it is not always possible. The maritime sector is one of them. Fluctuations in the production rate of renewable energy need to be addressed. Wind and solar energy production rates follow these natural sources. Energy needs to be captured and stored to provide a buffer for output imbalances and to unlock global distribution.

The ability to convert renewable energy into hydrogen via electrolysers gives it great potential as an energy carrier. Yet, its properties make for difficult handling and storage in pure form. A lot of energy is lost by compressing or cooling.
Renewable hydrogen can serve as component in production for a variety of fuels/ carriers. The energy is then contained in a completely different substance with other physical characteristics. There are a lot of possibilities in the form of solids, liquids & gasses.

The goal is to facilitate handling. Reducing energy losses during these conversions is an important area of research. Most hydrogen-based fuels or carriers are more likely to be used as-is.
The progress of developments is determined by a range of factors. From governmental support to innovation from companies. A lot of projects are running to test out different options.
Some are ahead of others which is normal.

Liquid organic hydrogen carrier technology exists today, but still has a lot of room for development. It is one of the few energy carriers that can be re-used. Because of the ease of handling and low risk, it shows great potential to play a major role in the energy transition.

The first chapter will explore different fuels. This cannot be neglected because in the near future a mix of solutions is more probable.
Afterwards more information is provided about the most common LOHCs and how they work.

Hydrogen forms the core of this matter, so it deserves its own chapter as well.
The following parts study the requirements to develop a working infrastructure for supplying ships. Small scale projects can give insights on technology advancements.

Finally, a bigger picture is shown, by describing different factors that influence the supply and demand.

2 Comparison of fuels

To put everything in perspective a comparison of the most promising and current fuels is needed. The characteristics of each fuel itself matter, but also different aspects that surround them such as transport and storage. The purpose of this chapter is to get a basic understanding of the impact on the environment by different alternative fuels. And investigate the capability to replace conventional fuels partly of completely.

2.1 Conventional fuels

Today the majority of ships sail on fossil fuels using internal combustion engines. This oil finds it origin over millions of years ago. When the remains of dead animals and plants were covered by mud. This crude oil is extracted by drilling in the underground reservoir and pumping it to the surface. The carbon that is contained in this fossil oil, does not form a part of the current atmosphere composition. All carbon emitted by burning this oil increases the total quantity of greenhouse gasses present (*GHG)* in the atmosphere. This forms the base of the climate change problem.

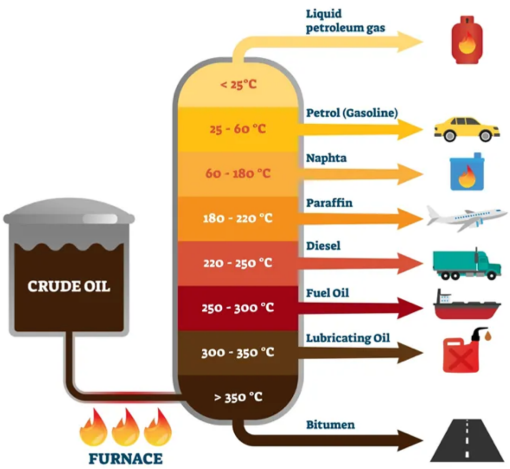


Figure 1 Fractional destillation
Source: Shalom Education (2023)

Crude oil is passed through a distillation unit to form distillates and residual fuel oil (Figure 1). Residual fuel oil is usually referred to as *HFO* or heavy fuel oil. Lighter fuels like gasoline, kerosene, diesel etc. are separated based on their different boiling points. Different blends are indicated by three letters. For example, DMA; 'D' stands for distillate and 'R' for residual. The 'M' stands for its application, in this case 'marine'. The final letter 'A' gives more information about its properties.

When a percentage of biofuel is mixed in, an 'F' is used instead representing FAME (see biofuel 2.5) (Vermeire, 2021). This is not a pure conventional fuel anymore and is categorized as biofuel.

The International Maritime Organisation aims to collect more statistics about emissions. New tools are developed to measure and collect data about the efficiency and emissions of a ship: the *EEXI* and *CII* (International Maritime Organization, 2019).
As of 1 January 2023, it is mandatory to calculate the *EEXI (*energy efficiency existing ship index). It is designed to ensure ships meet minimum energy efficiency requirements. The index is calculated by a formula that takes ship size, hull efficiency, engine power, etc. into account.
Ship operators must report carbon dioxide emissions by using the CII (Carbon Intesity Indicator). And measures should be implemented on board to keep the efficiencies as high as possible. This is done by the *SEEMP* (ship energy efficiency management plan).

2.1.1 Efforts to reduce emissions

If conventional fuel is used it's a real challenge to reduce the CO_2 output. Blending with biofuel and installing a carbon capture system are a few of the limited options. NOx and SOx emissions can be reduced more easily by using scrubbers, low sulphur fuel, and more recent engines.
The MARPOL sets out standards for engines to limit NOx emissions. Tier I engines have more relaxed limits as they are the oldest. Tier III limits are the most stringent because they are for more recent engines (from 2016).
Starting in 2020 new *IMO* guidelines regarding maximum sulphur content went into force. These are published by the *MEPC (Marine Environment Protection Committee).*
MEPC 74 states the following: "From 2020 ships are required to use fuel oils with a sulphur content of 0.50% m/m or lower, unless fitted with an approved equivalent means of compliance" (MEPC, 2019, 3.0.2).
Before this regulation, *HFO* with sulphur content up to 3,5% was allowed outside *ECA's* (emission control areas). Inside these ECA zones, only fuel with a maximum of 0,1% sulphur can be used. It is also possible to reduce these emissions by using exhaust treatment systems and still use high sulphur fuel. Washwater from a scrubber is discharged in the

ocean, impacting the aquatic ecosystems (Teuchies, Cox, Van Itterbeeck, Meysman, & Blust, 2020).
Still the sulphur content of these conventional fuels is higher than alternatives presented in the rest of this chapter (DNV GL, 2019).

In a life-cycle assessment researching the feasibility of a battery-powered passenger ferry (Guven & Kayalica, 2023), an interesting remark regarding low sulphur fuel is made.
0,1% sulphur fuel emits the lowest SOx emissions compared to higher sulphur-containing conventional fuels. Despite this improvement, the production of these fuels causes the highest CO_2 emissions and high energy and water consumption. The reason is the intensive refinery processes.
This is an excellent example to show how important it is to look at the complete cycle of fuels, including production, handling, etc.

2.1.2 Technology to reduce emissions

Another option to reduce the carbon footprint of conventional fuels is to synthesise it from renewable sources.
Franz Fisher and Hans Tropsch created the Fisher-Tropsch synthesis *(FTS)*. A wide variety of hydrocarbons can be made by combining hydrogen and carbon monoxide. This process can be paired with a carbon capture unit. Carbon can be captured directly from the atmosphere or at a carbon-rich exhaust stream from other processes. Directly from the atmosphere would be the most renewable option. Usually, carbon-rich exhaust streams originate from burning fossil fuels.
The original FTS uses CO, but when extra catalysts are used, CO_2 can also be hydrogenated into hydrocarbons. A mix of hydrocarbons is produced. Adjusting the temperature can promote diesel-like fuel production. Still a mixture of reaction products will be created. This reduces the overall efficiency (Mahmoudi et al., 2017).
Synthesising fuels are a great way to create *drop-in fuels* that can be used directly in existing propulsion systems. One of the biggest downsides is that only one out of three hydrogen molecules is stored in the synthesised fuel. The rest goes to ‘waste’ and forms water. Renewable hydrogen production is a highly energy-intensive process. Currently, the scale of production is still limited. Supplying world needs with renewable FTS fuels is therefore questionable.

2.2 LNG

LNG or liquefied natural gas is a well-known alternative fuel for ships. An easy transition was possible due to tankers transporting LNG. These ships already had the fuel on board as cargo. Boil off gas can be used or reliquefied. The next step came as a natural consequence. However, it has become more common to have a dual fuel diesel electric configuration on board LNG carriers (Lataire, 2022).

The LNG cargo is liquefied to increase the density, and automatically reduce the volume. In this cryogenic state (at a very low temperature) boil-off gas is always created. The amount can be reduced by optimizing insulation and reducing sloshing in tanks. Different possibilities are available to manage this boil-off gas (*BOG)*: consumption in an engine, burning, re-liquefaction…

The obvious choice for LNG carriers is to use the boil off gas as fuel. For other types of ships, cylindrical fuel tanks need to be installed. About two times the volume of LNG is needed for the same energy as in conventional fuel. And because the tank is cylindrical, even more space is taken from the limited space available on board a ship (DNV GL, 2019). Fuel tanks are therefore often installed on deck (Figure 2).

Liquefied natural gas consists mainly of methane ($\mathrm{CH_4}$). This molecule has the lowest carbon content of all hydrocarbons and is therefore the best fossil fuel option to reduce carbon emissions. The high hydrogen content in these molecules results in a relatively high heating value. A negative consequence of this high methane content is 'methane slip'. $\mathrm{CH_4}$ is a very strong greenhouse gas. Its lifetime present in the atmosphere is much shorter than carbon dioxide. About 12 years compared to centuries with $\mathrm{CO_2}$. Still, methane is responsible for 30% of the rise in temperature since the industrial revolution. This moment in history was the beginning of large-scale human emissions (IEA, 2023).

Through an increase in consumption, more methane is released into the atmosphere each year. Mainly due to leaks, but also by incomplete combustion. Engine manufacturers report possibilities to run a mix of hydrogen and natural gas in existing dual-fuel engines. This may significantly reduce the methane slip.

High-pressure two-stroke engines seem to have the least methane slip in their exhaust. The main benefits are the reduction of SOx emissions since natural gas is almost sulphur-free.

For now bunkering is mainly done by trucks and in the ARA-region (Amsterdam-Rotterdam-Antwerp) some bunker vessels are operational (DNV GL, 2019). Trucks are very flexible in terms of deployment, but capacity is limited. Of all alternative fuels listed in this chapter, LNG has the most developed infrastructure. A lot can be learned and applied to other fuels. For example, the handling of a cryogenic liquid is also needed when using hydrogen.

Figure 2 LNG truck to ship bunkering
Source: Safety4sea (2020)

With the Sabatier reaction methane can also be synthesised, which is then called *S-LNG*, where the letter 'S' stands for synthetic. When hydrogen and CO_2 are combined in the presence of the right catalyst at the right temperature and pressure, methane will be formed. This is an exothermic process, 165kJ/mol is released. Again, great potential is shown when using this technology in conjunction with carbon capture. But just as with the synthetic diesel or methanol (2.1.2 & 2.4) a part of the valuable hydrogen supply is lost, about 50% (Van Hoecke et al., 2021).

This approach would make no sense when the hydrogen supply comes from methane reforming. Methane reforming is a process where steam releases the hydrogen atoms from the CH_4 molecule. The hydrogen must be sourced from one of the other options. These include electrolysis and biomass. The scale of these production methods is still limited as seen in 4.3.

2.3 LPG

Liquified petroleum gas is a by-product of the oil and gas production industry. It is a mix of propane and butane. The global warming potential is about three to four times as high as carbon dioxide. Just like LNG there is an issue with unburned LPG escaping in the atmosphere via the exhaust.

There is virtually no sulphur emitted, particulate matter is also reduced significantly. NOx & CO_2 emissions are reduced both by about 10 - 20 % (DNV GL, 2019).

An LPG fuel system/ engine is cheaper to run than than LNG. The pressures and temperatures are not as extreme.
Infrastructure is already well established and production would have no problems to supply demand (DNV GL, 2019).

MAN currently has the first LPG two stroke marine engine commercially available. It also has dual fuel capabilities, can operate on methanol and would be a good option for converting to an ammonia engine (MAN Energy Solutions, 2018).

2.4 Methanol

Different methods to produce methanol include natural gas reforming. Which is unfortunately the most common method. Almost all yearly production uses fossil fuels (International Renewable Energy Agency & Methanol Institute, 2021). This is not a renewable method, requires a lot of energy. Thus, has substantial emissions. Coal and biomass gasification are other methods, where biomass would be the better option due to its ‘waste to energy’ capability.

Another promising method for renewable production is the hydrogenation of CO_2 (synthetic methanol). Not all hydrogen molecules react with the CO_2, one-third is lost due to forming water. The reaction is endothermic at around 230 °C and 50 bar (Bowker, 2019).

Methanol or CH_3OH contains carbon atoms. This will lead to CO_2 emissions when burned. The only method to make this a ‘zero carbon fuel’ is by only using carbon atoms that were already present above the earth’s surface/ in the atmosphere (not from fossil fuel) (Dalena et al., 2018).

Using CO_2 that ‘would otherwise be emitted nevertheless’ can be an option too. One should not forget that carbon-emitting processes in factories will also be carbon neutralized when possible. Then this way of capturing carbon will become limited. *DAC* or direct air capture (Figure 3) would be a renewable option to complete the carbon cycle. The required energy for DAC can vary depending on the technology used, but generally capturing CO_2 at the exhaust of a process is more energy efficient.

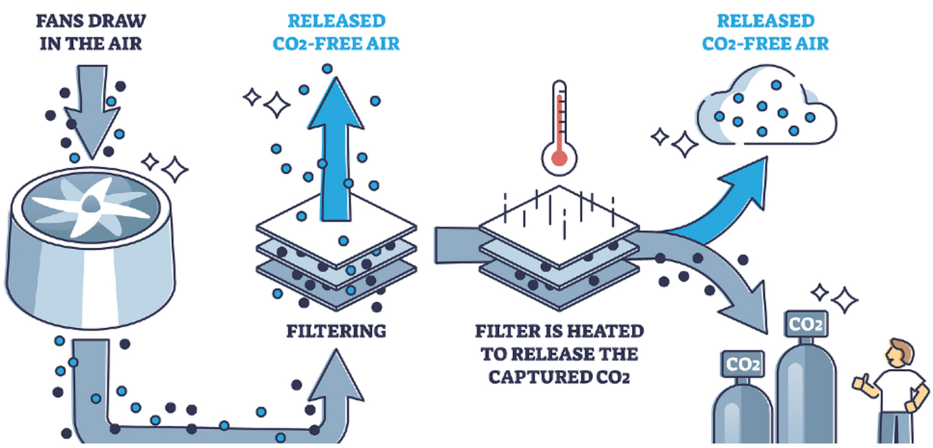


Figure 3 Direct air capture
Source: Nelthorpe (2021)

Methanol can be used in both internal combustion engines and fuel cells. There are direct methanol fuel cell possibilities (*DMFC).* Or methanol can first be reformed to hydrogen and then used in a high-temperature proton exchange membrane fuel cell (*HTPEM FC).* High temperatures have the advantage that the mixture has to be less pure. Impurities may exist after reforming. Both fuel cells release carbon dioxide. In HTPEM methanol basically is a hydrogen carrier molecule.

A downside of methanol is the carbon release, with both fuel cells and combustion engines. However, this problem is offset when renewable CO_2 is used, or captured and stored across the whole lifecycle.
It is an easy-to-handle liquid with a great energy density. The main downsides are the toxicity, flammability, and the fact that it is a carbon-containing molecule (Araya et al., 2020).

2.5 Biofuel

Biofuels use carbon that is already present in the atmosphere (plants, animals, organic waste) and thereby don't create more greenhouse gasses. For the production, harvesting, and processing, fossil fuels are still used.
A division of biofuels can be made based on the origin or processing method (geeksforgeeks, 2022).

First-generation biofuels are produced by extracting oil, or by traditional processing methods like fermentation of crops that can also be used for food production. These types raise questions about the proper use of agricultural land. The food versus fuel discussion. The use of agricultural land with the sole purpose of energy production is not very efficient. Photosynthesis by plants has an efficiency of about 1%. Photovoltaic cells (solar panels) have an efficiency of about 12-20% (Pimentel & Patzek, 2005). Since we cannot eat electricity, farming crops is still needed at this lower efficiency for food.

The main disadvantages of first-generation fuels are solved with second-generation fuels. They are made from crop waste material, organic waste, etc.
All organic material with fibre contents, called lignocellulosic material is used (Alalwan, Alminshid, & Aljaafari, 2019).

Third-generation fuels are made from microorganisms like algae. Algae absorb a lot of CO_2 and can grow at a very fast rate. A big disadvantage is the amount of water needed. They can also grow in salt water, wastewater, etc. In this case, more processing will be needed.

The fourth generation uses microorganisms combined with genetic modification.
Third and fourth-generation fuels are better options considering greenhouse gas reduction and food-fuel competition (Alalwan et al., 2019).
Figure 4 gives a schematic overview of how different generations can eventually produce the same fuel. A generation expresses the production pathway.

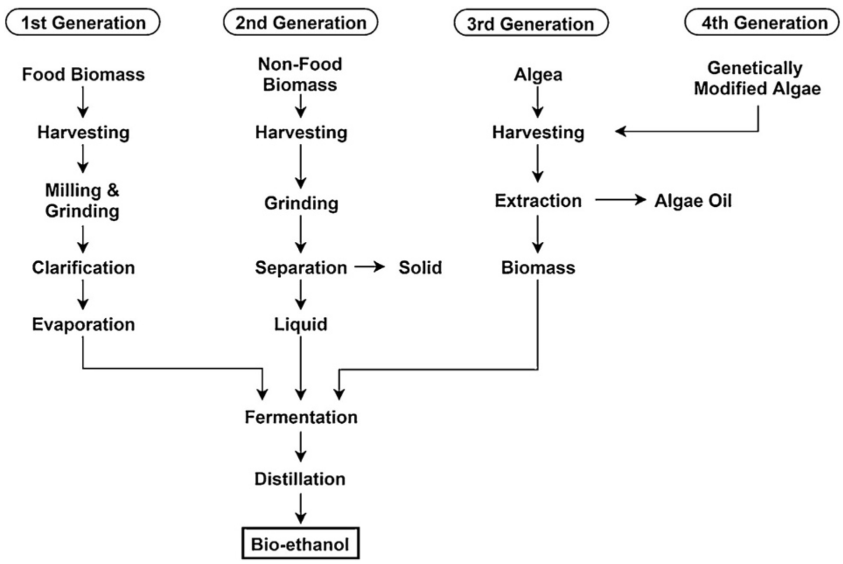


Figure 4 A schematic diagram of bioethanol production based on different generations
Source: H. A. Alalwan e.a. (2019)

Two important processes used to produce biofuels are fermentation and transesterification. With fermentation, microorganisms like bacteria and fungi convert biomass to fuel by chemical reactions. Transesterification (Figure 5) is a process where the R groups of an alcohol and an ester are exchanged.

Figure 5 Transesterification
Source: Wikipedia (2014)

The four most common types of biofuels are *HVO* (hydrotreated vegetable oil)*, FAME* (fatty acid methyl ester)*, LBG* (liquified biogas), and ethanol.
Drop-in fuels and blends can use existing infrastructures (DNV GL, 2019). The marine industry is mainly focussing on methanol due to a wider range of feedstock possibilities (Vedachalam, Baquerizo, & Dalai, 2022). Wartsilla states that ethanol can also be used by methanol engines with very little adjustments (Ship&Bunker, 2023).

2.5.1 HVO

*HVO (*Hydrotreated vegetable oil), or also known as green diesel, renewable diesel, or HEFA (hydro-processed esters & fatty acids). These terms refer to triglycerides that are split into fatty acids.

To further process this substance into a hydrocarbon, oxygen needs to be removed. This happens through hydro-deoxygenation *(*removing oxygen, forming water) and decarboxylation (removing carbon, forming CO_2). During this process, as one can derive from the name, hydrogen is needed as illustrated in Figure 6.

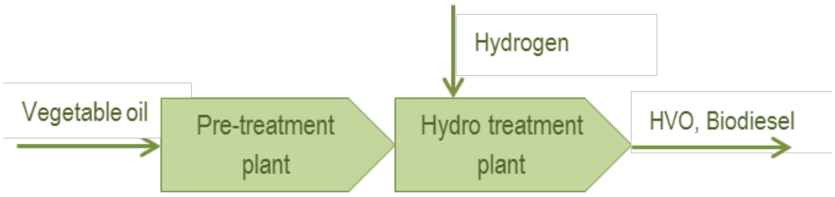


Figure 6 HVO production
Source: f3 innovation cluster (2016)

Then the problem shifts again to renewable hydrogen production and sourcing. There are regulations about the properties of this fuel since it is commonly mixed in with regular diesel. This normally gives no problems because renewable diesel is chemically the same as petroleum diesel. Most of the time about 5 – 10% is mixed in. On the European level, they are set by the *RED* (renewable energy directive) (European Technology and Innovation Platform, 2020).

2.5.2 FAME

FAME (fatty acid methyl esters), also referred to as biodiesel, is made by transesterification of an alcohol and an ester. This means the R-group of the organic molecule is exchanged. R represents a number of carbon atoms (ETIP Bioenergy, 2023). Methanol is an example of an alcohol that is used for the synthesis of FAME.
Biodiesel can be used in regular diesel engines (using compression as ignition), mixed to any percentage with petroleum diesel or pure (Bioenergy Technologies Office, 2023).

2.5.3 LBG

LBG (Liquified biogas) is essentially the same as liquefied natural gas. It originates from fermentation due to anaerobic bacteria (without oxygen), or from gasification (using heat but without combustion).

2.5.4 Ethanol

Ethanol has been used already a century ago around the 1900s, later people lost interest because of higher prices compared to oil. Then interest spiked again after the oil crisis in the 1970s. Until now, especially due to the search for alternative fuels, ethanol is used in some countries. Like the USA, Brazil & others (Alalwan et al., 2019). These two the biggest exporters of ethanol.

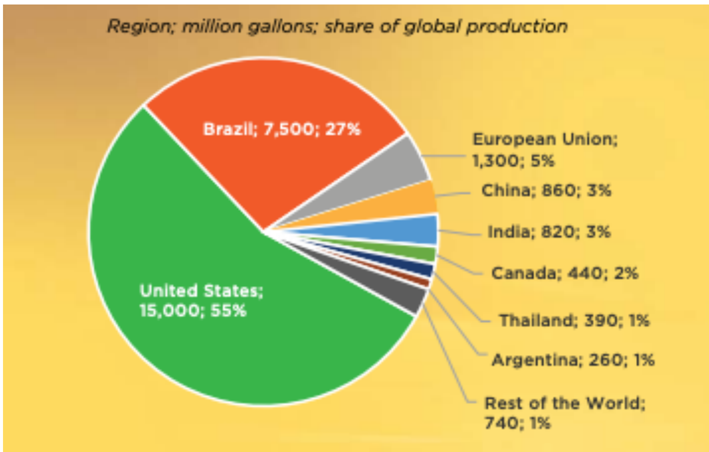


Figure 7 Global fuel ethanol production
Source: Renewable Fuel Association (2022)

Ethanol can again be produced by fermentation of biomass, or formed from a by-product of petroleum refining called ethylene. The latter will not be a good option to reduce carbon footprint. Ethanol would then be produced by the hydration of ethylene. Ethylene is used to produce polyethylene, which is a widely used type of plastic (Wikipedia, 2023a), (Hidzir, Som, & Abdullah, 2014).

Ethanol can be used in spark ignition engines as a blend with gasoline. Often 10 - 15% ethanol is mixed in with gasoline. This works fine for normal spark-ignited gasoline engines. Other blends can contain up to 85% ethanol. Already available for passenger cars and can be recognized by the 'E85' marking. Specially adapted engines are needed to run on this fuel (Renewable Fuel Association, 2022). The emissions will be less, but since the energy content of ethanol is lower than gasoline, the consumption will be higher.
The E85 ethanol-gasoline mix has a gravimetric energy density of 33,2 MJ/kg, regular gasoline has about 44,4 MJ/kg (Wikipedia, 2023b).
Experiments are done to increase the efficiency of these spark-ignited engines by injecting hydrogen in the air intake (Ayad et al., 2020).

The eventual product can most of the time be produced in different ways, depending on the "generation" as explained above. There is for example first/ second/ third/ fourth generation ethanol.

Biofuels also have some drawbacks. Fossil fuels are often used for production, processing, heating, ... This takes away the advantage regarding emission reduction and reduces the efficiency. Especially when considering that for example producing 1 litre of ethanol from corn takes 6,579kcal, while this ethanol only provides 5130kcal (Pimentel & Patzek, 2005). This cycle is not renewable.
A prediction in the Journal of Environmental Management estimates the total need for energy by 2050 and the potential of the earth's biomass (Ambaye et al., 2021). It shows there won't be enough to satisfy the world's needs. Still, biomass/ waste/ organic material is produced by farmers anyway. In this scenario, biofuel technology serves a good purpose.

These crops, like corn and sugar beet, need a lot of surface area with fertile soil, which means that some countries will have to import from others. Often this will be from poor countries where food is scarce. This raises some ethical questions. While people are hungry, fertile soil is used for fuel instead of food (Brussels instituut voor milieubeheer, 2009).

Most of these fuels can be used in regular combustion engines, or after some adaptations (e.g for E85). There are some common technical problems that arise;
Pure vegetable oils & animal fats polymerise because of aging or when in contact with lubrication oil. Then e.g., the proper functioning of the injection pumps is affected.
Some of these problems can be avoided by refining.

2.6 Power to fuel – synthetic fuel

The power to fuel/ synthetic fuel name has multiple meanings but generally, people who use this umbrella term refer to synthesis using renewable energy. As illustrated below (Figure 8).

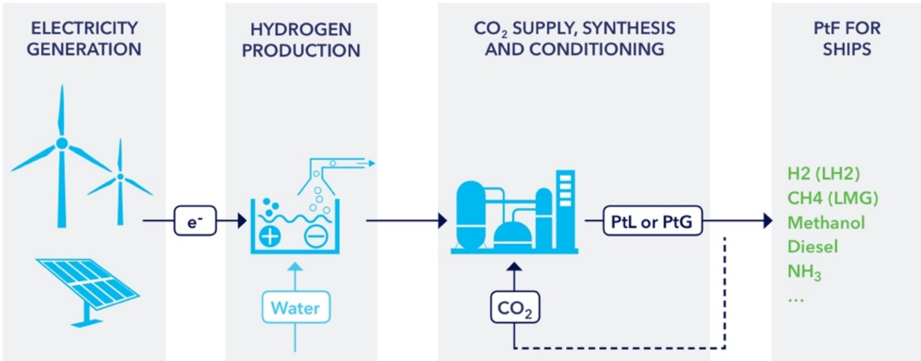


Figure 8 Principal production pathway for power to fuel (*PtF)*
Bron: DNV GL (2019)

The concept is to create fuels from water, carbon, and nitrogen, … using mainly electricity. A report of DNV GL uses power to fuel/ electro fuel/ e-fuel or synthetic fuel as umbrella terms (DNV GL, 2019).

This section's purpose is a clarification of the terms described. Further on in Chapter 3, some of these fuels will be categorized as hydrogen carriers. These substances all store the energy contained in hydrogen atoms. Synthetic diesel fuels, synthetic natural gas, methanol, and ammonia are some examples. Changing to these fuels as a user requires little to no effort. For example, synthetic diesel oil can use the same infrastructure and engine as fossil diesel oil. These interchangeable fuels are called *drop-in fuels*.

Using the primary renewable energy source directly, will always be more energy efficient than further processing it to a synthetic fuel & thus also cheaper. Electrification (with green electricity) is the most efficient. Some high energy demanding appliances like ships simply cannot be electrified with today state of battery technology (DNV GL, 2023). Projects exist on a smaller scale, for short-sea shipping on fixed routes (Guven & Kayalica, 2023).

2.7 Ammonia

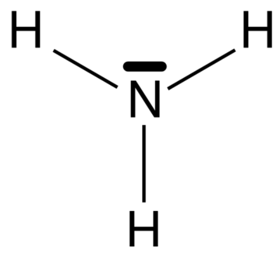


Figure 9 Ammonia's structure
Source: Solanki (2021)

Yearly over 200 million tonnes of ammonia are produced. These numbers are increasing every year (Statistica, 2022). Production happens by combining nitrogen and hydrogen via the Haber-Bosh process. It is a very old chemical process that is still used in modern production plants today. The Haber-Bosch process combines nitrogen with hydrogen under pressure at elevated temperatures (Smith, Hill, & Murciano, 2020). It is possible to produce hydrogen from electrolysis. Unfortunately, steam methane reforming *SMR* is cheaper and therefore used by most production plants. Chapter 3 explains why *SMR* is not a good option to reduce carbon emissions. Nitrogen can be captured with direct air capture systems.

2.7.1 Pure ammonia

Ammonia (NH_3) is a promising fuel for the shipping industry, trucks, and other heavy machinery to reach a carbon net zero. The molecule does not have any carbon and sulphur atoms (Figure 9). This means during combustion also no CO_2 or sulphur oxides will be formed. Nitrogen oxides will still be present.

NH_3 has a small flammability range of 16% to 25% (Airgas, 2019). Which is good for safety reasons but for combustion engines, pilot fuel is needed to make the combustion happen. Diesel is frequently used as pilot fuel. It helps ignition and lubricates the piston. In bigger engines, the longer piston stroke length helps to give the combustion more time. The stroke length of a ship's engine can be e.g. 2 meters or even more. For reference, in a car, it is only centimetres. H_2 can also be used as a pilot fuel but these systems are not compatible with normal diesel oil.

The diesel pilot fuel creates a dual fuel system that is flexible in the proportions of diesel/ ammonia mix. CMB is investing in this technology as seen on Figure 10 of the planned bulk carrier.

Figure 10 Ammonia powerd vessel by Bocimar, to be built by 2025-2026
Source: CMB.TECH (2023)

2.7.2 Cracked ammonia

Ammonia can also be cracked to release the hydrogen, but this is less common. High temperatures are needed, and pure hydrogen is not guaranteed. Hydrogen combustion engines or fuel cells can then be used. In this way, ammonia can also be seen as a carrier of hydrogen.

Direct ammonia fuel cells are still in development and combine the better efficiency of a fuel cell and no NOx emissions, with the advantage that no cracking is needed.

Since ammonia is already used in various sectors at a large scale. Infrastructure, transport, and safety procedures for handling already exist.

To liquify $\mathrm{NH_3}$ it should be cooled to -33°C at atmospheric pressure, or pressurized to 7,5 bar at an atmospheric temperature of 20°C. The main disadvantage of ammonia is its high toxicity, possible impact on human health and the possibility to damage ecosystems (Airgas, 2019).

2.8 Electricity

2.8.1 Electricity = energy

Energy in the form of electricity needs to be captured for better handling/ storage & transportation. Batteries & fuel cells are two promising technologies. They each have their advantages and disadvantages. Batteries are currently more developed and show great overall efficiencies.

Electricity plays a major role in the transition to renewable energy sources. Solar and wind power generate electricity year-round. Some areas on earth are more fitted for capturing solar/ wind energy. This fact also means long-distance transportation is required, here batteries fall short in their capabilities. A carrier molecule could be a possible solution. For example, hydrogen production via electrolysis.

The next problem is difficult transportation of hydrogen due to its properties. This is the reason hydrogen carriers exist, and the core of this research.

Another problem with renewable energy is the varying output.

When using wind and solar photovoltaic energy, the output varies according to the intensity of the sun or wind. Nuclear power is also a possibility, see 2.9.

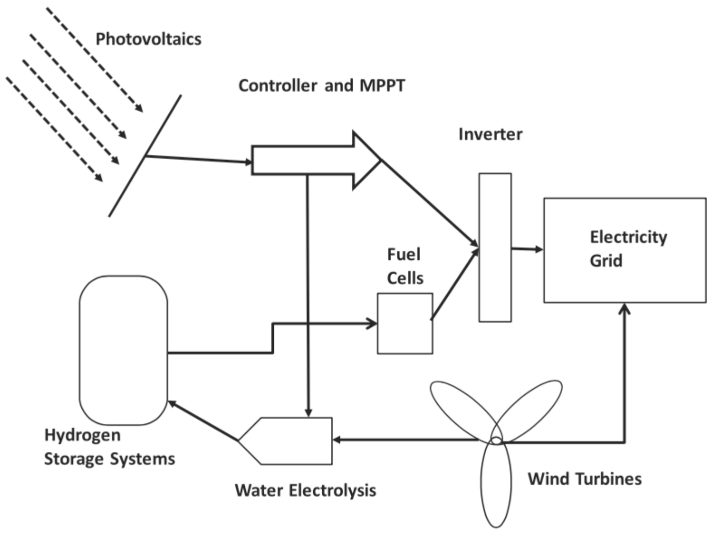


Figure 11: Schematic diagram of the system for the production, storage, and distribution of electric energy.
Source: Leonard, Michaelides, & Michaelides (2020)

Studies have shown that a transition to 100% renewable energy is feasible. The *IRENA* predicts renewables will supply 2/3 of the total energy by 2050 (International

Renewable Energy Agency, 2019). This will not happen without a proper storage system to absorb fluctuations of power generation. Hydrogen can play a role in this transition and storage system as illustrated by Figure 11.

2.8.2 Battery storage

Batteries are well known in their capabilities to store electricity.
Lithium-ion batteries are the most popular due to high power density. Different subcategories exist based on the material of the anode & cathode components. These materials have an impact on the properties of the battery. The LFP (Lithium Iron Phosphate) batteries appear to be the best option concerning greenhouse gas reduction, but for gravimetric energy density (energy per kg) NMC (Nickel Manganese Cobalt) appears the better option (Figure 12).

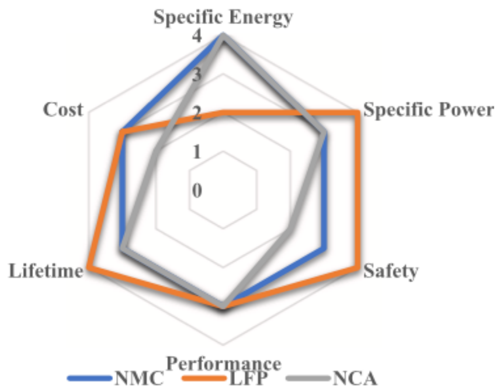


Figure 12 Comparison of different lithium-ion types
Source: Guven & Kayalica (2023)

The environmental impact of batteries is one of its strong points. A recent life-cycle assessment of a battery-powered passenger ferry gives a comparison between batteries and diesel engines of the emissions and water used over a whole lifecycle of the propulsion system (Guven & Kayalica, 2023).
For a battery-powered propulsion system, the main CO_2 emissions come from electricity production. This shows that when 100% renewable electricity is used this could be an attractive option. During the lifecycle, *PM*, *NOx* & *SOx* are still created, but significantly less than the diesel reference systems. The particulate matter that still is released comes mainly from electricity production and not as much from manufacturing.

The rest of the CO_2 emissions come from the production of batteries, but these are relatively low. During operation, no CO_2 is created.

Energy density is a problem. When designing an appliance, the needed capacity is calculated. It is important to remember that the state of charge of a battery has a minimum value. For example, a maximum discharge until 20% of the capacity is left. The aim is to extend the lifetime of the battery. Nevertheless, batteries should be renewed about every 10 years as they degrade over time. Something everyone using a smartphone can agree with.
While battery production keeps increasing, recycling does not keep up. In the near future it is necessary to improve recycling, raw materials will become scarce (Bae & Kim, 2021).
Energy density is the main reason why fuel cells are an interesting alternative. Heavy-load vehicles which need a long range like trucks, but also for cargo ships batteries are not an option (for now). Electrification is constantly pushing limits (DNV GL, 2023).

2.8.3 Fuel cells

As mentioned before, the energy contained in electricity can be stored into something more manageable. To convert the energy contained in a carrier back to electricity, fuel cells (FC) are needed.

Not only hydrogen FCs are being developed. Other types that use another fuel directly also exist. For example, DMFC (direct methanol fuel cells) or DAFC (direct ammonia fuel cells). The most common types of fuel cells used in applications today are *PEM* (proton exchange membrane) fuel cells. Toyota uses PEM FCs in their hydrogen vehicles (Toyota, 2023). Higher temperature options such as the *SOFC* (explained below) are becoming more popular. Especially for high energy demanding users. A higher temperature also means more waste heat which is an important advantage. Connection with other processes will increase the total efficiency. More impurities in the hydrogen are allowed due to these higher temperatures.

For marine or industrial applications with large energy demand on the megawatt scale, fuel cells are less developed than for the road transport sector (kW scale). It is also not possible to compare the use of a fuel cell on board a ship to MW-scale stationary power plants for the following reasons;

A ship is subject to the movements of the sea. Space on board is limited. Any mass of a propulsion system cannot be carried as cargo. Temperature differences can vary a lot every day. (Imagine sailing from the equator to higher latitudes.) The fuel itself needs to have a whole infrastructure built around shipping routes. The latter is a reason why a lot of experiments and new technologies are first seen on ferries and short-range shipping. High power fuel cells exist, but more development is needed for implementation on ships. Also see 'megawatt-scale fuels cells' in chapter 5.

Different types of fuel cells are explained below along with their main characteristics (Inal & Deniz, 2020).

2.8.3.1 PEMFC (proton exchange membrane fuel cell)

This type is the most common because of its flexibility, mainly due to a lower temperature (65-85°C instead of e.g. 800-1000°C with a SOFC). Start up times and energy are also less. The electrodes are platinum based. This is one of the main components of the cell. Therefore, it makes this option rather expensive.
To have some of the advantages of higher temperature fuel cells as well a high temperature version also exists (HT PEMFC). More impurities are allowed in the fuel at higher temperatures. These versions operate up to 200 °C which reduces flexibility in return of a higher impurity allowance.

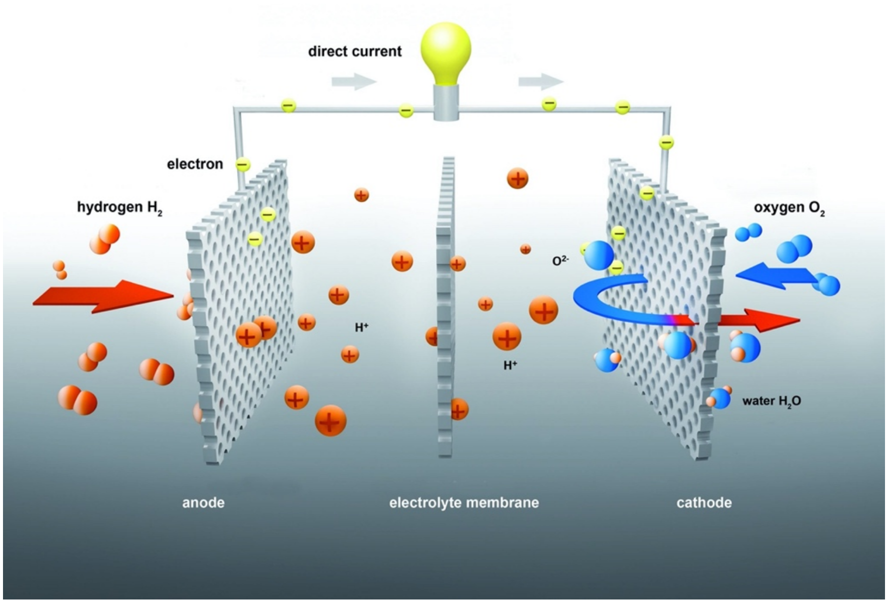


Figure 13 Fuel cell principle
Source: Viessmann (2020)

The protons travel through a membrane which is impermeable for electrons. These electrons then travel through a wire to meet the protons on the other side. This is how current is created. In the other types the same principle is more or less applied. Protons and electrons travel separately from cathode to anode. Figure 13 of a PEM FC illustrates this concept.

2.8.3.2 *AFC (*alkaline fuel cell)

These are the first fuel cells made. They work at low temperature and are relatively cheap, a disadvantage is the needed purity of fuel. Hydroxyl ions (OH-) are transported through the electrolyte solution.

Temperatures are generally below 100°C.

2.8.3.3 PAFC (phosphoric acid fuel cell)

Hydrogen protons are transported through a phosphoric acid electrolyte solution. The power density of this cell is relatively low. This means more volume/ space is required for the system for the same power generation than previous fuel cells.

Temperature ranges from 150-220°C so impurities are tolerable.

2.8.3.4 MCFC (molten carbonate fuel cell)

The molten carbonate fuel cell uses molten carbonates (CO3 containing substances) as electrolyte solution. An even higher temperature than the PAFC allows for more impurities Other fuels, like hydrocarbons can even be used without reforming beforehand. When using hydrocarbons, one should consider CO_2 will again be formed. An advantage over an internal combustion engine is the significant reduction in SOx, NOx & PM.

Another advantage of a higher temperature is the high energy in the flue gasses. These can even be used in a gas turbine for example to increase efficiency. Downsides are a longer start up time and wear of components because of thermal stresses.

2.8.3.5 SOFC (solide oxide fuel cell)

This type has an even higher operating temperature of around 800-1000°C. Heat recuperation and impurities thus form no problems. Advantages and disadvantages are similar as with the MCFC and it is a good fit for high energy demands.

A multi-criteria decision analysis by a university for the journal of cleaner production combines points given by experts from different relevant fields (Inal & Deniz, 2020). This way they made a ranking with advantages/ disadvantages of fuel cells for on board use of ships. Safety was found the most important and emissions the second most important criterion. Diesel oil powered high temperature FC's (like the MCFC & SOFC) eventually score best. The main reason being the hydrogen bunker problem and its availability around the world. Since the goal is to stop using fossil fuels this ranking can only be considered temporary. Biofuel is seen as a worthy alternative, but as seen in 2.5 'Biofuel' care must be taken.

Worth mentioning is that each setup is different. Ships differ greatly from stationary systems, so there is no 'one solution that fits all'.

2.9 Nuclear power

Nuclear power is a carbon free alternative to produce electricity. A very controversial topic where social acceptance is of major importance. Especially due to accidents in the past. Another consequence of these accidents are high safety standards like those from the *OECD* (Organisation for Economic Co-operation and Development) which comes with its costs. More safety always equals more costs. This aspect is a major problem concerning nuclear power.

The International Energy Agency *(IEA)* takes a period of 7 years to calculate building costs. In reality this is often a lot more. This results in highly expensive projects.

It seems that solar power is the better renewable electricity option for several reasons. It is better socially accepted compared to noisy wind turbines or nuclear power plants. Photovoltaic cells are very reliable, defective units can be replaced by an employee who is not highly trained and without extensive safety procedures. Finding manpower will not be a problem.

Wind & solar both have a consistent operation time in common. Nuclear power plants need to be shut down entirely when there is one small defect. A defect may be a problem with identical setups, those too then need to be shut down. (Boccard, 2022)

Nuclear power cannot be ruled out as an energy source. There are a lot of supporters of this technology for good reasons. A capsize bulk carrier for example could sail for 25 years without refueling. Nuclear waste after this period would be less then 200kg (Smith & NorthStandard, 2021). Some countries are planning to build new plants while others are sizing down. The controversy is holding back developments.

2.10 Wind assisted propulsion

As the name states, sails only offer assistance on commercial ships. Pure sailing vessels wouldn't be effective enough/ too time consuming/ dependent on the wind forecast…
Still, this is mentioned in the 'list of fuels' because it might serve a purpose to increase the maximum sailing range of every fuel. Most fuels will need more volume due to lower energy densities. Increasing range might become more important.

2.10.1 Types

2.10.1.1 Rigid wing sails

Rigid wing sails examples are: Flettner rotor, Turbosail, Multi-element wing sail (Milić Kralj & Klarin, 2016).
The principle with these three types is the same. Because of a combination of the design of the wing and the apparent wind through the ship's motion, the wind passing on the front of the wing (direction of the bow) has a higher velocity. A relative low pressure is created and has a lift force as a result.

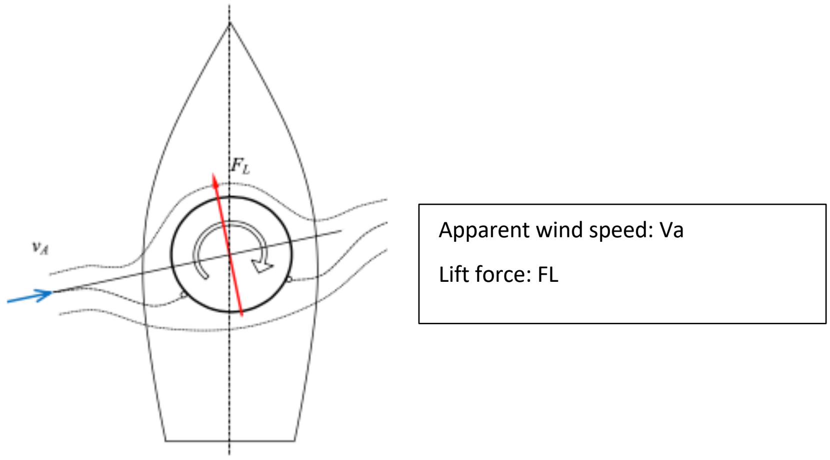


Figure 14 Basic principle of Flettner rotor
Source: Milić Kralj & Klarin (2016)

Figure 15 Flettner Rotor
Source: Wärtsilä Corporation (2020)

2.10.1.2 Kites

Kites are a more recent technology. Sails have been around even before the engine was invented. The ease of installation and little to no deck space occupation makes it an attractive choice. One downside is the range of sailing angles relative to the wind.
A static flight is not as effective as a dynamic flight (steering the kite). The latter needs more complex systems (Khan, Macklin, Peck, Morton, & Souppez, 2021). This means less reliability, more maintenance,…

Figure 16 Kite assisted ship
Source: Frangoul (2015)

2.11 The renewable colour spectrum

Often colours are used to refer to a production pathway. It is a simple method of categorising fuels based on their origin. Figure 17 shows the meaning of different colours for hydrogen production. These colours are not only used for hydrogen but also for other fuels, often based on hydrogen. For example 'green ammonia' means that it was produced using green hydrogen from electrolysis. 'Grey ammonia' would have its origin in fossil fuels etc.

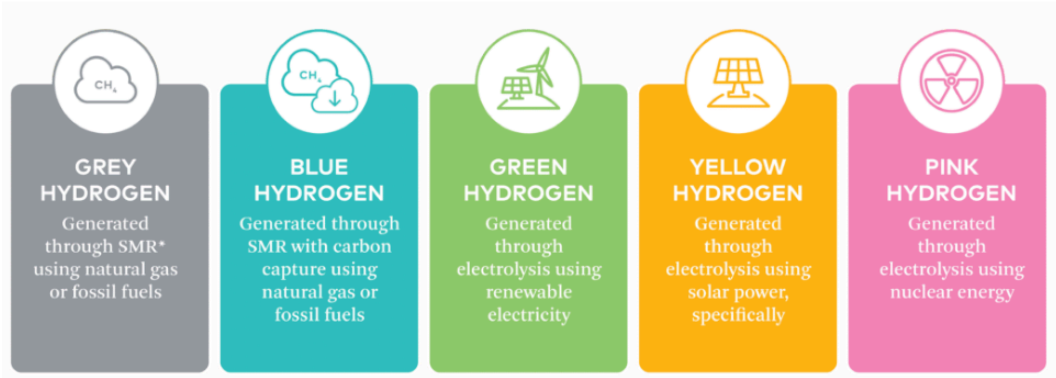


Figure 17 Hydrogen colour spectrum
Source: Meyer (2022)

These different production methods are explained in more detail in Chapter 4 'Why hydrogen'.

3 LOHC

LOHCs or Liquid Organic Hydrogen Carriers are cyclic organic compounds. These molecules can carry a few hydrogen atoms and release them again afterwards. The carrier molecules can be re-used after *dehydrogenation (*when the carried hydrogen is released). The process of storing hydrogen atoms in an LOHC is called *hydrogenation.*

3.1 Organic compounds

Organic compounds can be divided in cyclic and acyclic molecules. The carrier molecules have a cyclic structure. These cyclic compounds can again be divided in 2 categories. Homocyclic which means the ring is made of only carbon atoms, or heterocyclic which means another element can be part of the ring.
These cyclic hydrocarbons have a great advantage over other carriers due to their reversibility between hydrogenation and dehydrogenation.

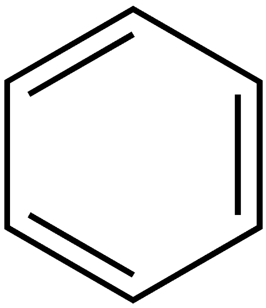


Figure 19 Example of a homocyclic compound
Wikipedia (2023)

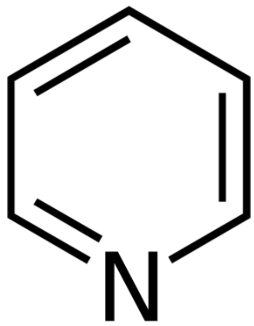


Figure 18 Example of a heterocyclic compound
Wikipedia (2023)

LOHCs are made from fossil fuels and since they are not burned, no direct emissions exist. As explained in 3.2 energy is needed for (de)hydrogenation. The efficiency and emissions can vary depending on the heat management and energy sources. Using heat exchangers to connect separate processes creates a lot of possibilities.
The carriers can be re-used numerous times and only degrade a little bit per cycle. For example with benzyltoluene this is only 0,1% per cycle (Tullo, 2022). Benzyltoluene is a type of LOHC. In 3.3 different types are discussed.

3.2 Hydrogenation & de-hydrogenation

Benzene-like or aromatic structures have double bonds in the ring. Two lines in the chemical notation as in Figure 19 & Figure 18 represent a double bond. These can be broken, and the free connections are then used by hydrogen atoms. This process is called hydrogenation and is an exothermic reaction. The reverse of this process is called de-hydrogenation. More energy is needed for the latter (endothermic reaction). Each step has their own reactor which is designed to optimize thermodynamic driving forces; A low temperature/ higher pressure for the exothermic hydrogenation, and a high temperature/ low pressure for the endothermic dehydrogenation. Catalysts are used to help speed up the reaction.
There are also possibilities to use only one reactor for the 2 steps. This is more efficient when LOHC is used as stationary hydrogen storage (Jorschick et al., 2017).

For the hydrogenation of benzyltoluene & dibenzyltoluene different catalysts were studied to determine the best performance. Ru-based catalysts (Ruthenium) are the best option for lower temperatures, below 200°C. Pt-based catalysts (platinum) work very good for higher temperatures, up to 320°C. Higher temperatures are not always more attractive. But when looking at the bigger picture, a higher temperature may be interesting. Waste heat still has a decent temperature to re-use or store in other processes.

For the hydrogenation of toluene, Rh – based (Rhodium) catalysts work best until the process reaches a temperature of 170 °C where the next best working catalyst in line is again Pt-based. (Jorschick, Preuster, Bosmann, & Wasserscheid, 2021).

The reaction speeds of the catalysts were measured by the *rate determining step.* This is the moment when the first hydrogen atom binds to the carrier. At this moment the aromatic nature of the molecule is lost. This means the benzene-like structure disappears.

3.3 Types

In this part the most common LOHCs for maritime application will be discussed. Most important aspects are (de)hydrogenation enthalpy. Which determines the energy consumption of (de)hydrogenation and possibilities to be implemented in other processes. All boiling points values indicate that all examples are liquid under normal atmospheric conditions.
Flammability is important for safety reasons. Toluene is the only one that stands out in this area (in a negative way).

3.3.1 Toluene/ MCH (methylcyclohexane)

Table 1 Specifications toluene
Source: edited from Van Hoecke et al. (2021)

	Toluene (H0)	MCH (H6)
density (kg/m^3)	867	770
Gravimetric hydrogen capacity (wt%)		7,2
Volumetric hydrogen capacity (g/L)		55,44
(De)hydrogenation enthalpy (kJ/ mol H_2)		68,3
Melting point (°C)	- 95	- 127
Boiling point (°C)	111	101
Flash point (°C)	4	- 4

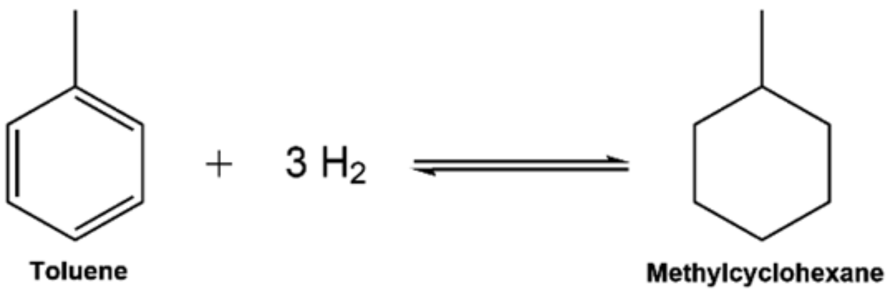


Figure 20 Hydrogen storage using Toluene/ MCH
Source: Jorschick et al. (2021)

This molecule has a relatively simple structure. It is almost the same as benzene, but one hydrogen atom is replaced by a methylgroup (CH_3). The hydrogenated version can carry six hydrogen atoms and is called MCH (methylcyclohexane). This highly aromatic structure provides a very stable molecule. Which is a downside for a carrier molecule. To break the double bonds a temperature of 250°C or higher needs to be reached. This temperature is higher than the boiling point of the carrier molecule itself, so all participating elements will be in the gas phase. Compared to e.g. DBT where the boiling point of DBT is higher than the dehydrogenation temperature, the situation is more complex and requires more energy.

Another disadvantage is the very low boiling point which increases safety hazards. The molecule is toxic, inhaling can cause severe lung problems. The toluene molecule is saturated when all double bonds are broken, and hydrogen has taken its place on "free connections". The hydrogenated product is called methylcyclohexane or MCH (Jorschick et al., 2021).

3.3.2 N-ethylcarbazole (H0-NEC) / perhydro-N-ethylcarbazole (H12-NEC)

Table 2 Specifications NEC
Source: edited from Van Hoecke et al. (2021)

	H0-NEC	H12-NEC
density (kg/m^3)	1158	937
Gravimetric hydrogen capacity (wt%)		5,7
Volumetric hydrogen capacity (g/L)		53,4
(De)hydrogenation enthalpy (kJ/ mol H_2)		50,6
Melting point (°C)	69	84
Boiling point (°C)	378	281
Flash point (°C)	186	NA

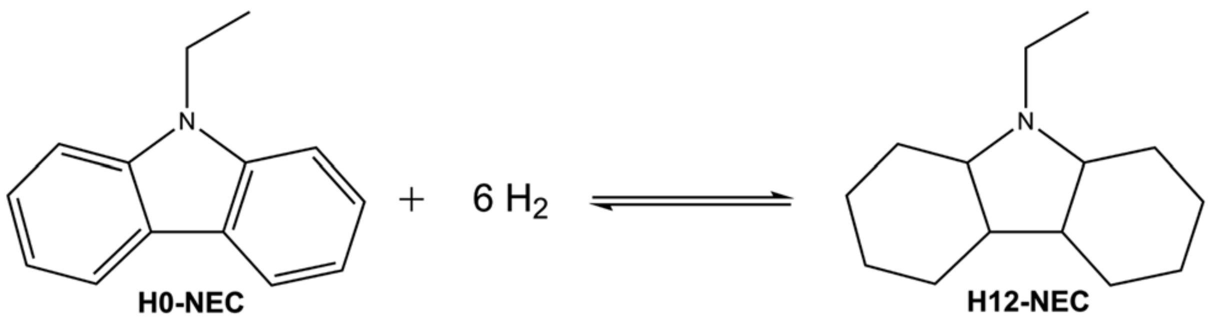


Figure 21 Hydrogen storage using NEC
Source: Jorschick et al. (2021)

NEC can carry 12 hydrogen atoms. The de-hydrogenated version is referred to as H0-NEC, and fully hydrogenated this becomes H12-NEC. Because of the nitrogen atom in the middle ring, it is less stable. Not as much energy is needed to release or load hydrogen. This fact is at the same time a disadvantage; the C-N bond is not as stable as the C-C bond.

Compared to pure hydrocarbon LOHCs the impact of NEC on the environment is worse. Pure hydrocarbons compounds only contain hydrogen and carbon.

Technology to provide constant quality during production is not available, and what is available is relatively expensive.
Most carbazoles are solid under ambient conditions. These compounds are not present in most conventional fuels that are used today. Today's liquid fuel infrastructure is not compatible with solid fuels. This takes away one of the biggest advantages of LOHCs (Jorschick et al., 2021). A solution could be to only dehydrogenate 90% to keep the H12-NEC in liquid form. This would then be 10% less efficient (Van Hoecke et al., 2021).

3.3.3 Dibenzyltoluene (H0-DBT) / Perhydro dibenzyltoluene (H18-DBT)

Table 3 Specifications DBT
Source: edited from Van Hoecke et al. (2021)

	H0-DBT	H18-DBT
density (kg/m^3)	1041	909
Gravimetric hydrogen capacity (wt%)		6,2
Volumetric hydrogen capacity (g/L)		56,358
(De)hydrogenation enthalpy (kJ/ mol H_2)		62
Melting point (°C)	-39	-58
Boiling point (°C)	390	371
Flash point (°C)	212	NA

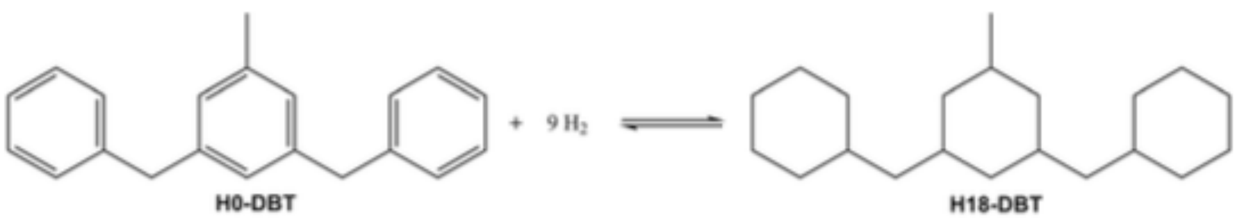


Figure 22 hydrogen storage using DBT
Source: H. Jorschick e.a. (2021)

This molecule can carry up to 18 hydrogen atoms as shown in Figure 22. The main advantage is that the boiling point of DBT is higher than the reaction temperature for dehydrogenation. Only hydrogen will become a gas, so an extra purification step is avoided. The main disadvantage is the high viscosity at low temperatures (Van Hoecke et al., 2021). For this reason, benzyltoluene can be a better option. It has a lower viscosity at low temperatures which facilitates pumping (Tullo, 2022).

3.3.4 Benzyltoluene (H0-BT)/ Perhydro benzyltoluene (H12-BT)

Table 4 Specifications BT
Source: edited from Rao & Yoon, (2020); Melcher, George, & Paetz, (2021)

	H0-BT	H12-BT
density (kg/m^3)	996	876
Gravimetric hydrogen capacity (wt%)		6,2
Volumetric hydrogen capacity (g/L)		54
(De)hydrogenation enthalpy (kJ/ mol H_2)		63,5
Melting point (°C)	-30	NA
Boiling point (°C)	280	270
Flash point (°C)	130	115

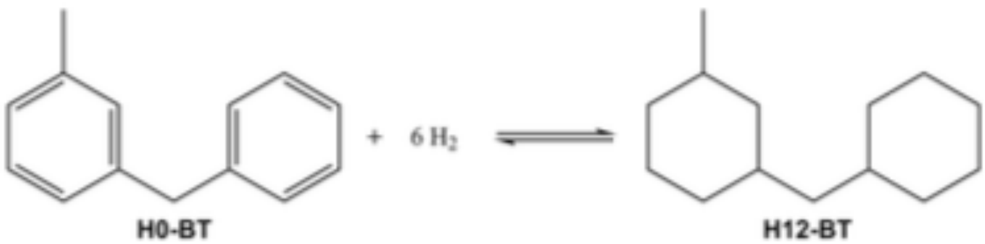


Figure 23 hydrogen storage using benzyltoluene
Source: Jorschick et al. (2021)

The boiling point of H12-BT is low compared to H18-DBT. This complicates dehydrogenation while remaining in the liquid phase. There are multiple advantages which make this carrier a strong competitor next to the other main carrier molecules. The dehydrogenation is faster

than H18-DBT, less complex intermediary structures are formed. (to get from H12 to H0 instead of H18 to H12), …(Rao & Yoon, 2020).
With a flashpoint of 130 °C benzyl toluene is hardly flammable and not even explosive. It remains non-explosive after hydrogenation.

To conclude:
NEC, DBT and BT are safe options concerning flammability, DBT & BT have more favourable advantages over NEC. It is also possible to mix DBT and BT to combine their advantages. A study showed that for example a 20 *wt%* (weight percentage) addition of benzyltoluene to dibenzyltoluene reduces the viscosity at 10°C by 80%. This was the main disadvantage of DBT. Other effects like better dehydrogenation were also observed (Jorschick et al., 2020).

For application on board ships more research towards reactors is needed. Specific challenges arise to deal with the movements of a ship etc. Removing hydrogen from the carrier is a crucial step that determines the success of LOHCs.

4 Why hydrogen?

4.1 Energy density

Hydrogen has a high gravimetric energy density, about three times as much as *HFO*. This characteristic is of big importance when designing a fuel. Hand in hand with the gravimetric energy density (MJ/Kg) goes volumetric energy density (MJ/m^3). The latter is also very important since it determines the ease of transportation/ how much you need of the fuel. (Alongside with other factors like toxicity/ flammability etc.)

The volumetric energy density is where the main challenge of hydrogen lies. For the same energy, five times the volume of liquified hydrogen compared to HFO is needed. Own calculation below (Table 5) shows how a higher gravimetric density does not immediately result in a higher volumetric energy density as well (Wikipedia, 2023c); (Huth & Heilos, 2013).

Table 5 Volumetric energy density of H_2 & HFO
Source: Own calculation

Energy in $1m^3$ liquid H_2	71 kg/m^3 * 120 MJ/kg =	8520 MJ/m^3
Energy in $1m^3$ HFO	1010 kg/m^3 * 41 MJ/kg =	41410 MJ/m^3

Another way to put this into perspective; pure compression (at 700 bar) of H_2 at ambient temperature has an energy density of +- 5,33 MJ/kg. This value takes the weight of the pressure vessel into consideration. Thick walls are needed to withstand 700bar. When comparing this to the *LHV (*lower heating value) of 120 MJ/kg, not much is left.

Still, this is significantly higher than batteries. A lithium-ion battery its gravimetric energy density is less than 1 MJ/kg (Samantaray, Putnam, & Stadie, 2021). Despite the lower value, electrification via batteries is very common. The reason being less conversion losses. Electricity – battery – electromotor. Instead of electricity – electrolysis - hydrogen handling – FC – electromotor.

4.2 Why, role of hydrogen

To answer the question “why hydrogen”: electrification has its limitations. According to the energy transition outlook of DNV (2023), hydrogen will serve the hard-to-electrify sectors. This means heavy, long distance road transport, shipping, aviation, etc.

As will be discussed in 4.3, to produce hydrogen via electrolysis, electricity is needed. Where it is possible to directly use renewable electricity, this will always be the cheaper option. Other methods for producing renewable hydrogen exist. For example, H_2 from biomass, but it is not as scalable.

Electric energy carried by batteries is not suitable for covering long distances. Think about trucks and ships. Added weight would compromise the cargo capacity. Aviation is even more sensitive to weight, but for short distance flights batteries still seem to be a strong competitor.

The transport sector takes up about 25% of total global greenhouse gas emissions, and for the next 30 years DNV (2023) even predicts a 35% increase of cargo carried at sea. The other transport sectors also see a significant increase in volume.

In the short-term drop-in fuels can be used, until infrastructure and technology allow hydrogen-based alternatives. Some of these alternatives are already used, but mostly without renewable hydrogen.

In most cases these alternative fuels are not called carriers of hydrogen, because they are not produced with the ‘capturing green energy by hydrogen’ - concept.

To solve the problem described above about the volumetric density of pure hydrogen, a carrier can be a good solution. This means that another substance, liquid/ solid or gaseous, serves as a medium to change energy density and aggregate state. In some cases, the carrier can be used directly as fuel. Otherwise a reactor is needed to extract the hydrogen from the carrier before consumption.

4.3 Hydrogen production

H_2 itself does not produce any harmful gasses when burnt, or when used in a fuel cell. The only reaction product formed is water. But the source of production is of great importance when determining the final emissions.

Most common methods for hydrogen production are the following (International Energy Agency, 2019):

4.3.1 Steam methane reforming

Almost all hydrogen today is produced by *SMR.* Steam is released at natural gas. Methane (CH_4) is the main component in this gas. Under the influence of steam, the hydrogen molecules are separated from the carbon.
With the help of catalysts, this reaction is made more efficient. CO_2 is formed as a by-product. For the steam production fossil fuels are used. To be renewable, the carbon must be recovered by a carbon capture, utilisation & storage (CCUS) system.

4.3.2 Electrolysis

Electrolysis essentially works in the same way as a fuel cell, but in the other direction. More detail in 2.8. Instead of supplying a fuel to the cell and collecting the current. Electricity (electrons) is supplied. Water is separated in H_2 and O_2. Some types work on high temperatures and efficiencies can be increased significantly when incorporating other processes.
Exothermic reactions like ammonia production or LOHC hydrogenation are some examples of potential processes that can be incorporated.

4.3.3 Thermal coal gasification

By applying high pressure and temperatures to coal, H_2, CO and CO_2 are released. This is a cheap option to create hydrogen. It is used by China to investigate and test the uses of hydrogen and how it can benefit in their economy (Nakano, 2022). Japan imports this type from Australia to supply a growing demand (Ohno, Nishida, Ishihara, & Hirose, 2022).

4.3.4 Hydrogen from biomass

Biomass is biological waste from animals, agriculture, sewage, etc. Biogas installations are already commonly used to process this waste. Most common methods are anaerobic digestion (a reaction by microorganisms in the absence of oxygen). And again, thermal gasification. Scaling up shows similar problems as with biofuel; shortages of material, food versus fuel, … Apart from this, it is an excellent method to convert waste in useable energy.

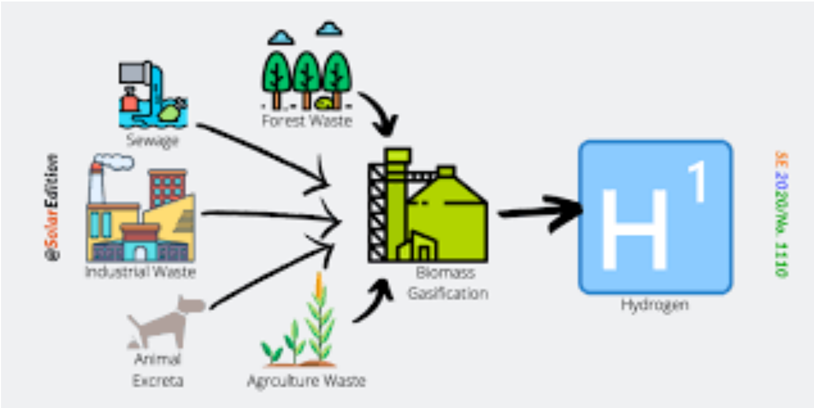


Figure 24 Gasification of biomass
Source: Solar_Edition (2020)

Of all methods mentioned above to produce hydrogen, electrolysis is the most logical choice. It is possible to scale up renewable electricity production. Wind and solar energy can be converted in a more versatile product. Efficiencies will suffer under extra conversions compared to electrification of end users. Still hydrogen will be necessary for heavier users and to compensate fluctuations in renewable energy production.

4.4 Hydrogen carriers

The term ‘carrier’ may seem a bit vague. Previously mentioned fuels like ammonia and methanol are suddenly called a carrier of hydrogen. This is because after synthesis there are possibilities to release the hydrogen again. In some fuels it is more obvious than others because the carrier itself can also directly be used as a fuel. In most cases this is the logical approach. Especially when considering total efficiencies across the supply chain.

A division can be made between physical storage (via adsorption) and chemical bounds. Chemical carrier molecules are more common than the adsorption method.
The difference is that with chemical bonding, the hydrogen molecule will react with another component and form a new substance, the hydrogen atom will be a part of the new molecule.

4.4.1 Physical adsorption

With physical adsorption the hydrogen molecules are attached on the surface area of the adsorbent material. Uptake capacity depends on available surface area. Hydrogen is attached by weak forces. An article states adsorption-based hydrogen storage at room temperature doesn’t have many advantages over pure compression. Also considering the extra complexity and thus costs (Samantaray et al., 2021).

4.4.2 Chemical bonding

Chemical carriers include ammonia, methanol, synthetic diesel, natural gas (methane) and liquid organic hydrogen carriers (*LOHC’s)*. Storage conditions determine the state, liquid or gaseous. More information about each carrier can be found in chapter 2, or chapter 3 for LOHC.
Liquid organic hydrogen carriers are discussed in a separate part because the carrier molecules themselves are not used as a fuel, as opposed to the possible direct use of the other options.

Solid state carriers also exist, most promising materials for the marine environment are metal hydrides and boron-based materials.
When metals react with hydrogen, they form metal hydrides. As one can expect, the gravimetric storage capacity (percentage of the weight that represents the hydrogen

quantity) is the main challenge. Generally, a trade-off must be made between hydrogen quantity and dehydrogenation temperature. Finding lighter metals usually also means higher dehydrogenation temperatures are required.

Boron is the fifth-lightest element in the periodic table, combined with a high hydrogen capacity. Very high gravimetric storage capacities are the result. Even the highest capacity of non-$\mathrm{CO_2}$-based hydrogen storage, up to 180kg/m^3 for $\mathrm{NH_3BH_3}$.
Dehydrogenation can be done by supplying heat or promoting a reaction with water.
The main problem with boron-based storage is that they are very difficult to hydrogenate due their stability. The ability to easily recycle the carrier is important for overall performance (Van Hoecke et al., 2021), (Zacharia & Rather, 2015).

4.5 Transition to hydrogen-based fuels

Actions from both regulatory organs and companies/ shipowners are required to make progress in the energy transition. The target set by the IMO is to reduce the annual *GHG* emissions by ships with 50% by 2050 (compared to the values from 2008) (MEPC, 2018).

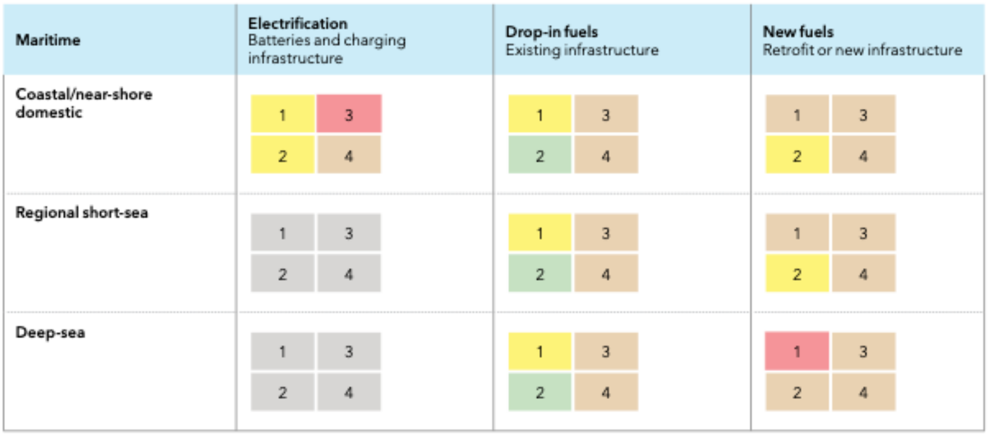
The push from regulations is needed to encourage investments in new technologies by making it more attractive. A specific example is seen in electrification of road transport in Norway. The government gives multiple benefits to users of electric vehicles (*EV's)*. They provide free parking, no toll on roads, free access to ferries and the ability to use the bus lanes in traffic. The government also provides fundings for a charging network. Meanwhile users of vehicles with internal combustion engines *(ICE)* must pay higher taxes.

After a while the *ICE* users will be a minority. Tax revenues are going to reduce significantly. The next move of the Norwegian government is then to decrease financial advantages of electric vehicles. At this moment the danger exists that *ICE* transportation will become the cheaper/ more attractive option again. Besides this potential problem, the proof is there that this push from the government worked. Norway has the highest uptake rate of passenger *EV's* (Norsk elbilforening, 2023).

A big difference between the maturity of technology and policies/ regulations of the road transportation and the maritime sector exists. There are limitations for electrification in the maritime sector (see part 4.1). Drop-in fuels or completely new fuels must be used.

Following table by DNV (2023) gives an overview of the progress in each domain that impacts progression.
Four aspects are discussed; they are all connected and influence each other.
Supply and uptake are worthless without each other. A ship (uptake) needs infrastructure to take in new bunkers. And vice versa, infrastructure is not feasible without uptake.
The 'policy push' means undertaking action. For example, by investing in infrastructure. The 'policy pull' must create measures to increase the demand of a certain fuel (see example above with *EV's* in Norway).

Table 6 Technology challenges and policy adequacy in maritime transport
Source: DNV GL (2023)



* Tiles 1 and 2 represent technology challenges. Tiles 3 and 4 represent adequacy of policies.

Technology maturity and challenges	Policies
1. **Supply** challenges and technology maturity for production and infrastructure	3. **Policy** push to address supply challenges for production and infrastructure
2. **Uptake** and demand challenges across all transport subsectors	4. **Policy** pull to address demand challenges across all transport subsectors

Technololgies		Policies
Existing technology or infrastructure		Well-defined policy, proven measures
Medium challenge		Defined policy, partial results
High challenge		Early policy, unclear results
Substantial challenge		Insufficient policy, no results
"Impossible" (no known tech.)		No defined policy

Drop-in fuels are currently closer to a fully working system with supply, demand and infrastructure compared to new fuels like ammonia, methanol, hydrogen, etc. For existing ships, the drop-in fuels are an excellent option. But when a shipowner faces the decision for a new propulsion system when ordering a new ship, the choice will still be very difficult. It takes time for renewable sources to reach a sufficient capacity to provide 100% green fuels for the maritime industry. Therefore, the blue version of these fuels could mainly be used in the beginning (production with carbon capture).

It is than a matter of policy decisions by governments, combined with efforts by leading companies investing in decarbonisation that will determine which propulsion system is the best investment. This illustrates the importance of policy decisions and support. A future shipowner will invest in best value for money, determined by factors mentioned above. The goal is to let the fuel with the least *well to wake emissions* be this option (DNV GL, 2023).

5 On board LOHC system setup

5.1 Energy balance on board of a ship

Detailed calculations are not yet possible. The goal is to explore various options for integrating LOHC as an on-board fuel. Unlike conventional fuels it needs to be dehydrogenated. A reactor is needed for this endothermic process (requires heat).

The feasibility of this setup is determined by waste heat and engine efficiency.
Waste heat should be used to power the dehydrogenation reactor. Available waste heat is determined by engine type and vessel type. Internal combustion engines, turbines & fuel cells all have different efficiencies. A higher efficiency means that more energy contained in the fuel can be converted to power at the propeller shaft. The type of vessel also matters. Tankers may carry cargo that require heating to prevent solidifying.

Figure 25 shows how much waste heat is available on a ship with a conventional combustion engine. All horizontal arrows are losses of the energy that was in the fuel. The waste heat boiler converts only 5% to steam. This figure represents the 'propulsion system-box' in Figure 26. Other options for this box will be discussed.

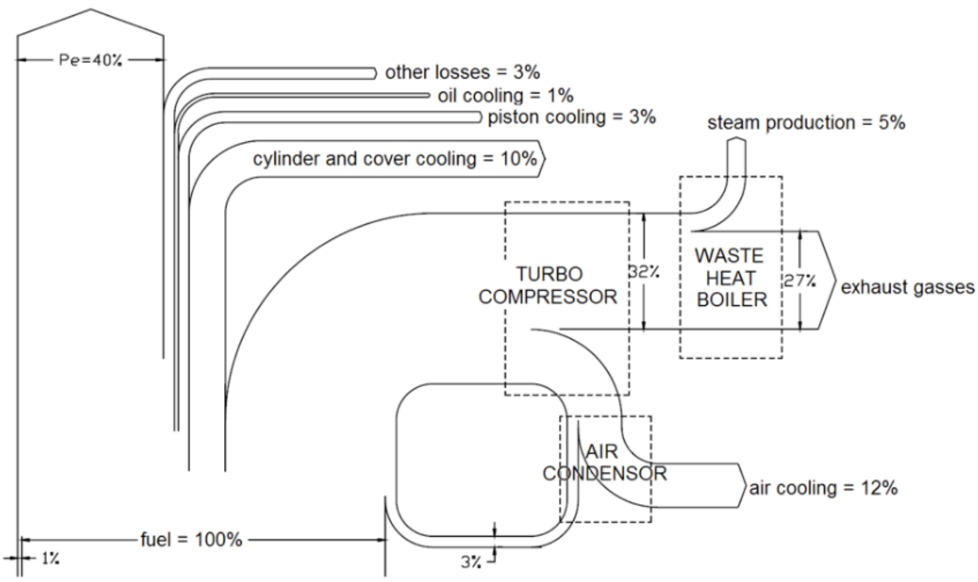


Figure 25 Sankey diagram conventional combustion engine
Source: Lataire (2022)

Two types of boilers are used for heating systems. Economisers use exhaust gasses as a heat source. This type reduces total fuel consumption unlike fired boilers. The fired boiler uses fuel burners to get up to the preferred temperatures. Extra fuel beyond the needs of the main engine is required. When in port, at anchor or manoeuvring, the main engine will usually not provide sufficient heat for the economisers.

Total heat demand is not a constant. It depends on seawater temperature and outside air. For tankers carrying heated cargo, demand changes with the carried quantity and changes each voyage (Bocheński & Kreft, 2020).

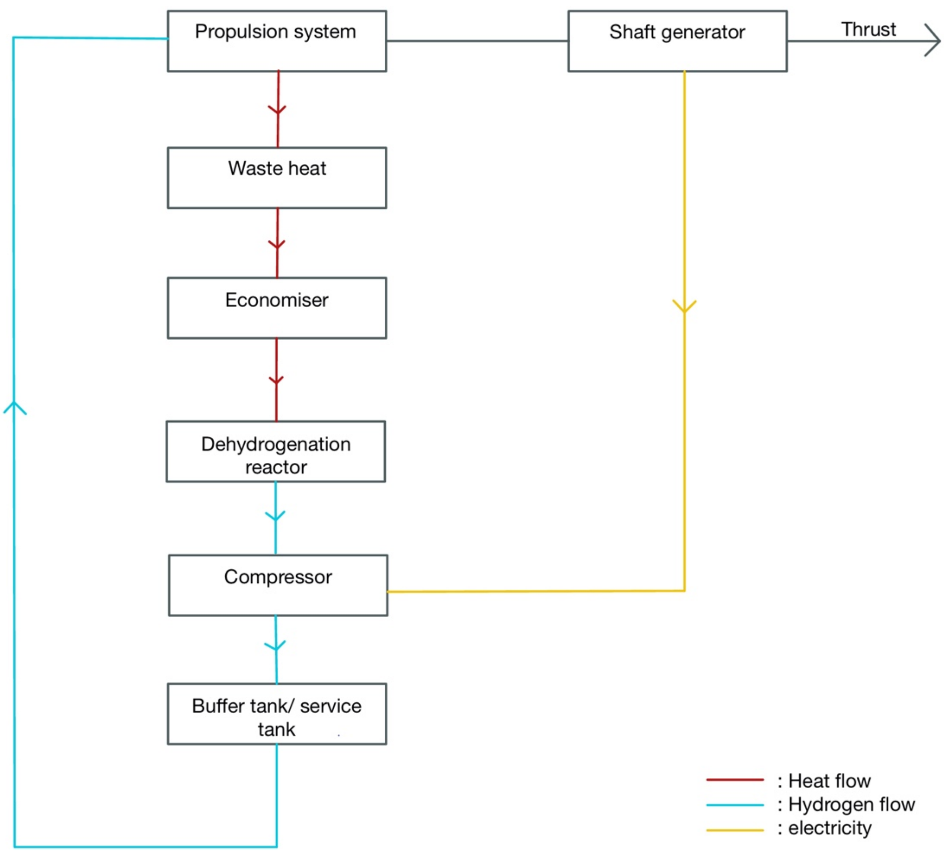


Figure 26 LOHC propulsion system
Source: own work

The diagram (Figure 26) shows energy flows a LOHC propulsion system to clarify the concept. Each part will be discussed in more detail below. This basic scheme assumes there is enough waste heat. When the main propulsion unit is not used in port, at anchor there will not be any heat available for dehydrogenation. A possible solution can be to build up an excess of hydrogen in the buffer tank. This is only possible when the hydrogen release rate

by the reactor exceeds consumption for propulsion. Then smaller fuel cells or gensets can provide the needed power.
More data is needed to calculate this in detail. Several factors determine the feasibility. Voyage length and required power during operations to name a few.
More detail follows about Figure 26 in 5.1.1, 5.1.2 & 5.1.3.

5.1.1 Propulsion system

5.1.1.1 Hydrogen combustion engines

When comparing diesel engines to steam & gas turbines. Diesel combustion engines have the highest *Carnot efficiency.* This means the maximum thermal efficiency of a certain engine without taking friction etc into account. It says something about the amount of energy in the fuel that can be converted to useful energy by the engine.
Carnot efficiencies for a diesel engine, steam & gas turbine are respectively 68%, 61% & 47%. In reality the following efficiencies are reached respectively: 45%, 30 & 25%. Due to internal friction and other losses (Lataire, 2022).

This shows the diesel engine is a very efficient propulsion system. One downside is the mass and size of the machine. Power density will reach about 30 kg/ kW while for a gas turbine these numbers can be as low as 1 Kg/kW. Overall, with lower RPM and thus stronger parts, diesel engines have proven to be a reliable choice for ship engines (Lataire, 2022).
Fuel cells reach even higher efficiencies and will be discussed below. A MCFC for example can reach (theoretical) thermal efficiencies of up to 77%.

Hydrogen internal combustion engines (*HICE*) have less energy in the exhaust compared to a conventional *ICE.* The reason is the high burning velocity. This means more heat will be transferred inside the cylinder, so it would be interesting to capture waste heat via the cooling liquid (X. Wang, Sun, & Luo, 2019). Generally cooling happens via a some closed loops with heat exchangers to the seawater (Abdelkareem et al., 2021).
Compression ignited dual fuel engines show better thermal efficiencies over spark ignited gaseous fuel engines. Since the diesel cycle is used, Carnot efficiencies are similar to a normal diesel (compression ignited engine) (Bakar et al., 2022).

If hydrogen and/ or another engine type is used, there will be a change in specific fuel consumption and resulting waste heat. These numbers have an effect of the amount of LOHC that needs to be supplied to a ship, and thus determines the whole fuel supply chain. Storage capacities in ports will be influenced.

5.1.1.2 Megawatt scale fuel cells

The question rises if a diesel type engine will still be the choice when changing to LOHC as a fuel.
To propel a vessel, megawatt scale power is needed. Ranging from 2-3MW for small coasters up to around 80MW like the Emma Maersk for example (http://www.emma-maersk.com/specification/). Fuels cells are mostly used & more developed on a smaller scale. An individual cell unit has low voltages, to increase the power output, the cells are combined to form a fuel cell stack. They are generally combined in series, which means the anode of a cell is connected to the cathode of the next.

Some examples of large-scale power plants are an 11 MW PAFC from Tokyo Electric Power Company. Siemens Westinghouse developed a SOFC power plant of 4,5 MW and even one of 500 MW. These examples use natural gas or coal as fuel. SOFC can also be used with pure hydrogen. (Das, Chowdhury, Li, & Tan, 2021).
These stationary plants do not always have a constant power consumption, fluctuations can be absorbed with batteries (Radmanesh & Samkan, 2018). On ships energy is always needed, but also has varying needs when at sea, in port, at anchor,…

Projects for building fuel cell powered vessels with LOHC already exist. Like ship-aH_2oy. The project is supported by 15 million euros funding from European Climate Infrastructure and Environment Executive Agency (*CINEA*). It was recently announced in a press release (Østensjø Rederi, Edda Wind, & Hydrogenious LOHC Technologies, 2023). Offshore service vessels will be equipped with an LOHC/ SOFC powertrain. This will be a first-of-a-kind. A period of five years is foreseen, starting from 2023.

Figure 27 Edda wind's vessel with a LOHC/SOFC powertrain
Source: Østensjø Rederi e.a. (2023)

H_2ship is one of many projects funded by the European Union. It started in January 2021, and they are currently in the planning stage. Their liquid hydrogen powered roro-vessel is planned for delivery by October 2023. A Norwegian company will be operating the vessel. This first vessel will have a 3MW PEM fuel cell. Later scale-up towards 20MW is planned (European Union, 2023a).

5.1.2 Waste heat → eonomiser

25,5 percent of waste heat as seen in Figure 28 would be available for use of LOHC dehydrogenation. This graphic from a paper about waste heat recycle systems on board a 9000 *TEU* container carrier (Pan et al., 2020) further simplifies Figure 25.

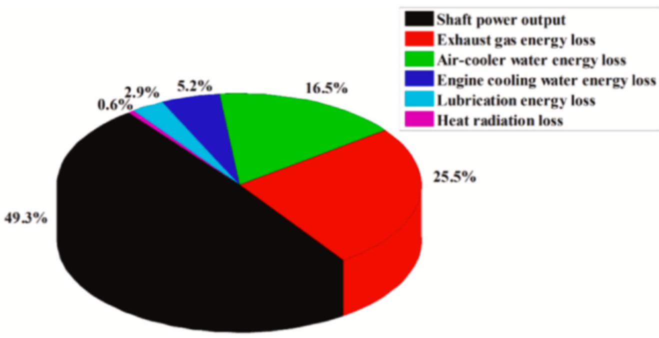


Figure 28 Energy balance of a low speed 2-stroke marine diesel engine
Source: P. Pan e.a. (2020)

Exhaust gas waste heat can be captured by the economiser. A lot of energy is also lost in the cooling water.

5.1.3 Dehydrogenation reactor → buffer tank

After dehydrogenation hydrogen is released. The flow starting here going to the hydrogen propulsion system needs to be controlled. An intermediary compressed storage/ buffer tank can be considered. For this compression there is also energy needed. Which can come from the shaft generator for example. Another option is a service tank with liquid hydrogen, but this seems less interesting. Some examples in the automotive industry like the BMW hydrogen 7 and GM Hydrogen3 reported a maximum storage length of 5 days. Even with very insulated tanks the boil-off is too much of a loss. Liquefying also requires a lot of energy. 37-45% of the lower heating value (*LHV)* is needed.
Compared to compressed storage depending on the pressure, losses go up to 10% of the *LHV* (Van Hoecke et al., 2021).

From this tank a fuel supply system delivers the hydrogen to the engine at correct pressure. Figure 29 below gives an example of hydrogen delivery to a fuel cell.

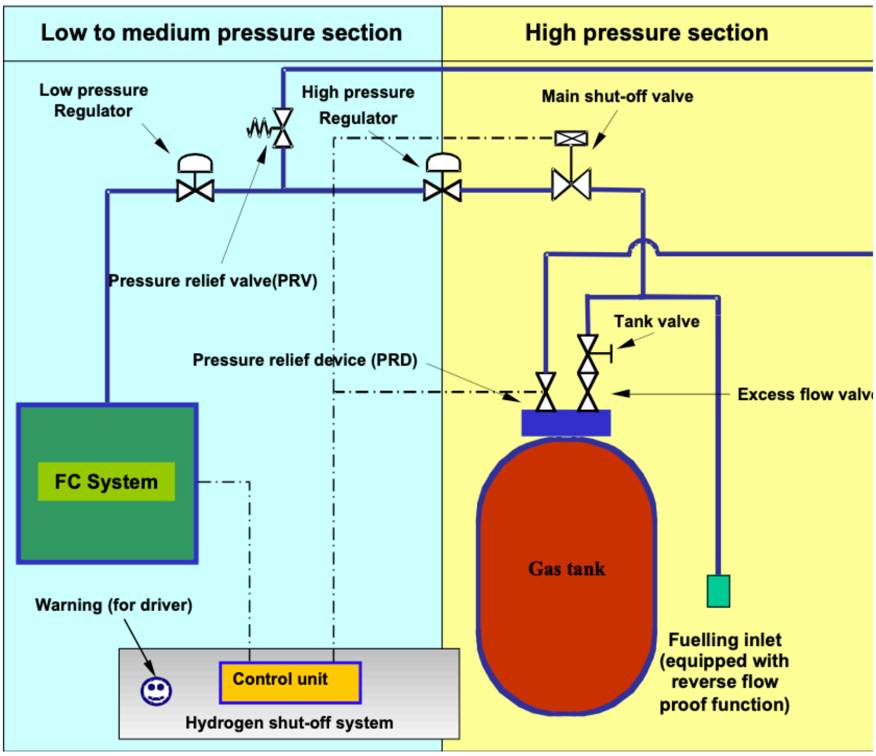


Figure 29 Example of hydrogen fuel supply system in fuel cell vehicle
Source: Van Den Bossche & Van Mierlo (2003)

If a LOHC propulsion system is feasible depends on many factors. Such as propulsion systems, heat recovery systems, reactor efficiencies, etc. The hydrogen release rate should be high enough to keep the system running.

5.2 Lost cargo volume & multiple fuel tanks.

More volume on board is required for the fuel tanks. This also translates to total capacities at bunker ports. Capacities for barges etc. Density-wise there are no exceptionally high values. Most LOHCs have a relative density around one compared to water (Chapter 3).

The main increase in bunker capacity is a result of the big difference in energy density. LOHC can contain 54kg of hydrogen per m^3(for BT). Which is 54kg*120MJ/kg = 6480MJ/m^3. Diesel contains 45,6MJ/kg and has a density of around 840kg/m^3. This results in around 38304 MJ/m^3 (Wikipedia, 2023d); (Innovation, Science and Economic Development Canada, 2018); (Hydrogenious LOHC Technologies, 2023a).
Diesel has roughly six times as much energy in one cubic metre.

There are two main possibilities to take on this challenge. The first one is increasing bunker frequency. Ships often take more fuel on board than necessary for the intended voyage. The other option is an increase in fuel tank volume. The relative share of total displacement of the ship remains limited. On vessels in the range of 100 000 tonnes deadweight only 1-2% of this volume is used for fuel storage (Van Hoecke et al., 2021).

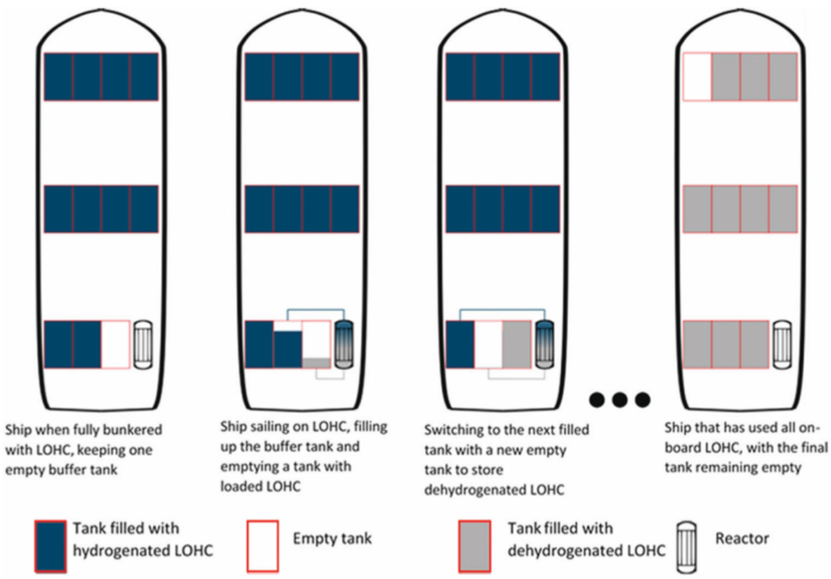


Figure 30 Use of a buffer tank for LOHC fuel systems on board of a ship.
Source: Van Hoecke et al. (2021)

Other alternative fuels all need more space on board. For gaseous products cylindrical tanks are required. Integrating a cylinder in the hull results in unused space. Therefore, these are often placed on deck. LOHC can be stored in regular tanks below deck.
There is one major difference, however. As seen in Figure 30; an extra buffer tank is required for storing used LOHC.

6 LOHC harbour infrastructure

The bunker data of the port of Antwerp-Bruges shows an average of around 4-5.000.000 tonnes of fuel bunkered yearly in Antwerp (Port of Antwerp-Bruges, 2022). This is huge, even when considering a reduction around covid times as seen on Figure 31. When transitioning to renewable fuels, these numbers need to be realistic in terms of “how many days a ship has power from ‘x’ amount of fuel”. Not the exact number of litres needs to be matched due to energy density and fuel consumption (efficiency) differences.

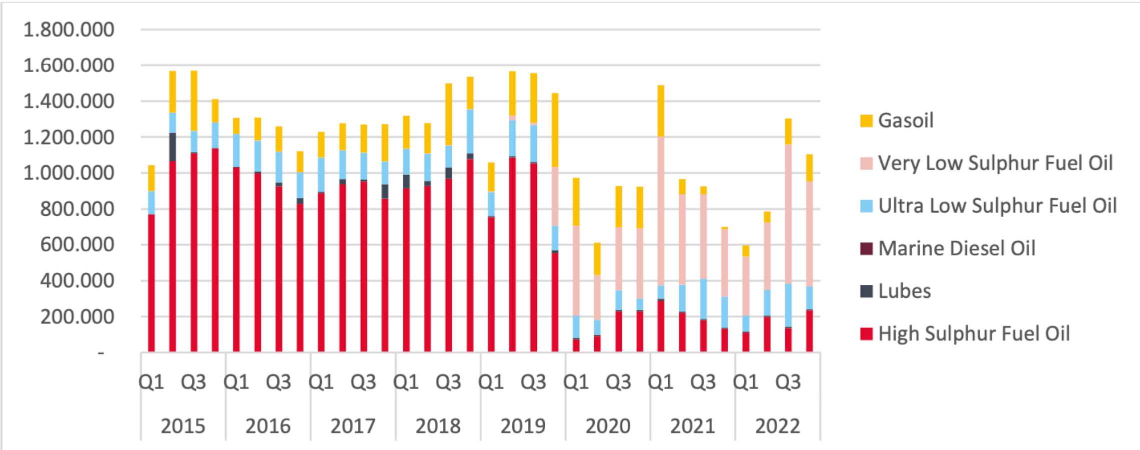


Figure 31 evolution fuel bunkering Port of Antwerp-Bruges: Platform Antwerp
Source: Port of Antwerp-Bruges (2022)

A transition needs to take place gradually. With dual fuel engines this becomes possible. The port of Antwerp-Bruges does not see one fuel as the solution. Methanol, ammonia, liquid hydrogen, LOHC… are all seen as part of the solution. Mentioned options already have well established operating infrastructure at the port today since these products are used in industries other than the transport sector as well. Except for LOHC, DBT is used as a thermal oil on a small scale compared to the other hydrogen carriers.

6.1 Terminal configuration

6.1.1 Tank capacities

To be able to supply the needs of a port like the one of Antwerp-Bruges, terminals need to be equipped with sufficient capacity. Figure 31 gives an idea of the amount fuel that is bunkered in the port.

As mentioned, these figures cannot be translated directly to LOHC to make a prediction of the needed capacity. The energy content of one ton of marine diesel oil differs from one ton of LOHC.

Another issue to make a prediction are the different efficiencies encountered in different propulsion systems. Comparing the fuels based on energy content does not make sense. A better option would be to compare the range on one fuel tank. The amount of energy required for a diesel combustion engine to deliver a certain thrust, is not equivalent to that of a dual fuel combustion engine, pure hydrogen engine, fuel cell, etc.

Re-using fuel is a new concept, which also influences the capacity. Once the hydrogen has left the carrier molecule it needs to be stored again. Total capacity will need to be bigger than the stored volume itself.

This is also the case for ship-to-ship bunkering operations. The barge will need to have the ability to receive used LOHC. The principle of having multiple fuel tanks and a buffer tank as illustrated in Figure 30 can also be adopted for terminals and barges.

The advantage over having two big separate tanks is that the total volume is only increased by the small buffer tank. On the other hand, is doubling the capacity with two equal tanks less complex.

6.1.2 Bunker barge capacities

The capacity of bunker barges corelates to the demand. Thus, it also depends on all what is mentioned above. Almost all renewable fuels will need more volume. This can also be illustrated by Table 7 in Chapter 7; a volumetric energy density comparison of most promising alternative fuels.

6.1.3 Loading-unloading gear

For unloading (ship to shore), pumps of the ship are used. For loading pumps of the shore/ bunker vessel are used. The connection is made at the manifold of the ship. It is possible to only make one connection for multiple tanks and load/ discharge from there. As seen on the illustration from a manifold plan of chemical tanker Gioconda of GEFO's fleet. '*CL'* stands for common line. All tanks are connected to this line. Switching over from tank to tank is done by operating the correct valves. In this manifold it is also possible to connect to all tanks from starboard or portside. This can facilitate mooring operations.

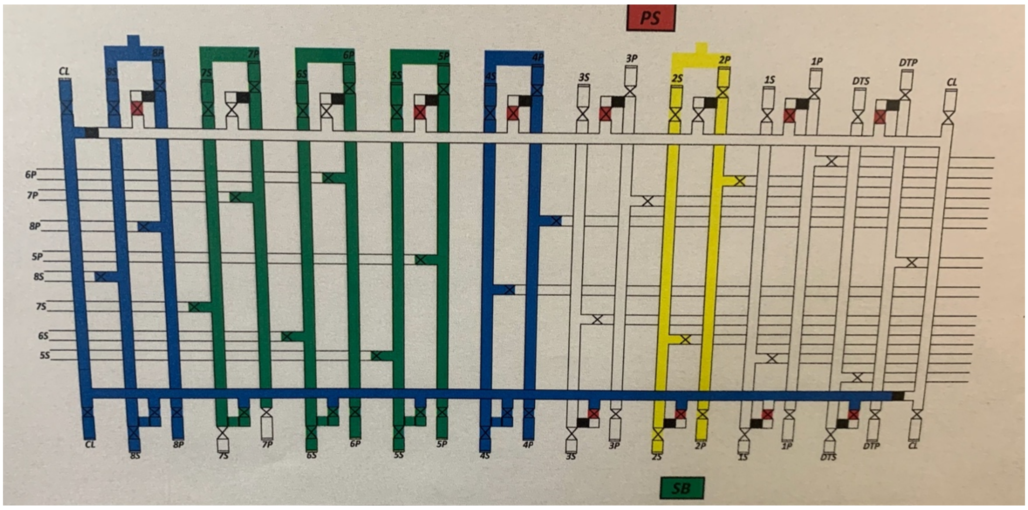


Figure 32 Manifold plan Gionconda
Source: Own work

Loading and unloading at the same time is possible. It's a matter of arranging correct fittings, pipes & valves.

6.2 Operations

The time a ship spends in port is always kept to a minimum for several reasons. Every hour spent alongside costs money. More vessels can be received by a terminal when operations are executed as efficiently as possible. For this reason, bunkering fuel is often done when alongside with a bunker vessel, simultaneously with cargo operations. While LOHC is not as dangerous as conventional fossil fuel, it needs a two-way flow.
Used LOHC needs to be discharged, while fresh H_2-rich LOHC is taken on board. This fact complicates the piping arrangements, but it is possible.

Another option is to split the two flows in separate operations. Which will double the operation time and occupation of a bunker barge. This is not ideal.

6.2.1 Safety measures

Before starting any operations, the material safety data sheet of the product needs to be thoroughly studied by both the shore- and ship side. Or by both ships when doing a ship-to-ship operation (by a bunker barge).

Vopak is part of an equally shared joint venture with hydrogenious LOHC technologies: LOHC Logistix, (Vopak, 2023). The joint venture wants to develop hydrogen transport via LOHC. Starting between Dormagen, Germany, and Rotterdam in The Netherlands. Vopak shared their procedures for handling benzyltoluene and dibenzyltoluene (see Annex).

Their procedures for handling products mainly consider vapour handling and appropriate *PPE* (Personal Protective Equipment). There are four methods for dealing with vapour: vapour processing, vapour return, vapour extraction and an open system. First three options should be considered for products with a high vapour pressure, flammability, or carcinogenicity. An open system is used for lower-risk products regarding exposure and vapour pressure.
A decision for vapour handling and PPE is made based on physical properties and H-phrases.

For LOHC, this amounts to the following:
(Benzyltoluene and Dibezyltoluene were used to determine safety measures as these are used by Hydrogenious LOHC Technologies.)

An open system can be used. The vapour pressure is less than 0,01mbar at 20°C (CHEMGROUP, 2014). Which is very low. The product can be stored without extra requirements. Only standard PPE and chemical resistant gloves.
Standard PPE at Vopak consists of a helmet, safety shoes, safety glasses, and an antistatic flame-retardant boilersuit.
Another important aspect of the terminal is that it is designed to prevent any spills to penetrate the soil. This way if a spill occurs it can be contained and cleaned up. Similar practice is standard on board of ships. Spilling liquid overboard is prevented by installing scupper plugs.

6.2.2 Bunkering LOHC

Bunkering LOHC can be compared to bunkering conventional fuels. For this reason, an explanation of the current checklists is not out of place. Afterwards, any recommendations and adjustments can be made.
The following information is based on a checklist by the *ISGOTT* (International Safety Guide for Oil Tankers & Terminals), (Oil Companies Marine Forum, International Chamber of Shipping, & International Association of Ports and Harbours, 2020).

The checklist is divided in different parts for each stage of the operation.
Part A and B are checks for the planning stage. All personnel must be aware of operations, mooring and fendering arrangement should be agreed. In this stage the bunker plan should also be exchanged. This plan contains details about emergency procedures, who is responsible for which part, and also information about the loading sequence which takes the ship's stability into account (Safety4sea, 2019). The loading sequence of LOHC would be different. Filling up the empty buffer tank, while discharging the first tank of used LOHC.

Part C & D check if the mooring is done correctly. When done incorrectly a spill can occur after breaking the hoses/ loading arm. Emergency procedures are in place for when this would happen so it is possible to react in time. A *SOPEP* kit (ship oil pollution emergency

plan) contains oil absorbent material and booms to keep the oil from spreading. The safety data sheet of a product contains instructions for handling a spill. Information included on a safety data sheet of (di)benzyltoluene is very similar to the information of a *HFO* safety data sheet. Methods for clean-up and containment use absorbent material and booms to contain the spill. The goal is to keep the spilled product on deck, not entering the water. This is the reason why scupper plugs need to be inserted in draining holes on deck. Further in this checklist it will be mentioned as a task as well.
On both safety data sheets is mentioned that the products can have long lasting harmful effects on aquatic life (H410 in the hazard statements).
The main difference is the emphasis on flammability. LOHC is also flammable, but almost all types have a higher flashpoint than HFO, 212°C (DBT) compared to 61°C (HFO). Toluene has a much lower flashpoint at 4°C which is one of its downsides. For this reason, along with other factors this is not a popular choice as LOHC molecule (see Chapter 3) (Hydrogenious LOHC Technologies, 2019); (BP, 2019).

At this stage (part E) in the checklist the ship is now moored to the terminal or barge is alongside. A pre-transfer-conference makes sure both parties have checked communication methods, safety data sheets, designated smoking areas etc. The agreement sheets contain important information about which tanks are going to be loaded, the maximum flow rate, the maximum line pressure. Each tank has its own line, where the volumes that are going to be loaded are described. The operators need to control the flow rates (starting and stopping) according to the values described in this part.
Changing from one tank to the next requires attention of the involved operators and the crew on deck. Correct valves need to be opened and closed.

For LOHC bunkering, tanks with used LOHC would also need to be discharged. Meanwhile ballast operations need to be done to keep the vessel at the correct trim. Most of the time the suction wells for the pumps are situated at the aft part of a tank and a positive trim should be kept (keep the aft draught the biggest).

Part F & Part G are the last pre-bunkering checks. All aspects to prevent spills, explosions or fire are checked. This includes the scupper plugs, overfill alarms, firefighting equipment, etc.

During the operations repetitive checks must be done at regular intervals to assure safe operations. When the previously agreed amounts have been transferred, bunkering is finished. A few post-bunkering checks must be done. Hoses, pipes, and manifold should be drained and correct valves must be closed before disconnecting.

7 From production to consumption at a harbour

7.1 Existing hydrogen infrastructure

Most logical step towards developing a new infrastructure system is by looking at what already exists first. Natural gas pipelines can be used to transport hydrogen. Smaller-scale projects and industries where new technology is slowly taking off can teach a lot. Infrastructure developments can be compared to the ‘chicken and egg theory’. Which one is going to develop first when they both need each other to exist, remains a difficult question to answer.

Japan was the first country to have a hydrogen strategy. In the opinion of the renewable energy institute, they take it a bit too far and are trying to power everything with hydrogen. Not every sector can get priority at the same time, which leads to a delayed transition (Ohno et al., 2022). Japan wants to build a ‘hydrogen society’. Despite these comments, significant investments have already been made. A lot of hydrogen is imported from other countries with the help of a carrier or in liquid form. One of these countries is Australia, where hydrogen is made by brown coal gasification and carbon is captured and stored. This is the only way to provide enough hydrogen until renewable hydrogen production is scaled-up. The world’s first liquefied hydrogen carrier completed a voyage from Australia to Japan in January 2022 (Hydrogen Council, 2022). The ship is part of a project called HESC: hydrogen energy supply chain. She was designed by Kawasaki Heavy Industries

Figure 33 World's first liquid hydrogen carrier
Source: Hydrogen Counci, (2022)

The strategy is to develop consumers first and expect the infrastructure to follow. This way of thinking states that first consumers are needed to get the ball rolling. Later conversion to CO_2-free hydrogen is planned (Iida & Sakata, 2019).

Several car manufacturers already have a hydrogen powered model. Toyota is a pioneer when it comes to fuel cell technology and sells the Toyota ‘Mirai’. A great example of hydrogen supply is seen in Paris with the Hype project. Hydrogen powered taxis (Toyota Mirai) are already driving around today. Air liquid is one of the main investors and a supplier for hydrogen. Different sources are used, and the goal is to increase the share of green production. An advantage of this mix of production methods, is that the demand can increase at a separate rate of green hydrogen production developments. This way the supply will not hold back hydrogen developments for end users. The same principle is used as the Japan hydrogen strategy.

Air Liquide is currently scaling up towards 100+ MW electrolysers, with a 200MW electrolyser under development in France. Worldwide they have already about 35 units in operation, but these are mostly of smaller scale (Yoshihiro & Air liquide, 2022). Electrolyser scale up equals green hydrogen scale up.

Figure 34 Hydrogen powerd taxi in Paris
Source: Varoquier (2019)

European projects are taking off due to EU-fundings: Volvo group, IVECO and Mercedes Benz are working on long range hydrogen powered trucks. Total, Shell, Everfuel, OMV and Linde will provide refueling stations which will be supplied by 8 new electrolysers. This will help to speed up a hydrogen network in Europe (Clean Hydrogen Partnership, 2023).

The list of hydrogen projects receiving fundings goes on. RH_2IWER in Finland is an example, the goal is to develop fuel cell powered vessels for inland navigation. This smaller scale is more interesting to test fuel cell powered ships. Seagoing vessels are generally much bigger and more expensive. A failure would also cost a lot more. They will build six vessels up to 2MW. The project only just started in March 2023. One of the partners is also Air Liquide, so the supplied hydrogen will depend on their used technique. (European Union, 2023b). Another interesting project takes place in Norway. SUSTAINCELL is going to look at fuel cell/ elektrolyser developments and is 100% funded by Europe. This shows how Europe believes in green hydrogen production via electrolysis. (European Union, 2023c)
Again, this will help to speed up infrastructure as hydrogen demand increases.

These projects demonstrate the possibilities. The hydrogen that is needed for the project can almost be seen as a separate project on its own. For example, the French taxis in Paris need to have their own fuel station built. For the long-range trucks, supply also needs to be possible on the used trajectory. When success has been proven these networks will automatically expand. Local electrolysers to supply fuel stations can be a great solution when a source of renewable energy is available. If not, hydrogen must be imported from another place.

Figure 35 Hydrogen tube trailer
Source: City Machine & Welding, Inc (2023)

For distribution in the hinterland tube trailers (Figure 35), pressurized tanks, etc. are used. Distribution by pipelines would show great benefits. No pressurization is needed. Inland vessels would show more flexibility. A private pipeline network of Air Liquide of about 1600km of pipelines is dedicated to hydrogen transport. Natural gas lines are compatible with hydrogen after little to no modification.

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Figure 36 Air liquide hydrogen networks in the north of Europe
Source: Bethoux (2020)

7.2 LOHC + / - flows

Importing & exporting of green hydrogen on a bigger scale will be necessary to supply the whole world with renewable energy. The hydrogen can be seen as a mean to equally spread out the energy contained in electricity from PV and wind power. LOHCs can give the needed flexibility and increase availability for a changing demand.

In part 7.4 the supply of LOHC by ships over long distance, in large quantities will be discussed. LOHC is very suitable for long term storage, thus also for long distance transport. Hydrogenation plants need to fill up these vessels with fresh LOHC, but also need to take back the used LOHC. This concept creates a balance: every ship, consumer or dehydrogenation plant over the world needs to give back an equal quantity of LOHC after using the carried hydrogen. Figure 37 illustrates this concept.

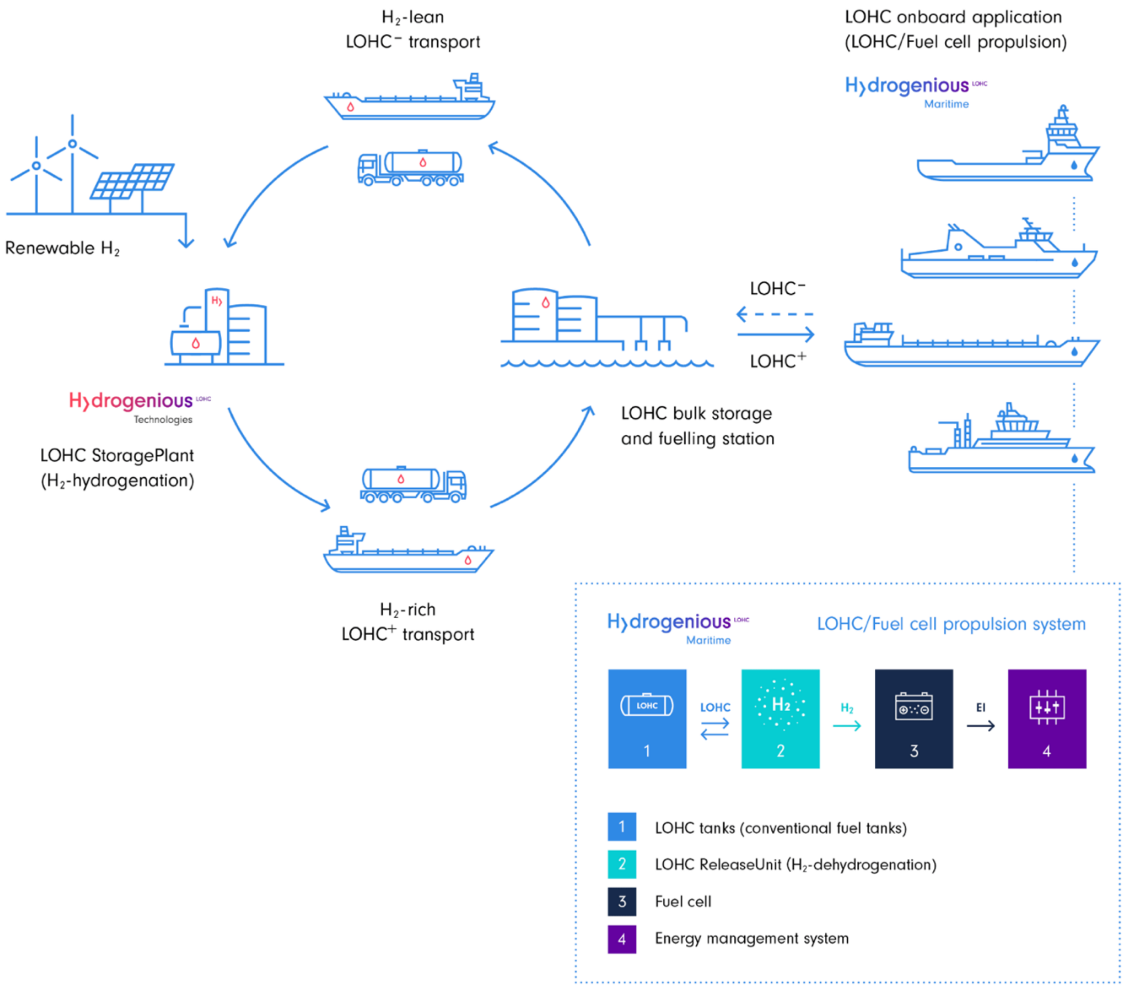

Figure 37 The LOHC cycle, from stationary to mobile maritime application
Source: Hydrogenious Maritime (2023)

When a certain quantity is lost which is possible due to e.g., a spill, the shortage then must be resupplied. This can be done by a ship that has to sail in ballast (empty) to a LOHC production facility.

Then LOHC should be loaded and carried to the hydrogenation plant to resupply its shortage. These trips are also needed when the hydrogenation plant is scaling up. Depending on the availability of the needed resources for LOHC production this extra transportation flow is needed or not

This extra flow can drive up the price compared to alternatives that are consumed as a whole (not dehydrogenated).

With synthetic fuel or ammonia for example, carbon or nitrogen can be supplied or captured at the production site itself.

The location of a LOHC production facility would therefore preferably be close to a hydrogenation plant (or even at the same location). A pipeline can be used instead of supplying by vessels.

7.3 Storage at the hydrogenation plant/ large scale production

For now, the biggest hydrogenation plant is the one that is being built for Hydrogenious in Germany at Chempark Dormagen. The planned capacity is 1800 tonnes of hydrogen that will be stored per year. This means the amount of hydrogen that will be stored in LOHCs. About 50 – 60kg of hydrogen can be stored in one cubic metre of LOHC (see Chapter 3).
One of the investors for this project is Royal Vopak. A company for storing chemicals, fuel oils, … with terminals all over the world. The head office is in Rotterdam. A supply chain will be developed between Dormagen and Rotterdam. These are the first steps towards a LOHC supply chain (Hydrogenious LOHC Technologies, 2021).

7.3.1 LOHC supply

To be able to store hydrogen in LOHC at a hydrogenation plant. A LOHC supply is needed to the hydrogenation plant. Preferably, this plant is located where the hydrogen is produced. See Figure 37 for a visualisation.

Scaling possibilities depend on availability of raw materials and production process.
For DBT and BT production, toluene and chlorine are needed.
Toluene can be made from crude oil by catalytic cracking. Catalytic cracking is a process used in crude oil refining where long hydrocarbons are split in shorter branches. Another option is capturing it as a by-product from coke production from coal. (Fuel cells and hydrogen Joint undertaking, 2019). Above options both use non-renewable resources. Research shows possibilities in renewable production of toluene (aromatic hydrocarbons in general) to become independent of fossil fuels (S. Wang et al., 2021).
However, using crude oil for LOHC production is 'not as bad' since it is not consumed/ burned. And it can be used over and over.

Chlorine is produced by electrolysis using NaCl. Hydrogen is a byproduct of this reaction which can be captured as a bonus (Wikipedia, 2022).
DBT & BT production today happens at small scale. According to a cost estimation study in context of European HySTOC project, there would be no problems to scale up the production. Raw materials (toluene and chlorine) already have a high production rate and are not scarce. (Fuel cells and hydrogen Joint undertaking, 2019)

7.3.2 Hydrogen supply

The purpose of using hydrogen carriers like LOHC is to facilitate transportation. Any compressed or liquified hydrogen transport should be avoided. This would massively decrease the effectiveness of the LOHC system.

Renewable hydrogen via electrolysis is a promising option. Onshore solar and wind power generation facilities can use existing high voltage networks and (converted natural gas) pipelines for distribution.
The electricity from offshore wind farms is transported through long distance subsea cables. Then onshore hydrogen production can supply LOHC hydrogenation.

The other option is offshore hydrogen production. However, the latter prolongs the distance from hydrogen production to the LOHC hydrogenation plant. Otherwise, hydrogenation should also take should also take place at sea. The harsh environment at sea makes everything more difficult. It should also be considered that hydrogen will probably have multiple uses concerning due to competition of a range of hydrogen-based alternative fuels. It seems more logical to only have an offshore electrolyser and do the rest of processing onshore.

This is the area of the cable versus pipeline dilemma (Figure 38).

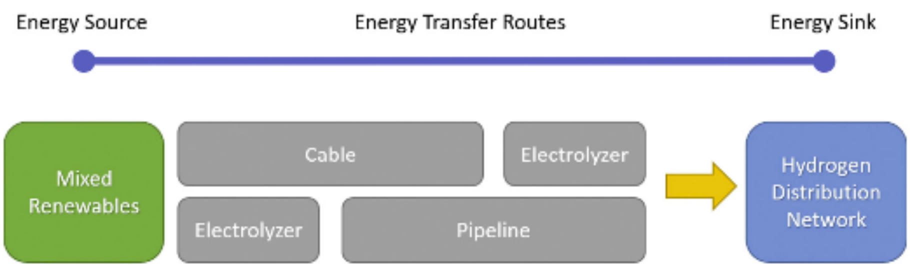

Figure 38 Cable versus pipeline dilemma
Source: Miao, Giordano, & Chan (2021)

Pipeline installation cost is higher than for cables. Cables have internal resistance, higher energy losses are observed, but the operation and maintenance cost is lower than for pipelines. Other factors like transportation length, scale of the market and utilization have an impact (Miao et al., 2021).

Renewable energy transport via cables is more mature for now; C-Power displays a cable in Ostend - Belgium for offshore electricity transportation. A network of 57 km of these cables is already installed for their wind turbines in the North Sea. It connects 54 turbines of each 6,15 MW (C-power, 2023).

Figure 39 C-power Seabed cable
Source: own work

Finally at the location where the hydrogen meets LOHC, hydrogenation takes place. An advantage of onshore hydrogenation would be more possibilities to use the waste heat. If the waste heat is utilized efficiently, the overall efficiency of LOHC could be very high because dehydrogenation only requires a little bit more energy. 10 kWh/ kg hydrogen for hydrogenation compared to 11kWh/ kg hydrogen for dehydrogenation (Hydrogenious LOHC Technologies, 2023b)

7.4 Large scale supply chain

Current traffic of ships is more dense at some places around the world. Where trading routes intersect. Todays' bunkering network is built along these trade lanes at strategic locations. Figure 40 by DNV shows the most common ports around the world where ships bunker new fuel. The amount a ship bunkers depends on the price of fuel at that moment. Fuel tanks (with conventional fuel) are big enough for multiple voyages; therefore, ships are less dependent on bunker hubs. This is an advantage for the shipowners because competition in fuel pricing is created. Future alternative fuels all need more volume and thus an increased bunker frequency. Increase in total volume also means an increase in transported volume.

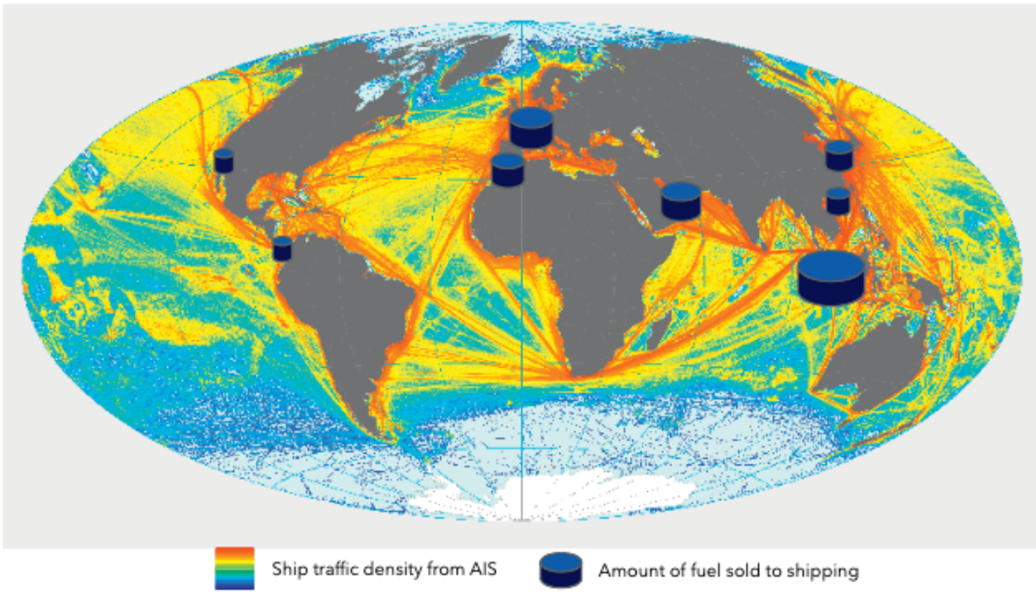

Figure 40 Major bunkering hubs on top of a heatmap of AIS data from ship traffic
Source: Ovrum et al. (2022)

The supply chain of any renewable fuel will be more complicated than the current oil supply. For one renewable fuel there are several different options for its source (biomass, electricity…) And one source is also supplying different kinds of fuel.

This creates a complicated network for energy transport and production. The flow of oil products is not as complex and requires only one direction. From the well to the refinery to the consumer (Figure 41). The direction of used LOHC is a new concept, but also used in a way by other alternative fuels: blue fuels. Blue means the carbon is captured and utilized or stored. These *CCUS* (carbon capture, utilization and storage) add another 'arrow' to the supply chain.

DAC (direct air capture) systems can replace this needed transport when installed at the production plant's location. The advantage of this technique is that it is a sustainable way of capturing carbon. Emitted carbon afterwards is not from fossil fuels and does not need to be captured. This puts the 'extra' LOHC transport in perspective. It shows more 'arrows' in different supply chains are needed, than what it seems at first sight.

Figure 41 A traditional fuel supply chain from energy source to ship
Source: Ovrum et al. (2022)

7.4.1 Ballast voyage versus dehydrogenated LOHC

Above simplification of the oil supply chain leaves out an important aspect for comparison. The ballast voyage of a crude oil carrier (she needs to sail back to the loading port without cargo). The next contract determines where a ship is going, which is usually again on the other side of the world.

An example of such ballast voyage is 23 days from Japan to Saudi Arabia. This data comes from a study using *AIS* (automatic identification system) to map out routes of tankers in ballast vs in loaded condition. (Prochazka, Adland, & Wolff, 2019). Optimisation is possible to minimize to sailing distance and reduce speed to reach certain delivery dates. Everything is connected and has an influence; available tonnage and oil production/ refining rates determine oil price. Digitalization has a lot of potential to optimize this supply & demand system. Both for current and future fuels.

This shows the supply chain of LOHC has more in common with the crude oil supply chain than what it seems. The main difference is the ballast voyages for an oil supply chain are replaced by dehydrogenated LOHC. The ballast voyage is replaced by a laden voyage. Worth mentioning is the dehydrogenated LOHC has a small difference in weight; For hydrogenated LOHC 5 – 7,2 percent of the weight of the carrier itself should be added (Van Hoecke et al., 2021).

The consequence of this main difference with the oil industry (the laden voyages) translates to a higher fuel consumption. A study looking the effect of periodic hull cleaning shares real data of an anonymous ship (ballast versus laden consumption). Speeds in ballast or loaded are usually not the same and depend on a lot of factors. For example, the effective fleet size is reduced when speed is reduced. This has an influence on the supply/ demand-balance and influences shipping costs for buyer and seller.
Speeds between 12 and 14knts gave an average of daily consumption of 37,79 tonnes loaded and 31,74 tonnes in ballast (Adland, Cariou, Jia, & Wolff, 2018). When in ballast this translates to a reduction of about 16%, this component cannot be overlooked.

Recently CWP Global and Hydrogenious LOHC Technologies partnered up. The main project of CWP Global has its focus on green ammonia. They are going to study the feasibility of a LOHC supply chain between Morocco and Europe. The goal is to transport 500 tonnes of green hydrogen per day (Sowmya, 2023).

7.4.2 A diversity of fuels

As explained in previous chapters a lot of different fuels are developing which will probably result in a mix of fuels. Fuel mix and infrastructure go hand-in-hand. Every fuel needs its own infrastructure, some already existing and others still need a lot of progress.
LOHC and methanol can use existing infrastructure with some minor adaptations. Ammonia has a substantial amount of infrastructure in place, but not for ship-to-ship bunkering. This is a major benefit LOHC and methanol have. With only minor adaptations the existing bunker vessels can be converted. Here lies a specific difficulty for LOHC; the bunker vessel must be capable of receiving used LOHC. It is a bit more complicated than pumping in only one direction. See 6.2 ‘operations’ for more information.

A comparative study has been done recently comparing the energy efficiency of maritime supply chains of the biggest candidates for the energy transition (Song et al., 2022). The following fuels where compared: liquid hydrogen (LH_2), ammonia ($\mathrm{NH_3}$), methanol (CH_3OH) and liquified natural gas (*LNG*). In the context of being climate friendly/ renewable natural gas is not really an option, only when it is created from renewable sources like biomass which has its limitations as seen in chapter 2.

They were compared on different 'sub-processes'; production, liquefaction, storage, loading, transportation and unloading. To have a constant reference the same vessel size and average voyage length etc was taken to compare.

To sum up the conclusions: LNG was the most efficient when considering the other fuels need natural gas for their production. They need hydrogen which is created from natural gas by a process called *SMR* (steam methane reforming). This process uses a lot of energy. When using a renewable energy source for production, the other three (LH_2, NH_3, CH_3OH) suddenly became very competitive (because previously LNG was used to produce the other options, instead of renewable hydrogen). Renewable hydrogen is made by electrolysis which is very efficient.
The cargo handling system has a big impact on the feasibility of a fuel. Trade is necessary for importing renewable energy from places on earth that have high wind and solar capabilities. The main reason for a reduction in efficiency for all fuels, is the boil-off gas (*BOG)*. Therefore, LNG and LH_2 are not suited for long term energy storage since they have higher boil-off rates *(BOR)*. Ammonia has a more acceptable boil-off rate. Methanol has a boiling point of about 65°C at ambient pressure. It can be handled and stored as a liquid and does not create any boil-off gas. A very good option for long term energy storage.

Another consequence of LH_2 and LNG having the higher boil-off rates are an increase in sensitivity to ambient temperatures, pipe length, etc where ammonia and methanol see very little effects as illustrated on F.

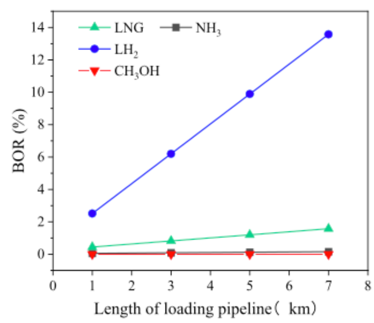

Figure 42 the effect of length of loading pipe on BOR and energy efficiency
Song et al. (2022)

This also means these two get the biggest jump in efficiency when a BOG handling installation is used. This inevitably results in a drop of efficiency compared to methanol which does not need any BOG handling. Downsides of liquefied cargo keep adding up, their cargo tanks need to be cooled before loading which complicated procedures and again consumes energy. More insulation reduces the volume in a tank etc.

7.4.3 Comparing LOHC to methanol

Final conclusion states methanol has the most efficient supply chain with a close second for ammonia. These options are also more suited for long term storage.
For all fuels a bigger vessel means a higher efficiency, even for the options that create more boil-off gas when the surface of the liquid is bigger. The propulsion system also needs more energy, but these factors are offset by the much bigger amount that is transported at once.
The properties of methanol that make it so efficient are also seen with LOHC's. The main difference on efficiency can be found in its production and energy density. Following table is made to give more context on the energy content (by using the lower heating values) in one cubic meter of some of the most popular/ promising fuels (Air Liquide, 2023); (Wikipedia, 2023e); (Hydrogenious LOHC Technologies, 2023a); (Gas Encyclopedia Air Liquide, 2023).

Table 7 Volumetric engergy density comparison
Source: own work

	Liquid hydrogen (120MJ/kg)	Liquefied natural gas (45MJ/kg)	Methanol (20MJ/kg)	Ammonia (19MJ/kg)	LOHC – hydrogen rich(H12-BT)
MJ/m^3	71kg/m^3 = 8520MJ/m^3	+- 455kg/m^3 = 20 475MJ/m^3	+- 748kg/m^3= 14960 MJ/m^3	+- 682kg/m^3= 12958MJ/m^3	54kgH_2/m^3 = 6480 MJ/m^3

8 Conclusions

Hydrogen will have an important role as an energy carrier in the energy transition. More and more projects are launched. Technology for hydrogen transportation and storage is a hot topic. The need for a solution to bring supply of renewable energy sources and demand in balance is the source of major research. Any possibility to capture, store and transport energy is the holy grail.

For now, renewable energy has scaling issues. There is an enormous market of fossil fuels that needs to be replaced. Different pilot projects are demonstrating the role of hydrogen in various sectors.

The number one benefit of liquid organic hydrogen carriers is the ease of handling, they make a very difficult product like hydrogen easy to handle.
Safety procedures are standard, pressures are atmospheric, flammability is very limited, an open system for vapours can be used etc. Long term storage of hydrogen is also possible. Existing infrastructure is ready to use with minor adaptations to handle a two-way flow. This flow of hydrogen rich and hydrogen poor LOHC translates to the entire supply chain.

The maritime industry is not a frontrunner in new technologies. Vessels are serious investments and have a lifespan of about 25 years. Industries that are less capital-intensive take steps into the unknown more easily. Scale up from smaller projects to the whole (maritime) industry takes time. International trade confronts shipowners with the need for global availability of alternative fuels before they can be used.

Regulations can push technological evolution. For the maritime industry this is the IMO. A lot of different methods for reducing emissions exist. Some have advantages over others. But not one stands out as a clear winner yet.
The best, most efficient solution cannot be chosen based on a scientific comparison. The evolution of different options does not happen at the same rate. Some are ahead, some are behind. Advantages & disadvantages are difficult to compare because they are in different areas with each fuel. A choice has to be made which areas are more important; toxicity, handling, production impact, carbon content, worldwide availibiity, etc. LOHC scores relatively good on all areas.

Energy density is not the highest, but still better than compressed hydrogen storage.

A mix of fuels is more probable than one ‘winner’. Renewable hydrogen is an ingredient in most alternative fuels. LOHC was studied as a hydrogen carrier and developing infrastructure seems feasible. On-board LOHC propulsion systems are in the infant stage, while other fuels are already way further in their developments, testing and even operational.

More projects are needed to gain knowledge beyond literature. Maritime LOHC projects are very limited. The maturity of LOHC technology is lacking compared to most alternatives.

Still LOHCs have an enormous potential. It is important to recognize this and follow up (the very limited) projects.
Efficient MW-scale fuels cells are an interesting area of research to help reduce the effect of a lower energy density. Reactor development with specific attention for application on board is relevant. Projects are planned and will provide interesting data.

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10 Annex

Van:
Onderwerp:
Datum:
Aan:
Kopie:

Dag Elian,

Dag Elian,

In de beoordeling van de producten, aangaande welzijn en milieu, houden we vnl. rekening met de mogelijke vrijstelling van dampen en de hierbij benodigde technische aspecten m.b.t. de installatie en het gebruik van persoonlijke beschermingsmiddelen

Deze aandachtspunten worden aan de hand van de producteigenschappen (o.a. fysische gegevens en de H-zinnen) bepaald; in eerste instantie komende uit de e-SDS van de klant.

Naar behandeling van dampen zijn er 4 mogelijkheden:

- Dampverwerking
- Dampretour
- Dampafzuiging (naar veilige locatie)
- Open systeem

Naar welzijn van de medewerkers toe kunnen, afhankelijk van de H-zinnen en de fysische eigenschappen van het product, technische voorzieningen aan de installatie geëist worden. Tegelijkertijd kunnen de persoonlijke beschermingsmiddelen vastgelegd worden.

Naar luchtemissies zijn de dampspanning bij 35°C, het vlampunt, informatie over de geurproblematiek en cancerogeniteit belangrijk.

Voor de producten die je in bijlage hebt meegestuurd komt dit op volgende neer:

1) Benzyltoluene *

Het product is geklasseerd als irriterend bij huidcontact en aspiratiegevaarlijk. Vlampunt 137°C.

Er is geen grenswaarde naar bloostelling toe en het product heeft een zeer lage dampspanning (< 0,01 mbar a 20°C). Dit mag in open systeem behandeld worden.

Naar persoonlijke beschermingsmiddelen toe schrijven wij voor onze manipulaties enkel de standaard PBM en chemiehandschoenen toe. Extra PBM of adembescherming zijn niet nodig.

Dit product kan in opslag genomen worden zonder bijkomende voorwaarden. Volgens de SDS is het naar transport toe niet gereglementeerd.

**Aandachtspunt: De SDS in bijlage is vermoedelijk een Amerikaanse en al ouder dan 5 jaar.*
Volgens REACH wordt dit product ook geclassificeerd als (H410) milieugevaarlijk met langdurige / chronische gevolgen (https://echa.europa.eu/nl/home).

2) Dibenzyl toluene

Het product is geklasseerd als aspiratiegevaarlijk. Vlampunt 212°C.

Er is geen grenswaarde naar bloostelling toe en het product heeft een zeer lage dampspanning (< 0,01 mbar a 20°C). Dit mag in open systeem behandeld worden.

Naar persoonlijke beschermingsmiddelen toe schrijven wij voor onze manipulaties enkel de standaard PBM en chemiehandschoenen toe. Extra PBM of adembescherming zijn niet nodig.

De densiteit van het product is niet weergegeven in de SDS, dus moet nagevraagd worden. De vullingsgraad en het high-level alarm moeten aangepast worden indien de constructiesterkte van de tank lager is dan de densiteit van het product.

Indien de densiteit ok is, kan dit product in opslag genomen worden zonder bijkomende voorwaarden.
Volgens de SDS is het naar transport toe niet gereglementeerd.

**Ook hier aandachtspunt: De SDS in bijlage is vermoedelijk een Amerikaanse. Volgens REACH wordt dit product ook geclassificeerd als (H410) milieugevaarlijk met langdurige / chronische gevolgen (https://echa.europa.eu/nl/home).*

Hopelijk kan je hiermee verder.

Succes met je thesis.

Met vriendelijke groeten, Kind regards, Cordialement,

Vopak