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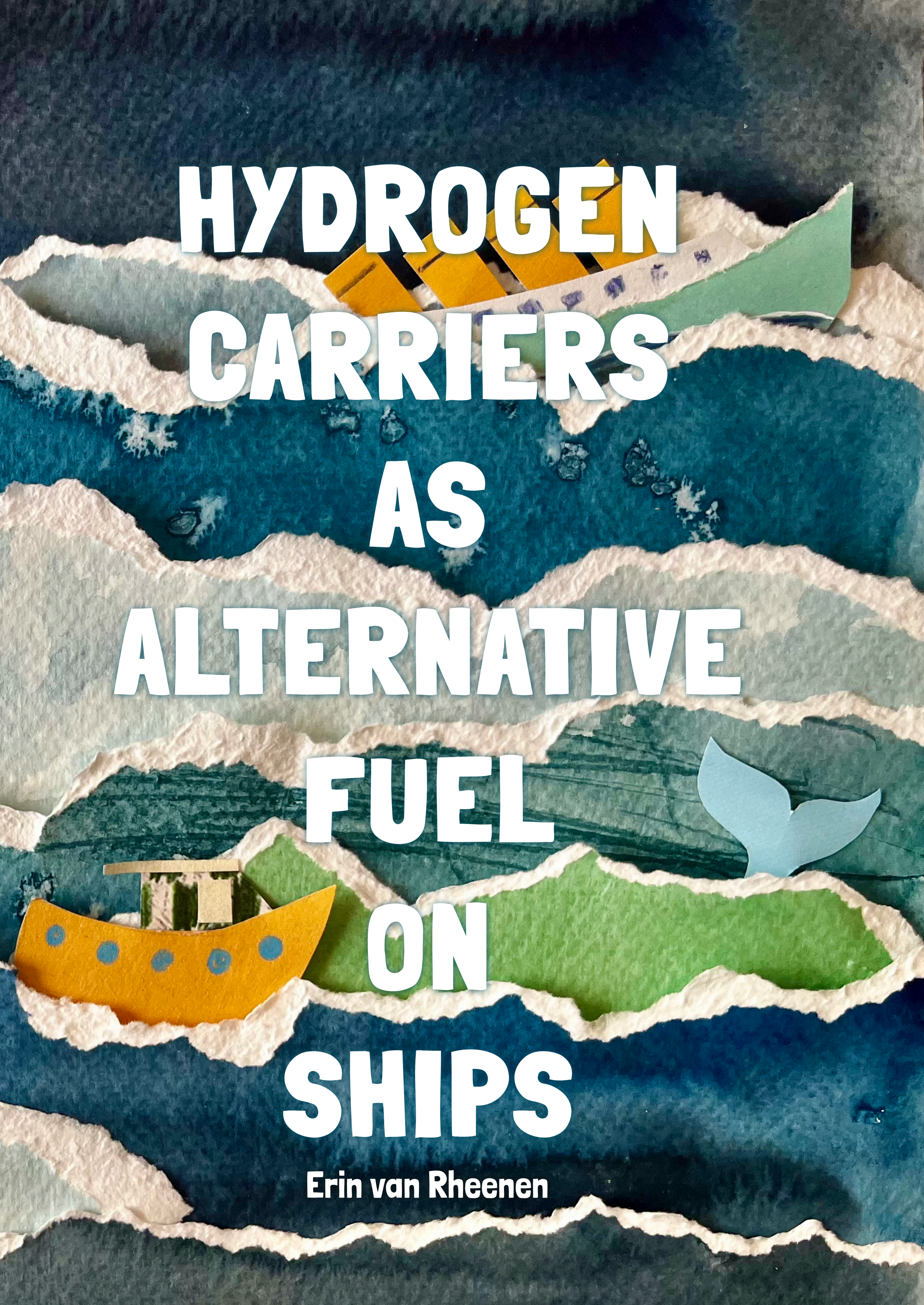

HYDROGEN CARRIERS AS ALTERNATIVE FUEL ON SHIPS

Erin van Rheenen

Propositions

accompanying the dissertation

HYDROGEN CARRIERS AS ALTERNATIVE FUELS ON SHIPS

by

Erin Susanna VAN RHEENEN

1. Going back in time in terms of design regarding old load capacities and increased size of propulsion systems is a necessity for the shipping industry to become sustainable. How far to go back in time depends on the alternative fuel chosen *(based on this dissertation)*
2. Alternative fuels such as hydrogen carriers score highly on many values, but fail on the most important value of all: timeliness *(based on this dissertation)*
3. In the context of alternative fuels for shipping, safety is a relative value: a fuel that increases safety for the marine environment will reduce it for the crew *(based on this dissertation)*
4. In maritime propulsion, pursuing a single alternative fuel as a universal solution is counterproductive *(based on this dissertation)*
5. To enhance safety, investigating and sharing about near misses is more important for the shipping industry than investigating disasters
6. The Global South is often ignored in the maritime industry; yet a successful and safe energy transition in the maritime industry requires the interests of both the Global South and North to be taken into account
7. Interdisciplinary work is said to be in high regard, but in practice not valued at all
8. The Arabian horse, prince of the winds, can blow away all ones sorrows, or fiercely increase them. There is no in between
9. In an environment governed by values that differ from your own, you have to either accept acting against your personality or accept not reaching your goal at all
10. Perfectionism is the main enemy of good enough. To reach a goal, perfectionism is a nuisance, good enough will do the job.

These propositions are regarded as opposable and defendable, and have been approved as such by the promotors prof. dr. ir. J.T. Padding and dr. A.A. Kana.

HYDROGEN CARRIERS AS ALTERNATIVE FUELS ON SHIPS

HYDROGEN CARRIERS AS ALTERNATIVE FUELS ON SHIPS

DISSERTATION

for the purpose of obtaining the degree of doctor
at Technische Universiteit Delft,
by the authority of the Rector Magnificus
prof.dr.ir. H. Bijl,
chair of the Board for Doctorates,
to be defended publicly on
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BY

Erin Susanna VAN RHEENEN

This dissertation has been approved by the promotors.

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SH2IPDRIVE
HYDROGEN FOR MARITIME

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Niet meer zijn wij dan
schippers van uw dromen
Geen commandanten
maar lieden die het anker lichten
en dan met trossen los
de steven richten
naar wond're havens waar
slechts zelden mensen komen

Pierdomenico Baccalario

PREFACE

When I started this project, I knew very little about ships. Of course, I did know about the Titanic, the unsinkable ship. While trying to learn more about the shipping industry in general, I, of course, also looked at the Titanic and was astonished at the pride the designers had when saying the ship was unsinkable. In Dutch, we have a saying, *hoogmoed komt voor de val* (Pride goes before the downfall). However, the disaster of the Titanic was in 1912; we are now 100 years later, so I was certain we had learnt several lessons from it. Over time, I realised that this was perhaps too optimistic. It started small, with sentences like: "These [insert chemical] are considered safe". I often found sentences like these in papers, as little more than a side note. Safety is important, so it is mentioned, and then the authors would continue with their main message. But the sentence triggered me; I wanted to know why these chemicals were considered safe. And then it dawned on me, what is safe? How do we define safety in a maritime context?

Slowly but steadily, this question became more pressing. I asked around, but I never received very clear and concrete answers. So, I decided to look into it myself. Only then did I start to understand the size of the rabbit hole I was falling into.

So, over time, a large part of my research shifted towards safety. After all, when we transport thousands of tonnes of fuel, we must also realise that we will transport thousands of tonnes of alternative fuel. And it is of the utmost importance that we do this in a safe (whatever it may mean) and sustainable way. Future, alternative fuels should not become the bane of our existence.

Somewhere in that rabbit hole I began to see a delicate balance emerging. These new alternative fuels carry the promise of being both more sustainable and safer than the systems we rely on today, yet their novelty naturally brings uncertainties with it. They behave in ways we have not fully charted, and the challenge lies in acknowledging those uncertainties without letting them eclipse the potential these fuels hold.

I am very happy that my supervisors understood this as well and encouraged me to explore it further. As I dug deeper, I realised that even though we have come far, there is still much to learn. Enhancing safety comes from a large part from learning from mistakes in the past, and only a small part of totally novel things. But how much have we really learned from our past? How much have we learned from safety science, a research topic with lessons we appear to ignore? How much have we learned from aviation, which should have similar issues, but counters by saying these are no issues at all for them? How much have we learned from maritime disasters in the past? The Titanic was supposed to have watertight compartments. The Edmund Fitzgerald, built in the 1950s and sank 50 years ago in 1975 in a November gale, did not have watertight compartments in her hold, which may have contributed to her sinking. Although 50 years may seem like a long time, the memory of the Edmund Fitzgerald remains very much alive in the Great Lakes region.

Now that we stand on the brink of a new era of alternative fuels, this is our opportunity to do better. By understanding the past and embracing the lessons of safety science, we can ensure that the fuels of tomorrow do not become the hazards of tomorrow. It is my hope that this work contributes, even in a small way, to that journey. The path to a better world begins with the choices we make today.

SUMMARY

The shipping industry is responsible for a approximately 2 to 3% of the global greenhouse gas emissions. The International Maritime Organization (IMO) has set a goal in 2023 to reduce these emissions. This goal entails that the sector becomes net-zero by 2050, which should be partly realized by adding alternative fuels to the energy mix. In general, methanol, ammonia and hydrogen are considered as promising alternative fuels. However, all three have challenges, such as toxicity (methanol and ammonia) or explosivity (hydrogen). Additionally, none of them have volumetric and gravimetric energy densities that are close to the current standards of heavy fuel oil (HFO) and marine diesel oil (MDO).

Hydrogen carriers can solve these challenges. Hydrogen carriers are chemicals that store and release hydrogen on demand. There is only very little pure hydrogen gas on board, which reduces safety risks. Additionally, hydrogen carriers can store a relatively large amount of hydrogen, up to over 20 wt%, enhancing the volumetric and gravimetric energy density. Finally, the inherent properties of each hydrogen carrier determine their applicability. Since some carriers behave similarly to oil, they offer a significant advantage for existing bunkering and fuel-transport infrastructure.

This thesis looks at hydrogen carriers as alternative fuels on ships. As safety and size of the overall system are the most important values for successful integration on a ship, these are the two main themes of this thesis. In this way, the thesis identifies the optimal combinations of hydrogen carriers and energy converters for different types of ships, such as container vessels, fishing vessels or ferries.

The research objective of this thesis is to identify and evaluate optimal combinations of hydrogen carriers and energy converters for various ship types, with a focus on technical feasibility and safety considerations.

To reach this goal, a selection and evaluation of hydrogen carriers in general is made. Many different hydrogen carriers are classified into categories, based on their chemical and physical characteristics. This way, choices regarding promising hydrogen carriers can be made for large groups of substances at the same time, reducing the required time and energy. Of these categories, two

appear to be promising for the shipping industry, namely liquid organic hydrogen carriers (LOHCs) and boron-based carriers. The LOHCs are extremely similar to current fuels and often safer, despite having a relatively low (6-7 wt%) energy density. The boron-based carriers, sodium borohydride (SB) and ammonia borane (AB) are powders, making them more difficult to handle, but they have extremely high energy densities (around 20 wt%).

The next part of this thesis deals with the technical and system-level evaluation. The effective energy densities of these carriers are calculated and enhanced by using heat integration. The size (both in weight and volume) of these total systems are assessed. This analysis results in the energy density and power density of these carriers. Finally, these carriers are then technically evaluated on their use for different ship types, as each ship type has its own operational needs.

From a safety perspective, the hydrogen carriers are evaluated as well. Starting with a hazard identification to determine the most pressing issues, several maritime related advantages and disadvantages are investigated, both from a theoretical and an experimental perspective. Next, the importance of safety from a design and operational perspective is discussed. Finally, to make an overarching assessment of these hydrogen carriers on safety and sustainability, they are assessed on many values relating to these two value-sets.

The main technical finding is that hydrogen carriers can reach sufficiently high energy and power densities for use on ships. The additional equipment is unlikely to be a large issue, as this equipment does not occupy significant space. LOHCs can achieve improved energy densities through proper waste heat integration; however, these remain relatively low; approximately a factor of five lower than conventional fuels such as MDO. The energy density of the boron-based carriers, especially ammonia borane (AB), is almost on par with MDO, with differences of roughly a factor 1.4 by mass and 3 by volume. However, because the spent carrier must also be stored onboard until offloading, the overall effective difference (both volume and weight based) is approximately a factor of two. This results in very good compatibility with ship's operational needs. Thus, it is also clear that these fuels can be used on various different types of ships, ranging from large container vessels to ferries.

Regarding safety, it is important to realise that some specifics remain unknown today, owning to the novelty and low production amount of these fuels; they do not need to be checked thoroughly, as dedicated by ECHA's REACH system. This results in a very limited ability to actually assess these fuels on safety.

Furthermore, specific maritime hazards are missing as well. For example, spill behaviour of these carriers was unknown. Experiments showed that LOHCs are hard to detect in (sea)water, and empty LOHCs usually sink, while full LOHCs float. Clean up is thus extremely difficult. SB and AB would theoretically react with seawater, albeit in a slower rate than with normal water. However, experiments showed that AB does not react at all with seawater (nor fresh water) without catalysts. SB, on the other hand, reacts faster with seawater. Finally, the spent fuels of SB and AB could theoretically be used as mitigation against impact, as these powders are fire-reducing.

Finally, comparing all these alternative fuels in terms of safety is nearly impossible as safety is multi-faceted. Each value varies in importance across different maritime environments and depending on own personal values, so the framework provides context-specific assessments rather than universal rankings. In the end, it appears that many carriers exhibit mixed or uncertain aspects, with no clear "best" option emerging. However, these findings underscore the importance of value-based reasoning and stakeholder dialogue.

To assess the perfect hydrogen carrier, all the above-mentioned values are of importance, from safety for the crew to environmental impact, from energy and power density to long-term viability, justice and economic impact. Some of these values are assessed in more detail in this thesis than others, but all of them influence the choice of hydrogen carrier. However, in the end it may be that one value trumps them all: timeliness. The shipping industry is much like a large container vessel: slow-moving, hard to alter but set on a clear course so the lock-in of alternative fuels may well occur. Once a choice is made, it is likely to persist. So, for hydrogen carriers to become part of the mix, the most important thing is that they are on time. Too late could easily become never, which would be a shame, as these hydrogen carriers have shown to be extremely promising as alternative fuels to make the shipping sector more sustainable.

SAMENVATTING

De scheepvaart is verantwoordelijk voor een significant deel van de wereldwijde uitstoot van broeikasgassen. In 2023 heeft de International Maritime Organization (IMO) daarom als doel gesteld om deze uitstoot sterk te verminderen. Gewenst is dat de uitstoot naar net-zero gaat rond het jaar 2050. Dit moet gedeeltelijk bereikt worden door het gebruik van alternatieve brandstoffen, naast conventionele brandstoffen. Ammoniak, methanol en waterstof worden vaak gezien als mogelijke opties voor alternatieve brandstoffen in de scheepvaart. Deze drie brandstoffen hebben echter alle drie eigen uitdagingen, zoals toxiciteit (ammoniak en methanol) of explosiviteit (waterstof). Daarnaast hebben alle drie deze brandstoffen veel lagere energiedichtheden, zowel in volume als in gewicht, die niet in de buurt komen van de energiedichtheiden van de huidige, conventionele brandstoffen zoals mariene diesel (MDO) en zware stookolie (HFO).

Waterstofdragers zouden deze uitdagingen, zowel veiligheids- als energietechnisch, op kunnen lossen. Waterstofdragers zijn chemicaliën die waterstof kunnen opslaan en weer kunnen loslaten wanneer dit gewenst is. Er is daarom maar weinig puur waterstofgas aan boord, en veiligheidsrisico's worden zo verminderd. Daarnaast kunnen waterstofdragers vrij grote hoeveelheden waterstof opslaan per gewicht (tot meer dan 20 wt%) en volume; zo wordt de energiedichtheid van het geheel hoger. Omdat de waterstof is opgesloten in de waterstofdrager, zijn het de chemische en fysische eigenschappen van de waterstofdrager die hun toepasbaarheid bepalen. Sommige waterstofdragers, bijvoorbeeld, lijken veel op olie. Dit betekent dat de huidige opslag en bevoorradingsstructuur gebruikt kan worden, wat zeer voordelig is.

Deze thesis kijkt naar waterstofdragers als alternatieve brandstof op schepen. De twee hoofdonderdelen van deze thesis zijn veiligheid en de grootte en gewicht van het systeem, aangezien deze bij de belangrijkste waarden horen om deze dragers succesvol te implementeren op schepen. Op deze manier kan deze thesis de optimale combinaties van waterstofdragers en energieomzettingssystemen identificeren voor verschillende scheepstypes.

Het onderzoeksdoel van deze thesis is het identificeren en evalueren van optimale waterstofdrager en energieomzettingssysteem combinaties voor

verscheidene scheepstypes met een focus op technische haalbaarheid en veiligheid.

Om dit onderzoeksdoel te bereiken, wordt als eerste een selectie en evaluatie van waterstofdragers gemaakt. Een grote hoeveelheid waterstofdragers wordt opgedeeld in categorieën, gebaseerd op hun chemische en fysische eigenschappen. Zo kunnen veel verschillende waterstofdragers snel en eenvoudig worden beoordeeld op hun bruikbaarheid. Twee van deze categorieën lijken zeer veelbelovend te zijn voor de scheepvaart. Dit zijn vloeibare organische waterstofdragers (LOHCs) en waterstofdragers gebaseerd op boor. De LOHCs lijken heel erg op huidige brandstoffen, in de zin dat het ook een soort oliën zijn, echter zijn ze over het algemeen veiliger, maar wel veel minder energiedicht dan huidige brandstoffen. Zij slaan ongeveer 6 tot 7 wt% aan waterstof op. De waterstofdragers gebaseerd op boor zijn natriumboorhydride (SB) en ammoniak boraat (NH3BH3, AB). Deze twee stoffen zijn poeders, wat het gebruik bemoeilijkt, maar hebben zeer hoge energiedichtheden (tot ongeveer 20 wt%), in de buurt van huidige brandstoffen.

Het volgende deel van de thesis evalueert de technische haalbaarheid op een systeemniveau. De effectieve energiedichtheden, dat wil zeggen de energie dichtheid van de waterstofdrager wanneer gecombineerd met een energieomzettingssysteem, worden berekend en geoptimaliseerd door gebruik te maken van overtollige warmte. De grootte en het gewicht van het totale systeem kan vervolgens worden berekend. Deze analyse resulteert in de energiedichtheid en vermogensdichtheid van het totale system. Vervolgens wordt dit gebruikt om de waterstofdragers te evalueren op hun bruikbaarheid voor verschillende scheepstypes, aangezien elk scheepstype een eigen set van eisen heeft.

Het derde deel van de thesis behandelt de veiligheid van waterstofdragers. Dit deel begint met een identificatie van alle mogelijke gevaren die gepaard gaan met waterstofdragers. Op deze manier worden de meest belangrijke problemen in kaart gebracht. Daarna worden verschillende voor- en nadelen met betrekking tot het gebruik van deze waterstofdragers in een maritieme context behandeld, vanuit een theoretisch en experimenteel kader. Het belang van veiligheid voor zowel een ontwerp als operationeel perspectief wordt ook bekeken. Dit deel van de thesis eindigt met een alomvattende beoordeling van waterstofdragers voor veiligheid en duurzaamheid en de daar bijbehorende waarden.

De technische evaluatie laat zien dat waterstofdragers voldoende energie en vermogensdichtheid kunnen leveren om gebruikt te worden op schepen. De uitrusting die extra benodigd is voor het gebruik van waterstofdragers zal hoogstwaarschijnlijk geen problematisch ruimte (of gewichts)beslag opleveren. De energiedichtheid van de LOHCs kan sterk verbeterd worden met goede warmte integratie, maar blijft lager wanneer vergeleken met de andere waterstofdragers of MDO (ongeveer een factor 5 lager dan MDO). De energiedichtheden van de andere waterstofdragers, SB en met name AB, komen dicht in de buurt van MDO. Zij zijn ongeveer 1.4 maal (gewicht) en 3 maal (volume) minder energiedicht dan MDO. Wanneer echter ook rekening wordt gehouden met de opslag van de lege waterstofdrager aan boord, verandert dit in een effectief verschil van ongeveer een factor twee voor zowel massa als volume ten opzichte van MDO. Deze waterstofdragers kunnen daarom goed voldoen aan de operationele eisen van schepen. Dit betekent dat zij toepasbaar kunnen zijn op verschillende scheepstypen, variërend van veerboten tot grote containerschepen.

Wat veiligheid betreft is het belangrijk om te realiseren dat sommige specifieke kenmerken helaas onbekend zijn. De waterstofdragers zijn erg nieuw en worden in kleine oplage geproduceerd. Hierdoor vallen ze onder minder strenge eisen dan andere stoffen, volgens het REACH systeem van ECHA. Dit resulteert in minder mogelijkheden om deze brandstoffen correct te evalueren op veiligheidsgebied.

Daarnaast missen veel specifiek maritieme veiligheidsaspecten. Het gedrag van deze waterstofdragers bij lekkage is bijvoorbeeld onbekend. Experimenten lieten zien dat LOHCs lastig te detecteren zijn in (zee)water, daarnaast drijft de volle LOHC waar de lege LOHC zinkt. Dit vermoeilijkt opruimen van deze brandstoffen. SB en AB reageren in theorie met zeewater, maar wel langzamer dan normaal. De praktijk wijst echter uit dat AB niet reageert met zeewater (of puur water) zonder katalysator. Aan de andere kant reageert SB sneller met zeewater dan met puur water. Als laatste lijken de lege vormen van SB en AB in elk geval in theorie gebruikt kunnen worden om impact te verminderen of te dempen, aangezien deze poeders brandvertragend zijn.

Vergelijken van al deze alternatieve brandstoffen op veiligheidsgebied is vrijwel onmogelijk, ook omdat veiligheid een veelomvattend begrijp is. Elk onderdeel van veiligheid heeft een andere invloed op maritieme omgevingen en is afhankelijk van persoonlijke waarden. Het framework ontwikkeld voor deze studie geeft daarom context-specifieke evaluaties in plaats van een universele rangorde. Uiteindelijk hebben vrijwel alle waterstofdragers gemixte of onzekere aspecten, waardoor er geen eenduidige beste optie uitkomt. Deze uitkomst benadrukt het belang van waarde-gebaseerde argumentatie en stakeholder dialogen.

Om de beste waterstofdrager in het algemeen te vinden, zijn alle waarden die hierboven genoemd zijn van belang; van de veiligheid van het personeel tot de impact op het milieu, van energiedichtheid en vermogensdichtheid tot lange termijn levensvatbaarheid, eerlijkheid en economische impact. Deze waarden worden allen beoordeeld in deze thesis, op verschillende niveaus van diepgang. Allemaal beïnvloeden ze de keuze van welke waterstofdrager het beste is. Echter, het kan zijn dat één waarde al deze anderen overschaduwd: timeliness oftewel op tijd zijn. De scheepvaartindustrie is soms net een groot containerschip; het beweegt langzaam, verandering van koers is lastig, maar eenmaal op een duidelijke koers is afwijken daarvan lastig. Daarmee is het gevaar van lock-in zeer aanwezig; wanneer een keuze wordt gemaakt zal die misschien niet snel meer veranderen. Dus, als waterstofdragers onderdeel willen worden van de energiemix, is het belangrijkste dat ze op tijd zijn. Te laat kan algauw veranderen in nooit; iets wat zeer jammer zou zijn gezien deze waterstofdragers laten zien dat ze zeer veelbelovende alternatieve brandstoffen zijn, die de scheepvaart industrie vooruit kunnen helpen om duurzamer te worden.

CONTENTS

1

INTRODUCTION

> *"Just because something seems impossible*
> *does not make it untrue"*
>
> — Deborah Harkness, *A Discovery of Witches*

CHAPTER SUMMARY

The maritime industry is responsible for about 3% of global greenhouse gas emissions. It also releases pollutants such as sulfur and nitrogen oxides, although recent regulations have already significantly reduced these. The International Maritime Organization (IMO) has therefore set a target of net-zero emissions by 2050. Achieving this goal will require cleaner propulsion options, with alternative fuels—ranging from lower-carbon LNG to carbon-free options like ammonia and hydrogen—offering the most promising pathway. However, these fuels often have lower gravimetric or volumetric energy densities than conventional fuels. Hydrogen carriers provide a potential solution, as they can store and release hydrogen on demand while achieving higher overall energy densities. This research therefore aims to identify and evaluate optimal combinations of hydrogen carriers and energy converters for various ship types, focusing on their technical feasibility and safety considerations.

Evidence of early sea-faring is difficult to assess, yet there is ample evidence that humans have been sailing for ages, dating back to at least 40,000 BC or possibly even earlier. For a very long time, the sailing vessel was the main way of transportation across large bodies of water. The first types of ships were all handmade for single purposes; mass production only occurred much more recently. Over time, ships got larger and were able to carry more cargo, with the *Grace Dieu* (1420) having a capacity of 1400 tons, but were still being built using personal experience and estimations - not fully designed [1]. The latter is required for mass production; without a design, mass production is not possible. Additionally, all of these ships were either powered by human strength, wind, or a combination of both.

The start of the Industrial Era changed both; the transition to steam engines enabled ships that could be mass-produced and operated by those steam engines. The first steam engine was patented in 1698 by Thomas Savery. The principle of this engine still was used for pulsometer pumps in at least the 1970s [2]. The first sea-going ship operating with a steam engine was the *Élise*, built in 1814 [3], while the first boat propelled by steam-power already sailed in 1787 [2]. In these times, ships were often still made of wood; only after 1850 ships were generally made of iron. Furthermore, owners and sailors did not have much faith in the engines, which was often justified. So, most ships, including the *Great Eastern* from 1858, were designed as sailing vessel, with the engine used as backup when the wind was not favourable [2]. In naval shipbuilding, this period also marked the transition to steam-screw propulsion, exemplified by the Dutch cruiser *Atjeh* of 1877 (designed by Tideman), the first national vessel built with this system [4], [5]. At the same time, ship design began to adopt a more scientific foundation, supported by systematic model testing and the growing influence of the work of Froude and Tideman [5]. The move from sail to steam was thus driven by the need for reliability rather than speed. Steam engines were updated in later years, allowing steam-powered ships to become competitive with sail-powered vessels. These new engines were triple-expanded, using coal as their power source. Steamships were used for a long time, with many advances on the propulsion system further down the line, from paddle boards to propellers [6].

Optimisation of this process also happened due to a change of fuel. Oil has a much higher energy density than coal and is easier to handle. The first step in converting marine steam boilers from coal-fired to oil-fired was already underway in the 1860s [7]. In 1898, the first oil-fired marine boilers were introduced; however, in those early stages the supply of oil was still an issue [7]. Only after World War 2 did oil-fired ships (including those using diesel) become the majority [6].

The next advancement in ship propulsion were two different engines: the gas turbine and internal combustion engine. The adoption of these engines followed a similar timeline as fuel oil. Up until World War 2, over 70% of the ships (by tonnage) consisted of steam-powered ships, even though the diesel engine was used on ships before World War 1 [6]. The first gas-turbine propelled ship, *Adm. Wm. M. Callaghan* was only built in 1967.

This effectively marked the end of the invention of new mechanical engine types. From that point onward, propulsion developments focused primarily on refining existing combustion systems and, in parallel, on exploring fundamentally different propulsion concepts; including electric drives and fuel cells [8]. These technologies introduced an electrochemical rather than a thermal form of energy conversion, marking the beginning of a new era in ship propulsion.

Yet the transition toward more powerful and efficient engines also revealed an unintended consequence. Marine diesel oil (MDO) and heavy fuel oil (HFO) appeared to be the perfect fuels, with their high energy density, safe operation, and ability to fuel powerful engines. They seemed, at least for a while, to be the final solution to the long-standing issue of ship propulsion innovations [2]. However, a major issue was discovered: the polluting of the world - both land and oceans - that is inherent with using these fuels.

1.1 NEED FOR EMISSION REDUCTION

The maritime industry currently generates a negative impact on the overall environment; it emits 3% of total greenhouse gas emissions, pollutants like sulfur oxides (SO_x) and nitrogen oxides (NO_x), as well as regularly spilling fuel or oil into the environment [9], [10], [11], [12]. The shipping industry is governed by the International Maritime Organization (IMO), a specialised agency of the United Nations (UN). As a UN member, the IMO has set a goal of emission reduction. The target set in July 2023 (at MEPC 80) is to reach a reduction of 40% of total greenhouse gas (GHG) emissions by 2030, and achieve GHG emission neutrality by 2050 [13]. To reach these goals, the shipping industry still has large steps to take. Many options have been researched, including design changes to reduce fuel consumption, optimisation of onboard energy systems, hybridisation of the energy system, and the use of alternative fuels [14], [15]. Most of these solutions offer emission reduction by making the ship more efficient. These efficiency gains can significant (for example when using wind-assistance, an efficiency gain of 40% can be reached), but often are around 2-10% efficient [14]. The most promising way of achieving net GHG neutrality is the use of alternative fuels. Consequently, the IMO has set a target for the use of alternative fuels, aiming to have alternative fuels account for at least 5% of total energy usage by 2030 [13]. The IMO has not specified which alternative fuel should be used; however, the ideal alternative fuel should obviously not exacerbate the current negative impact. Ideally, the new alternative would be greenhouse gas emissions neutral, not emit pollutants like SO_x or NO_x, not negatively impact the environment during spills, and not be worse than diesel from an overall safety perspective. However, it has also been noted by DNV in their maritime forecast that there is no single solution, or "silver bullet," for decarbonization [15]; therefore, a silver bullet that solves all these current issues is likely impossible to find. As alternative fuels are likely to impact all of these aforementioned issues, they remain a promising solution and are thus worth investigating.

1.2 TRADITIONAL ALTERNATIVE FUELS

Currently, many alternative fuels are considered for usage on ships, with the main options being ammonia, methanol, liquid natural gas (LNG) and hydrogen [15]. Of these, LNG is currently the most widely applied for ships (approximately 7.8% of gross tonnage in operation), with several methanol ships (70) also sailing [15]. The first hydrogen and ammonia-powered ocean-going ships are in early trials, while these fuels are currently already being used on smaller ships [15].

However, as mentioned above, no single fuel is likely to become the new MDO or HFO - all of these fuels have drawbacks hampering their widespread use. None of them have the same energy density as MDO or HFO; for all of these fuels a larger quantity is required to comply with the same operational profile. Additionally, ammonia is a toxic gas, which is unlikely to be allowed on inland ships due to their proximity to large public agglomerations. Furthermore, safe operation of an ammonia-fueled ship requires several design changes to prevent the crew from coming into contact with ammonia. The major issue with methanol is its carbon content - methanol is only zero-emission if it either is biomethanol or carbon capture is involved, either directly at the ship or during the production of green methanol. Similarly, LNG is not a zero-emission fuel due to its carbon compound, and it often involves methane slip, where methane, a greenhouse gas, is emitted. Hydrogen in its pure form is explosive and has a very low density. To store it as a fuel it either needs to be compressed up to 700 bar or liquefied (involving temperatures of around -250 °C) [16].

In addition to alternative fuels, various options for converting chemical energy into usable energy are being investigated. Energy converters such as proton exchange membrane fuel cells (PEMFC), solid oxide fuel cells (SOFC) or internal combustion engines (ICE) can reduce NOx emissions to values compliant with Stage V or Euro7 standards [17]. However, as most alternative fuels have very different combustion characteristics and a lower energy density, a more efficient energy converter might be beneficial. Fuel cells are generally more efficient but face technical challenges [18].

1.3 HYDROGEN CARRIERS AS ALTERNATIVE FUELS

Hydrogen can be stored and transported in various forms, often through so-called hydrogen carriers. These are chemical substances capable of storing hydrogen and releasing it on demand. When hydrogen is stored in such carriers, the chemical and physical properties of the carrier itself become crucial, since no pure hydrogen is present in the storage system.

From a theoretical standpoint, fuels such as methanol and ammonia can also be considered hydrogen carriers. In fuel-cell applications, these fuels are typically first decomposed (or “cracked”) to release hydrogen, which is then used to generate electricity. Beyond methanol and ammonia, tens of other hydrogen carriers have been identified, and new candidates continue to emerge through ongoing research. Each of these carriers possesses distinct chemical and physical properties, along with specific advantages, disadvantages, and challenges that must be addressed before they can be adopted as viable marine fuels.

Because the exploration of hydrogen carriers is still a relatively recent field, and even more so in the maritime sector, many potential carriers remain at early stages of development, ranging from proof-of-concept experiments to initial system prototypes. Nevertheless, identifying the fundamental trade-offs and eventual optimal hydrogen carrier could address several of the challenges currently associated with hydrogen-based propulsion and potentially lead to the development of an ideal, zero-emission, and sustainable shipping fuel.

1.4 CONSEQUENCES AND GAPS WHEN USING HYDROGEN CARRIERS

Using hydrogen carriers means introducing entirely new fuels on board ships. This transition has significant implications for the technical, economic, and safety feasibility of maritime operations. However, the economic feasibility is extremely difficult to assess; it is influenced by numerous uncertainties such as hydrogen carrier development, infrastructure availability and regulatory evolution. Therefore, it is excluded from the scope of this research.

Instead, this work focuses on two key aspects: the technical feasibility and the safety implications of using hydrogen carriers on board ships. Each hydrogen carrier has distinct properties (such as energy density, storage temperature and pressure, and chemical reactivity) that lead to different technical and safety challenges when applied on board. Understanding these consequential differences is therefore essential for developing feasible ship designs and safety measures.

However, before these influences can be analysed, it is essential to identify which hydrogen carriers are suitable for use as alternative fuels on ships. Prior to this thesis, no comprehensive overview of hydrogen carriers suitable for use on ships had been published. Existing studies often discuss only a few hydrogen carriers [19], [20] or compare several hydrogen carriers without considering the maritime context [21]. Accordingly, this research aims to provide an overview of various hydrogen carriers and to evaluate their suitability for use on ships. This overview serves as the foundation for the subsequent analyses from both technical and safety perspectives, where safety encompasses both immediate and long-term (sustainability-related) aspects.

1.4.1 TECHNICAL PERSPECTIVE

Assessing hydrogen carriers from a technical perspective enables the evaluation of whether a hydrogen carrier is suitable for different ship types with different operational profiles. Several publications have compared several conventional fuels (e.g., liquid hydrogen, methanol, ammonia) with different converters (ICE, gas turbine, PEMFC, SOFC). However, these focus mainly on fuel cells and omit hydrogen carriers or heat integration [18], [22]. Most existing studies concentrate on a single fuel family, such as liquid organic hydrogen carriers (LOHCs) [21], [23], [24], [25], [26]. Others provide limited multi-fuel comparisons [27], [28], [29], or only broad, high-level overviews [19], [30]. Finally, some single-fuel marine studies incorporate detailed integration, but without cross-fuel comparisons [31], [32].

This thesis aims to provide an overview of the technical suitability of different hydrogen carrier and energy converter combinations for different ship types.

1.4.2 SAFETY AND SUSTAINABILITY PERSPECTIVE

Although the transition towards hydrogen carriers originates from the need for more sustainable energy sources, other societal values, in particular safety, also play a crucial role in this process. In fact, sustainability and safety are closely intertwined: a technology cannot be considered truly sustainable if it poses unacceptable safety risks to people, assets, or the environment. Safety represents the short-term, operational dimension of sustainability, ensuring that the immediate risks associated with hydrogen carriers remain manageable and acceptable.

Many studies have evaluated and compared alternative fuels in the maritime sector [33], [34], [35], [36], [37], [38], [39], [40], [41], [42], [43]. One category of these studies employs Multi-Criteria Decision Making (MCDM) or methods closely related to it. These studies utilise rankings to assess a multitude of criteria for each of the fuels [34], [35], [36], [37], [38], [39]. Applying relative weight factors enables them to compare the fuels based on these multiple criteria [34]. This approach provides a practical way to quantitatively compare fuels. It is usually applied to relatively mature alternative fuels [36], [37], [38], [39], likely due to the information requirements for the entire process. Other ways of studying alternative fuels in the maritime sector include studies looking at life cycle analyses [40], economics [41], [42], or the required changes to legal frameworks [43].

These research approaches, while providing valuable quantitative comparisons, reveal fundamental limitations for the maritime fuel transition. Firstly, there are practical limitations, such as the choice of the criteria and their corresponding weight factors [35]. Regarding criteria, safety and or sustainability are not always taken into account [44], not specifically mentioned [34], or only superficially considered (using parameters such as flammability, ignition temperatures or ecotoxicity) [45]. In addition, current assessment frameworks tend to be rigid and evaluative rather than exploratory, and may not fully capture the complex value considerations that are relevant in maritime contexts.

In response to these limitations, this thesis aims to explore how the introduction of hydrogen carriers affects both safety and, by extension, long-term sustainability in maritime operations. The study seeks to compare different hydrogen carriers from a safety perspective, emphasizing their practical implications for onboard systems and human operations. By treating safety as a cornerstone of sustainability, this work highlights that achieving truly sustainable ship propulsion systems requires not only low emissions but also the reliable, safe, and acceptable handling of new fuels throughout their lifecycle.

1.5 RESEARCH OBJECTIVES

This thesis addresses the challenge of using hydrogen carriers as alternative fuels for ships. The effective integration of these carriers could lead to a fuel that is zero-emission, safe for both the marine environment and those on board, and characterised by high volumetric and gravimetric energy density as well as high power density. The overall research objective of this thesis is:

To identify and evaluate optimal combinations of hydrogen carriers and energy converters for various ship types, with a focus on technical feasibility and safety considerations.

To achieve this aim, the research has been divided into four specific subobjectives. Each objective is associated with a concrete contribution that supports the overall objective of the thesis.

The first objective is to *assess a large set of hydrogen carriers in terms of their suitability for use on board ships*. This includes characterising their chemical and physical properties and determining which types may be feasible in a maritime context. The scientific contribution is *the development of a categorization of hydrogen carriers and an overview of how general categories of hydrogen carriers may be suitable for ships as well as a detailed list of suitable hydrogen carriers, safety, and operational feasibility.* This approach results in an overview of general hydrogen carrier applicability to ships and a selection of the most promising categories.

The second objective is to *evaluate the technical feasibility of integrating hydrogen carriers with different energy converters.* This involves examining both the power and energy density that can be achieved when these systems are fully integrated on board ships. The corresponding scientific contribution is a *detailed comparison of hydrogen carriers, energy converters, and conventional alternative fuels under realistic integration conditions.* This analysis reveals how fuel properties, conversion efficiencies, and system layouts interact to determine the energy density and thus compliance with the operational profile.

The third objective is to *assess the safety and sustainability of hydrogen carriers used on ships.* This part of the research develops an approach to compare novel fuels even when limited information is available. The scientific contribution is *an approach of evaluating the safety and sustainability of novel alternative fuels to compare them without having large amounts of information, additional relevant fuel-specific maritime information, and an emphasis on the importance of operation over design.* This approach enables early-stage assessment on safety and sustainability of emerging hydrogen carriers under real-world uncertainty.

Finally, the fourth objective is *to identify the most suitable hydrogen carrier and energy-converter combinations for different ship types.* The scientific contribution is *a conceptual and philosophical analysis of hydrogen-based propulsion for shipping, integrating the technical, energy, safety, and sustainability analyses presented in this thesis.* By combining technical performance with broader contextual factors (such as safety and environmental ethics), this part of the research reframes optimisation as a multidimensional decision process, reflecting the diversity of operational contexts in the maritime sector.

Together, these four objectives establish a structured pathway from identifying potential hydrogen carriers to technical and safety assessments, culminating in a holistic evaluation of their applicability across various ship types.

1.6 OUTLINE

This thesis is organized into four main parts, each corresponding to one of the objectives described above and shown schematically in Figure 1.1. The structure reflects the logical progression of the research, beginning with the selection of suitable hydrogen carriers and concluding with the evaluation of their overall suitability for different ship types. Part 1 introduces hydrogen carriers and focuses on their selection for maritime applications. It consists of chapter 2. This chapter characterises the chemical and physical properties of a large set of carriers, providing an overview of which type of carrier can be considered most promising for use on ships. Furthermore, a set of initially promising hydrogen carriers is also briefly evaluated here.

Part 2 deals with the technical integration of hydrogen carriers with energy converters. The focus of chapter 3 is to integrate the hydrogen carriers and optimally utilise the available heat and mass flows to enhance the overall energy density of the system. By using several types of waste heat recovery, as well as water recovery, the system's efficiency is enhanced, and an optimal combination of hydrogen carriers and energy converters is made. This heat integration requires several heat exchangers, whereas the removal of hydrogen from the hydrogen carrier (dehydrogenation) necessitates a chemical reactor; all these components impact the power density. Chapter 4 evaluates the size of these components for a certain power output; this forms the basis of estimating the power density. Finally, chapter 5 combines the energy and power density of several combinations, compares them using Ragone plots and evaluates their suitability for different operational requirements.

Part 3 explores the safety and sustainability implications of using hydrogen carriers on ships. This part begins with a discussion of general safety hazards and an assessment of their suitability, highlighting the knowledge gaps in Chapter 6. The specific safety hazards of which information is missing, as well as specific maritime safety hazards, are explored from an experimental and theoretical perspective in chapter 7. Chapter 8 discusses the importance of safety during the design phase and where the maritime industry can learn from other sectors to enhance the overall safety. Finally, chapter 9 evaluates hydrogen carriers from a safety and sustainability perspective, providing a framework for comparison when limited data are available.

Part 4 discusses, from a philosophical and integrative perspective, the most suitable hydrogen carrier–converter combinations for various types of ships in chapter 10.

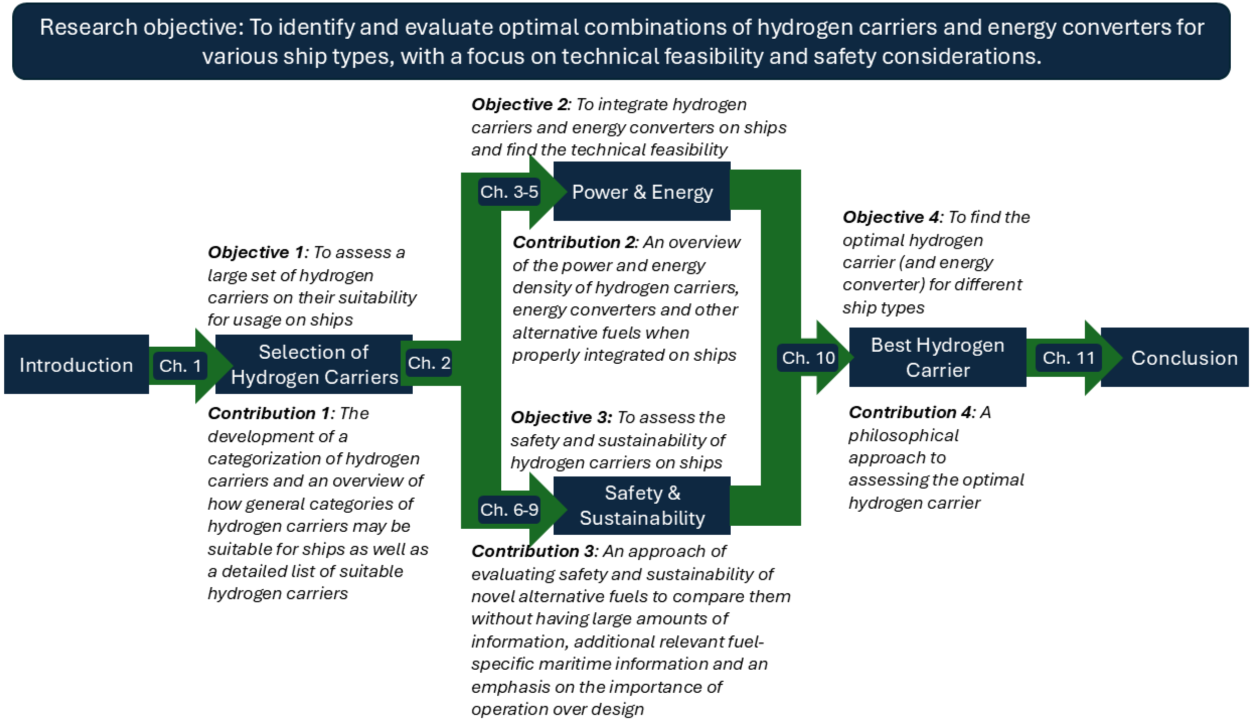

Figure 1.1: Outline of thesis research objectives, corresponding chapters and overview of contributions

PART 1: OVERVIEW AND SELECTION OF HYDROGEN CARRIERS

"The highway is alive tonight
Where it's headed, everybody knows
I'm sitting down here in the campfire light
Waiting on the ghost of Tom Joad"
— Bruce Springsteen, *The Ghost of Tom Joad*

PART SUMMARY

This part characterises the chemical and physical properties of a large set of carriers, providing an overview of which type of carrier can be considered most promising for use on ships. Furthermore, a set of initially promising hydrogen carriers is briefly evaluated in this section.

2

SELECTION OF HYDROGEN CARRIERS

> *"There's nothing like looking, if you want to find something. You certainly usually find something, if you look, but it is not always the something you were after"*
>
> — J.R.R. Tolkien, *The Hobbit, or There and Back Again*

CHAPTER SUMMARY

Hydrogen storage faces challenges, including low volumetric density, fire and explosion risks and transport challenges. In this chapter, over fifteen hydrogen carriers are evaluated based on their maritime performance characteristics to determine their suitability for shipboard use. Evaluation criteria included energy density, locally zero-emission, circularity of process, safety, dehydrogenation, logistic availability and handling. Borohydrides, liquid organic hydrogen carriers (LOHCs), and ammonia borane (AB) are found to be the most promising hydrogen carriers to use on ships with PEMFCs. Given varying operational demands, this research proposes a framework to assess the suitability of hydrogen carriers for use in different ship categories. Evaluating the three types of hydrogen carriers, using the proposed framework and considering current practices, shows that these are viable options for almost all ship types.

2.1 INTRODUCTION

As the shipping sector is not on track to reach its sustainability goals, there is a need for research on alternative power sources [46]. Batteries are not a viable solution for the shipping industry, due to their low gravimetric and volumetric energy density; for example, a container ship would need to use about 45% of the weight and 16% of the volume of the cargo hold by the batteries for the ship to be able to comply with its original operational profile [20]. This means that other alternatives have to be found. These alternative future fuels should meet specific requirements and criteria.:

- Safe (from a toxicity and fire hazard perspective)
- Zero emission (GHG and hazardous pollutants)
- High volumetric and gravimetric energy density
- Good logistic availability and easy handling
- Regenerative or circular produced - not one time use only

The United States (U.S.) Department of Energy (DoE) has set a goal for energy density, and even though this goal is set mainly for lightweight vehicles, it is used more generally to discuss the viability of hydrogen storage methods [16, 47, 48]. The goal is to reach an energy density of 9MJ/kg and 8.4MJ/L for the entire system [16, 49]. As gravimetric energy density is often expressed in weight percentage or wt%, the minimum weight percentage of hydrogen in a molecule should be 7.5 wt%. The gravimetric energy is then calculated by multiplying the weight percentage with the lower heating value of hydrogen (120MJ/kg). This is still excluding the rest of the system, meaning that 7.5wt% is a lower limit that should always be reached, as the rest of the system will only decrease the energy density.

The content of this chapter is based on the following article:
E. S. van Rheenen, J. T. Padding, J. C. Slootweg, and K. Visser, "Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation," J. Marine Engineering and Technology, vol. 23, no. 3, pp. 166–183, 2023. doi:10.1080/20464177.2023.2282691
The journal paper in turn is based on the following conference article:
E.S. van Rheenen, J.T. Padding, J.C. Slootweg, and K. Visser, "A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems," Institute of Marine Engineering, Science and Technology (IMarEST), presented at the International Naval Engineering Conference (INEC), 2022. doi:10.24868/10649

Currently, the shipping sector looks mainly at alternatives like hydrogen, ammonia and methanol, as well as batteries [46]. Of these alternatives (excluding batteries), hydrogen itself is the only one that is completely zero-emission when used in combination with fuel cells [18]. Also, when using a PEMFC, less noise and vibrations are produced compared to an internal combustion engine [18, 50]. Additional advantages are high electrical efficiency (40-60%), silence, operation at low temperatures (338 to 358 K) and modularity, causing gradual degradation [18, 20].

Therefore, this chapter focuses on the application of hydrogen combined with PEMFCs for ship applications. As storing pure hydrogen, even if pressurized or liquified, may not reach the volumetric energy density targets, this research will also consider other options, called hydrogen carriers [16]. Hydrogen carriers store hydrogen in their structure, for example by chemical bonding or physical adsorption [51]. To comply with the zero-emission target, it is important that hydrogen can be extracted without emitting harmful substances and that the original hydrogen carrier can be reused.

These hydrogen carriers have been researched before, however never specifically for use on ships, despite the additional characteristics that ships add, such as volume limitations and the need for autonomy. Current research either focuses on detailed descriptions of hydrogen carriers but with a different goal, such as storage with undefined purpose [21, 25, 47, 52, 53, 54] or storage for mobility [16, 48, 55]. With regards to the shipping sector, either more conventional alternative fuels—such as pure hydrogen, ammonia, or methanol—together with one or two types of hydrogen carriers are researched [19, 20, 56], or studies focus solely on one single type of hydrogen carrier [31, 57, 58].

This chapter aims to contribute to current research by first classifying the different hydrogen carriers based on their engineering characteristics. Then, the hydrogen carriers are evaluated on their viability in the shipping sector. For some viable hydrogen carriers, the effective energy density will be discussed and compared to the current fuels used. Additionally, a framework is developed to evaluate the application of hydrogen carriers for different ship types and ship operations, and discuss the challenges that still remain. This framework is then used to assess the suitability of certain promising hydrogen carriers for different ship types. Finally, in appendix B, several state-of-the-art industrial and scientific examples are discussed. Overall, this chapter aims to provide an overview of the hydrogen carriers that merit investment as alternative fuels to reduce greenhouse gas emissions in the shipping industry.

2.2 CLASSIFICATION OF HYDROGEN CARRIERS

The storage of hydrogen in general can be split into different methods. The exact definition of the storage methods is under debate [48, 49, 53, 54, 55, 59]. Often hydrogen storage is defined as storing hydrogen as a chemical hydride or using physical sorption (material-based storage) [48, 54], however, what is meant precisely by these terms can be different per author [48, 49, 53, 54, 55, 59]. Additionally, some authors define metal hydrides as hydrogen connected to metals, in all sorts of forms [48], whereas other authors see it as hydrogen-bonded into metals, making it behave similarly to physical sorption storage [54]. In this review, metal hydrides will be defined as part of material-based solid hydrogen carriers. The term chemical hydrides, even though extensively used, will be avoided due to its ambiguity [51, 54, 59, 60, 61].

These types of discussions are the reason that in this review, a classification based on figure 2.1 is proposed. Hydrogen storage is defined as either material or physical-based, with physical-based being the storage of pure hydrogen. Material-based storage is split up into liquid and solid material-based storage. This is more of an engineering approach, as liquid and solid storage methods require different handling. Such an engineering approach is required to address existing challenges. Metal hydrides can now be a part of solid storage, together with complex hydrides and physical adsorption methods. Next to handling, the material classification also provides groups of storage with similar dehydrogenation processes and gravimetric energy density storage. From an engineering point of view, these materials can be treated in similar ways for both storage, hydrogenation and dehydrogenation. The overall properties of these groups are discussed in the following subsections.

2.2.1 LIQUID CARRIERS

Liquid hydrogen carriers are carriers that are usually stored as liquid. Both the hydrogenated and dehydrogenated version of the hydrogen carrier has to be liquid to be considered in this category. They do not necessarily have to be

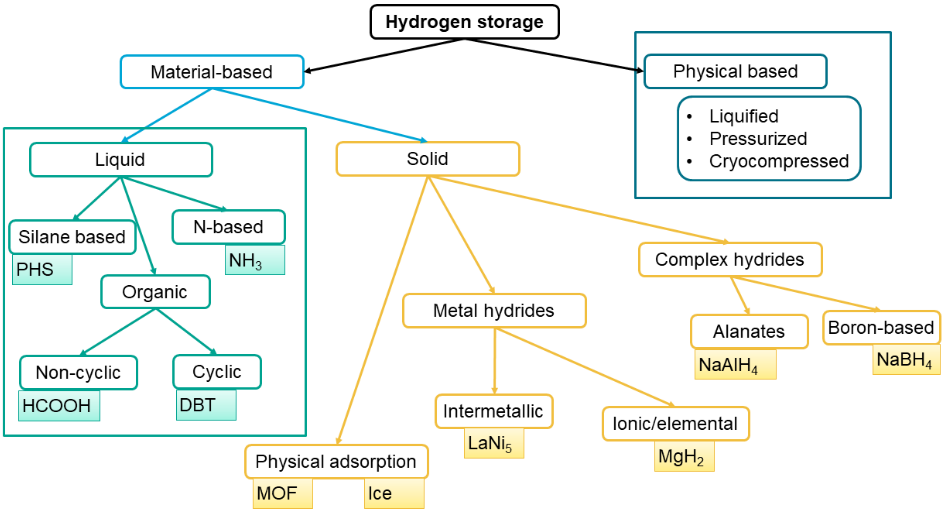

Figure 2.1: Proposed classification of hydrogen carriers for engineering purposes, including examples

a liquid at ambient conditions, as some gases such as ammonia require only slight modifications from ambient conditions to become liquid, which is why they are usually stored as a liquid. The main advantages of liquids are the use of current infrastructure and material handling, especially if the liquid carriers have similar toxicity to diesel. Generally speaking, storage is easier because liquids do not require set shapes.

Silane based

Silanes are inorganic compounds formed from silicon and hydrogen. It is possible to produce hydrogen from organosilanes, hydroxysilanes and (poly)silanes [62, 63, 64]. Dehydrogenation is usually through hydrolysis and is exothermic, but still requires a catalyst [62]. Organosilanes generally have a low boiling point and are gas state at atmospheric conditions, making them generally less safe [65]. The vapour pressure decreases with increased chain lengths [62], so larger molecules are more likely to be liquid. More complex organosilanes, such as polymethylhydrosiloxane (PMHS) have higher boiling points but also lower hydrogen weight percentages, of only 3.7 to 4.6 wt% [64, 65], whilst silane gas (SiH_4) can carry up to 12.5 wt% of hydrogen.

Unfortunately, silane gas is also highly flammable [62]. Other examples are polyhydrosiloxane (PHS) and pentasilane (Si_5H_{12}), which are both very promising alternatives for hydrogen storage [62]. PHS has a volumetric energy density of 10 MJ/L and pentasilane of 20 MJ/L, whereas PMHS, the more complicated molecule, only has a volumetric energy density of 2MJ/L [62]. The hydrogen weight percentage of pentasilane is 7.9 wt%, whereas that of PHS is less than 4 wt% [62]. Even though silanes are generally easy to handle and not toxic [66], public research on the use of polysilanes and organosilanes is limited [62, 63]. However, there is currently a company, called Hysilabs, investigating and patenting the use of silanes, mainly organosilanes, as a hydrogen carrier. The use of silanes in this practical application will be discussed in appendix B.

Non-cyclic organic (CO_2-based) carriers

Hydrogen can be stored chemically in non-cyclic organic molecules such as methanol (often abbreviated as MeOH) or formic acid [19, 47, 67]. Such compounds can potentially be produced from CO_2. Rather than using a chemical dehydrogenation step, most of them can be used directly in engine systems [19]. However, if they are used in PEMFCs, they have to be split. They can be used directly in other fuel cell systems, but at present these have low performance and low TRL [18]. CO_2 and hydrogen are products of the splitting and separation of these two gasses is required because CO_2 is poisonous for (especially low temperature) fuel cells [18]. As 90% of hydrogen (in 2016) was made using steam reforming, the separation process is highly researched [68]. Generally, pressure swing adsorption or cryogenic distillation are used, which require high amounts of energy and are expensive [68, 69]. Selective membranes to separate CO_2 and hydrogen are currently under research, as these are less costly and energy-intensive [68, 69]. On the other hand, an advantage of the CO_2-based hydrogen carriers is that they have been researched extensively, especially methanol [47]. However, as they emit CO_2 upon chemical dehydrogenation or combustion, they are only carbon neutral if green hydrogen and atmospheric CO_2 are used for their production [67]. Thus, only the complete cycle is potentially carbon neutral, while there are still local emissions. These local emissions can only be avoided by onboard CO_2 capture, which is not expected to be developed at the required scale [19].

Additionally, CO_2 capture and storage onboard ships would be challenging, although research projects have started to look at how this could be done [19].

Cyclic organic

Cyclic organic carriers are usually aromatic molecules that store hydrogen in their double bonds [19]. Unlike non-cyclic organic hydrogen carriers, cyclic organic not only dehydrogenate but can also hydrogenate, i.e. take up hydrogen, making them completely circular [19, 25]. The cyclic organic hydrogen carriers are often referred to as LOHCs (liquid organic hydrogen carriers) [19, 25, 47], a term also used in this thesis. Most of these LOHCs are cycloalkanes [70]. LOHCs can usually store about 5 to 8 wt% of hydrogen [70] and are generally safe and easy to handle, due to their oil-like physical properties [25, 70, 71]. However, the release of hydrogen is through an endothermic reaction, requiring high temperatures of over 420 K [25, 70]. There is an abundance of LOHCs, although mainly toluene (TOL) and its pair methylcyclohexane, N-ethylcarbazole (NEC) and its pair dodecahydro-N-ethylcarbazole and dibenzyltoluene (DBT) and its pair H18-DBT are considered [19, 25, 70]. Of these, toluene is often left out due to its carcinogenicity, low flashpoint (277 K) and low boiling point (384 K), even though it is the simplest molecule considered [19]. The other two are researched and reviewed a lot [19, 25]. Additionally, the company Hydrogenious is currently focussing on benzyltoluene (BT) and its counter pair perhydrobenzyltoluene, instead of DBT [72]. For all LOHCs, a major challenge is to find a catalyst that reduces the temperature for both dehydrogenation and hydrogenation, while still having high conversion rates [25, 47, 73, 74, 75].

N-based (Amines)

Amines are saturated nitrogen hydrides [76]. Of these, ammonia is the most well-known. It is also the only amine that is in gas form at ambient conditions, as amines with higher molecular weights are in the liquid form [77]. Amines generally have a high energy density because of the relatively low weight of the nitrogen atom compared to metals [77]. However, as amines are generally explosive and often toxic, they pose safety concerns [77, 78, 79]. Because of the decreasing energy density for larger molecules, the lack of safety and the elaborate research into ammonia as a hydrogen carrier, only ammonia will be discussed further here.

2.2.2 SOLID CARRIERS

There are a large variety of solids that can store hydrogen. Despite the large variety, it is always considered good practice to keep solid hydrogen storage away from water [19]. Compared to current fuels, which are liquids, new or different infrastructures may be required to refuel ships when solid hydrogen carriers are used.

Physical adsorption

Physical adsorption is defined as storing hydrogen without the splitting of the H-H bond [51]. There are many different mechanisms that can store hydrogen this way, but usually, the hydrogen is stored inside the molecule itself [80]. Generally speaking, physical adsorption processes are hard to scale up and require either high pressures or extreme temperatures to get sufficiently ($\geq$ 5 wt%) high energy density [16, 48]. Reversibility is a general issue [16, 80]. Substances that can physically adsorb hydrogen well generally have high porosity and large specific surface area [16, 80]. Despite the drawbacks, several physical adsorption substances will be discussed in further detail, as there is a large variety of them and they are well-researched and cannot be left out of an overview of hydrogen carriers.

Metal hydrides

There are two types of metal hydrides, intermetallic and ionic metal hydrides. Of the metal hydrides, ionic metal hydrides exhibit an average gravimetric energy density (up to 8 wt% or 9.6 MJ/kg), and a high volumetric energy density. Intermetallic metal hydrides, on the other hand, have a poor gravimetric energy density, with a maximum of 2wt% or 2.4 MJ/kg [55, 81]. Desorption of hydrogen occurs at extreme temperatures [16, 55] and the reversibility of the process is under debate and thus requires more attention [48, 55]. Because metal hydrides have been used on ships before [55, 82], they have a high technology readiness level and will thus be discussed in further detail.

Boron-based complex hydrides

Boranes and borohydrides are molecules that have either a BH_3 or BH_4 moiety [83]. The most common borohydrides are sodium and lithium borohydride, although potassium borohydride is also well researched [48, 84]. Boranes and borohydrides are promising storage materials due to their high hydrogen content, of up to 18 wt% [85]. They are usually safe to store as well [86]. The regeneration of boron-based complex hydrides is currently a major challenge, as the B-O bonds formed during dehydrogenation are hard to split [73]. Borohydrides and boranes release hydrogen in multiple ways, but the two main reaction paths are thermolysis and hydrolysis. Hydrogen release through thermolysis is done by heating the borohydride or borane. However, the temperatures required to release the hydrogen are extremely high: 953 K for lithium borohydride and 807 K for sodium borohydride [16, 48, 87]. As this is not a practical way of releasing hydrogen, this will not be discussed further in this review.

More promising is the release of hydrogen through hydrolysis. Both boranes and borohydrides react with water, producing hydrogen and borate [85], which has a great advantage in shipping, as the ship actually sails in the reactant needed for hydrogen production. The reaction is exothermic and can happen spontaneously, although for high conversion rates catalysts or acids are necessary [53, 85]. The reaction rate depends on the temperature and the catalyst used [19, 53, 84]. Because of the nature of the reaction, both the hydrogen stored in the borane/borohydride as well as the hydrogen originating from the water is released. This results in an effective hydrogen storage capacity of up to 36 wt% based on the weight of the borohydride, excluding the weight of water [84].

Alanates

Even though alanates have the possibility to store up to 10.6 wt% of hydrogen, most of them are not able to store more than 5 wt%, which means they do not have very high capacities [16, 88, 89]. The thermal release of hydrogen from alanates is endothermic and usually happens in multiple steps, with the first step requiring temperatures of 383 to 573K [16, 90]. The last desorption step takes place at higher temperatures, which depends on the alanate and may be too high for practical applications [91]. Doping can reduce this high dehydrogenation temperature, but always comes at a cost of less hydrogen storage [88, 90, 92]. Doping also appears to be required for dehydrogenation [90, 91, 92, 93], except for $KAlH_4$, which is reversible at relatively low temperatures and pressures, but there is only little research about this alanate [91].

Additionally, alanates usually react violently with water and are classified as dangerous [94], even though they are said to be stable [53].

2.3 DETAILED DESCRIPTIONS OF SPECIFIC HYDROGEN CARRIERS

In this section, certain hydrogen carriers that are generally considered to be relevant are discussed. The hydrogen carriers will be reviewed on the demands that are placed by the shipping industry and will include safety, emissions, volumetric and gravimetric energy density, ease and speed of generation of hydrogen from the carrier, and recyclability of the carrier (circularity). The U.S. DoE has defined a goal for both the gravimetric and volumetric energy density of the entire hydrogen carrier system, including the tank and other subsystems. This goal is set at a minimum of 7.5wt% of hydrogen per kg of the carrier (9MJ/kg) and 2.3kWh/L for light-duty vehicles [49]. This goal will be taken as a guideline in this chapter.

2.3.1 LIQUID HYDROGEN CARRIERS

Dibenzyltoluene and benzyltoluene

Dibenzyltoluene (DBT) is a promising LOHC, with a real-life storage capacity of about 6 wt% (theoretically 6.2 wt%) [19, 25]. It is cheap, stable during dehydrogenation and has a very high TRL (Technology Readiness Level) [25]. Additionally, it is not very toxic and widely available [19, 25]. DBT has a dehydrogenation temperature of 583 K when using Pd/C catalyst [25]. This can be reduced to 543 K, but then only 58% of the hydrogen is released [75]. It is thought that platinum could be a better catalyst for DBT [73, 74, 75]. The high dehydrogenation temperature is a point of concern for DBT. Another disadvantage of DBT is its high viscosity [95, 96]. As a result, BT is currently considered to be a good alternative for DBT. BT has very similar properties, but a much lower viscosity and a higher level of dehydrogenation under similar circumstances [95, 96]. However, BT has disadvantages as well, of which the low boiling point of only 538K (at ambient pressure) is the most problematic [96]. This low boiling point means that during the dehydrogenation gas by-products are formed, which is undesirable [96]. Thus, DBT with its high energy density, good availability and easy handling is often regarded as one of the most promising LOHCs [25].

N-ethylcarbazole

N-ethyl carbazole (NEC) is also thought to be one of the most promising LOHCs [73]. NEC has a dehydrogenation temperature of 453-523 K and stores about 5.8 wt% of hydrogen in theory, 5.2 wt% in practice [25]. Complete dehydrogenation can be achieved already from 453 K [25]. The dehydrogenation temperature of NEC can be reduced to 423 K when using iridium complexes as catalysts, but this does not result in complete dehydrogenation [73]. It has a TRL of only 3 on a scale of 1-9 and is not widely available [19, 25]. Additionally, the hydrogenated form is solid at room temperature, requiring either innovative handling solutions or continuous heating for the substance to remain liquid. Both options will result in additional cost and likely less efficient operations [19].

Methanol

Methanol is a low-toxic alcohol, which is liquid at ambient conditions and stores 12.6 wt% of hydrogen [19]. Due to its inertness, it can be stored in the double hull of a ship [19]. Another main advantage of methanol is that it is commercially available, making it cost-attractive [47]. However, methanol will pose safety challenges, as it has a low flashpoint and is dangerous to inhale or digest, resulting in the requirement of safety measures [19]. Just like formic acid, methanol releases CO_2 when dehydrogenated. Methanol can be used directly in combustion engines and direct methanol fuel cells but needs to be reformed and purified when used in combination with a PEMFC [18, 19]. Additionally, similar to formic acid, the emission of CO_2 means that having a ship that does not emit any CO_2 can only be achieved by using carbon capturing onboard, reducing the overall energy density of the system. If only circular production is desired, carbon capturing on land is sufficient [19]. Thus, even though methanol is a very interesting hydrogen carrier, it will not be reviewed further, as the main goal here is to have a fuel onboard which does not produce emissions.

Formic Acid

Formic acid (HCOOH) is a semi-non-toxic acid, which is liquid at ambient conditions [47]. It is highly corrosive [19]. It stores hydrogen at about 4.4 wt% [19, 47]. Formic acid is made from the hydrogenation of CO_2, which is theoretically 100% effective [19, 47]. It decomposes at about 373 K. At decomposition, it either forms CO_2 and H_2 or CO and H_2O [47]. The latter process is not desirable. As mentioned before, having a zero-emission ship running on formic acid is extremely difficult, which, combined with its relatively low gravimetric energy densit, means that formic acid will not be considered further in this review chapter.

2.3.2 PHYSICAL ADSORPTION

There exists a multitude of substances that are capable of physically adsorbing hydrogen, and a focus will lie on four specific types due to their unique and compelling characteristics. Metal-Organic Frameworks (MOFs), with their broad range of structural diversity, are suitable for a wide range of applications. Metal-decorated structures show great promise due to their high hydrogen uptake capacity. Nanostructures were previously considered interesting but have become a controversy in hydrogen storage research [97]. Finally, ice is also of interest because of the sustainable way of storing hydrogen in water.

Metal-organic frameworks

Metal-organic frameworks, also known as MOFs, are crystalline structures that are able to adsorb hydrogen in their voids [98]. MOFs pose a very promising way of storing hydrogen [51]. MOFs have a large structural diversity and thus, dependent on the application, different MOFs can be used [80]. MOFs are usually highly porous (to store the hydrogen inside their voids) and have a high specific surface area [16, 80]. The conditions at which MOFs store hydrogen ranges from cryogenic temperatures to room temperatures and ambient pressures [80]. A great advantage of MOFs is their fast release and adsorption of hydrogen, which is usually in the scale of seconds [16, 80]. The storage of hydrogen inside MOFs is reversible, however, after multiple cycles, the amount of hydrogen that can be stored inside the MOF can drop substantially [16, 80]. For MOFs to become a suitable option for hydrogen storage, considerable research is still needed, as current solutions are not practical and difficult to scale up [16, 80].

Additionally, a lot of light elements such as Li, Na and Mg cannot be used for MOFs as they are susceptible to hydrolysis, resulting in violent reactions with water [19, 48, 53]. The amount of hydrogen that can be stored in MOFs is also generally an issue. MOFs at room temperature are only able to store about 1wt% of hydrogen if they are at 20 bar [16, 80]. In order for MOFs to store higher quantities of hydrogen, they have to be at very low temperatures and high pressures [16, 80]. The hydrogen uptake of MOFs is proportional to the pressure [98]. The relationship between temperature and storage capacity is different, as physisorption decreases at higher temperatures [98]. At room temperature, using iron MOFs 6 wt% at 101 bar was reported [48], whereas at 77K and 70 bar, for example, NU-100 can store up to 16 wt% of hydrogen (which reaches the U.S. DoE target of 7.5 wt%) [99]. Keeping the MOFs at such low temperatures and high pressures is very costly and energy-consuming, even though MOFs generally have extremely low thermal conductivity [16].

Metal decorated structures

Structures such as silicon clusters or honeycomb borophene are capable of storing hydrogen as well, in a very similar way to MOFs [100, 101]. The working principle is very similar to that of MOFs, as metal decorated structures also adsorb molecular hydrogen physically [100, 101]. When alkali metals are added to these structures they can store up to 18 wt% of hydrogen at 100 K and 6000 kPa for a silicon lithium structure [101]. When borophene oxide is bonded with the metal lithium, a gravimetric density of 8.3 wt% can be reached at 100 K [100]. However, at room temperature and low pressure (300 kPa) the hydrogen storage is greatly reduced, to a maximum of 5.5 wt% [101]. A similar phenomenon applies to the borophene honeycomb structure, although the difference there is smaller, as at room temperature and relatively low pressures (about 3000 kPa) still 5.2 wt% of hydrogen can be stored [100]. The volumetric energy density is not mentioned in the papers by [100] and [101]. In order for both of these types of storage to become a solution to the hydrogen storage issue, a lot more research has to be done on the exact nature of the structures and how to enhance the hydrogen storage at room temperature and relatively low pressures.

Nanostructures

Nanostructures are not materials, but a way of physical storage. Nanostructures are usually made of carbon [48, 81]. There are several types of nanostructures [48]. Nanomaterials can, amongst others, be based on carbon, silicon carbide, boron and boron nitride [48, 97]. The storage principle behind these materials is the same, but the properties are different [48]. Carbon nanostructures are the most researched type of nanomaterials, usually they are designed as nanotubes [97]. It is not entirely clear how much hydrogen these materials can store as several results are not reproducible [48, 97]. Nanomaterials started with activated carbon, which can hold only about 3.2 wt% hydrogen at 18900 kPa and room temperatures [48]. Studies have shown that it is not possible to reach the U.S. DoE limit using carbon nanotubes at room temperatures [97]. Like MOFs, at lower temperature these carbon nanostructures are more effective, with storage of up to 8 wt% hydrogen at 77 K [48]. Regeneration is complicated, as it is difficult to add hydrogen to these types of structures [48]. Additionally, the dehydrogenation process is slow, with a 50% hydrogen release taking an hour and complete hydrogen release taking over 200 h [81]. An additional issue is the collapse of nanotubes during dehydrogenation, as well as fracture and strain which influence the size of the tubes that can be used [48]. As the carbon nanotubes will not reach the target, other types of nanotubes have been researched [97]. These were still insufficient in reaching the energy density target [97]. There is a lot of research into nanostructures, both carbon based and non-carbon based [48].

Ice

Another way of storing hydrogen is in clathrates [48]. A common clathrate is ice, which can store hydrogen inside its lattice. The official name of this clathrate is clathrate hydrate [48]. The amount of hydrogen stored in a clathrate depends on the pressure and temperature; high pressures are required to store larger amounts of hydrogen [48, 102]. Depending on the pressure, between 5.2 and 12.9 wt% of hydrogen can be stored in ice. The volumetric energy density is then 1.5 to 3.5 kWh/kg, reaching the target set by the U.S. DoE [48, 49, 103]. In order to store higher weight percentages of hydrogen, however, enormous amounts of pressure are required (at least 700MPa) [48]. The main advantages of storing hydrogen in ice are the required storage material (water) is cheap and the safety of the storage: it has a low environmental impact and is self-extinguishing [48]. However, the high pressure and low temperature required form a major complication [48, 102]. For example, to store 4 wt% of hydrogen, a pressure of 4000 kPa and a temperature of 114 K is required [102].

The storage can be improved by using promotors [104]. When adding a second component, such as tetrahydrofuran (THF), the hydrogen can be stored at lower pressure and ambient temperatures [104]. It is thought that by adding THF, 4 wt% of hydrogen can be stored inside the ice, at about 297 K and 5000 kPa [104]. The main issue of storing hydrogen in ice, with or without a promotor, remains the low energy densities. Studies have not shown hydrogen storage capacities beyond 5 wt%, which is significantly below the target.

2.3.3 METAL HYDRIDES

In this review, metal hydrides are split into two types: ionic or elemental hydrides and intermetallic hydrides. Elemental hydrides consist of an element combined with hydrogen. Examples of these are magnesium hydride and lithium hydride [52]. Elemental hydrides such as LiH and MgH_2 have similar properties. They store relative high amounts of hydrogen (i.e. MgH_2 stores 7.6 wt% [52]) and require rather high dehydrogenation temperatures [19, 52]. Hydrogen is stored in metal hydrides inside the structure, by occupying interstitial sites in the metal [52].

LiH and MgH_2

Lithium hydride is a material with a theoretically good hydrogen storage capacity as it can store up to 12 wt% of hydrogen [105]. However, LiH requires very high temperatures of about 973 K to release the hydrogen [19, 105]. Additionally, lithium hydride reacts violently with water, making it rather dangerous [53]. When combining LiH with nanoconfinement, release temperatures of 473 K have been reported, but then only 1.9 wt% of the hydrogen was released, which does not come close to the goal of the U.S. DoE [105]. This, however, is a promising technology if more hydrogen can be released.

MgH_2 is also often considered, as it is more stable, safer and has lower release temperatures than LiH [106]. MgH_2 can store about 7.6 wt% of hydrogen [19, 106]. It again has a rather high decomposition temperature (573 K) and it is hard to completely hydrogenate magnesium, as it is a surface reaction [19]. This can all be tackled by using catalysts, resulting in better hydrogenation [19]. The dehydrogenation process, however, seems to require a minimum temperature of 523 K [59]. When additives are used, this can be lowered to about 323 K, but additives also reduce the weight percentage of hydrogen that can be stored [107, 108].

Intermetallic metal hydrides

Intermetallic metal hydrides can be grouped according to the type of material. Usually they consist of one or more A atoms (usually a rare-earth or alkaline-earth metal) and B atoms (typically a transition metal) [54]. Combined, these form the following combinations: AB_5, AB_2, AB and A_2B types of metal hydrides [51, 54, 59, 60]. Typical intermetallic metal hydrides are $LaNi_5H_{6.7}$, Ti-Zr alloys (such as $Ti_{0.93}Zr_{0.05}Mn_{0.73}V_{0.22}Fe_{0.04})_2$, Sn_2Co, Ti-Fe alloys ($FeTiH_{0.95}$) [19, 48, 54]. The main issue of metal hydrides is their very low gravimetric energy density; usually only a few wt% [20, 48, 54]. For example, $LaNi_5H_{6.7}$ only stores 1.4 wt% hydrogen [54] Metal hydrides generally have favourable operating conditions, as they do store and release hydrogen at temperatures in the range of 298 to 353K) and do not need elevated pressures with their equilibrium pressures of 1 to 10 bar [48, 54]. However, their high weight makes them unsuitable for shipping [20]. Metal hydrides are much more suitable for land-based hydrogen storage [54]. A case study was performed, in which metal hydrides were looked at as effective hydrogen carriers onboard a ship; for the specific case this would result in 40% of the total storage mass taken by metal hydrides to provide the required amount of energy [20].

2.3.4 COMPLEX HYDRIDES

Complex hydrides such as $NaAlH_4$ and $NaBH_4$ are named as promising candidates for hydrogen storage [88]. Complex hydrides that are formed with aluminum are also named alanates [88], those formed with boron are named borohydrides. Both $LiAlH_4$ and $NaAlH_4$ are available and cheap [90, 93].

Ammoniaborane

Ammoniaborane (AB) is a widely researched borane [83]. AB has a very high hydrogen content of 19.6 wt% [83, 109, 110]. AB can be used as an anodic fuel, but also as a hydrogen carrier. Hydrogen can be released from AB using hydrolysis, pyrolysis and alcoholysis [110]. Hydrolysis is thought to be the best process, as it requires a mild temperature and no additional fuel [110]. The amount of hydrogen released by hydrolysis is limited. One source cites 7.8 wt% [73], while another says that only 5.8 wt% is released [66]. At this moment there is no catalyst that is both active and long-lived [109]. The hydrolysis reaction of AB is as follows [111]:

$$H_3NBH_3 + 3H_2O \rightarrow NH_3 + B(OH)_3 + 3H_2 \tag{2.1}$$

There is also another reaction noted, in which the borate and ammonia react and become ions [73]. It can be seen from reaction 2.1 that there are two main products, a borate and ammonia. For a PEMFC, which is assumed in this review, ammonia is very difficult. It is, however, a hydrogen carrier and will be discussed in further detail in section 2.3.5. In the case of AB there are a few options for the use of ammonia. The ammonia can be stored on board and taken back to shore; it can be cracked and used inside a fuel cell; or it can be burned in an internal combustion engine together with hydrogen [20]. This is, however, outside of the scope of this review.

Additionally, regeneration of AB is very difficult, due to the B-O bonds that are formed during dehydrogenation [73]. This also makes this process extremely costly [83]. So while AB has an extremely high hydrogen content, it may be hard to use in practical applications.

Sodiumborohydride

Sodiumborohydride (SB) can store up to 10.7 wt% of hydrogen in theory [53]. SB, with chemical formula $NaBH_4$, releases its hydrogen at moderate temperatures (298-333 K) with high hydrogen purity and good control [112, 113]. The release of hydrogen is done using hydrolysis, which is a spontaneous, exothermic, albeit slow, reaction [114]. The speed of the reaction can be enhanced by using catalysts or acids, both of which are very well researched [113]. There are many catalysts available, but ruthenium is used mostly [113]. Currently there is also interest in Pd/carbon dots, as these can be easily recycled, as well as cobalt based catalysators as they show good reaction kinetics [113]. The main aim of the catalysts is to enhance the reaction activity, not to reduce the temperature as the reaction happens at low temperatures already [113]. The hydrolysis reaction of SB is as follows:

$$NaBH_4 + (2+x)\ H_2O \rightarrow 4H_2 + NaBO_2 \cdot xH_2O \tag{2.2}$$

where x is either 2 or 4, depending on the reaction [115]. On a ship, water does not have to be brought along, but can be purified onboard and recycled from hydrogen-fed fuel cells. This means that twice as much hydrogen is produced as is carried inside $NaBH_4$. The spent fuel, $NaBO_2$, however, has to be brought back as well, which is 2.7 to 3.6 times heavier than the original fuel, depending on the hydrogenation of the spent fuel [115]. Regenerating this spent fuel is much under debate. According to some it is simple [113], whereas others say it is very expensive [73, 112] or even that there is no evidence at all of its working principle [114]. However, it is most likely difficult for the same reason as regeneration of AB is difficult, due to the B-O bonds that are formed during dehydrogenation [73]. The dehydrogenation is currently under active research at TU Delft and the University of Amsterdam [116].

Potassiumborohydride

Some sources have mentioned potassiumborohyrdie (KB, KBH_4) as an alternative for SB [84, 117, 118]. It has very similar properties to SB, it stores about 7.4 wt% of hydrogen theoretically and releases it by hydrolysis, releasing the hydrogen from water as well [84]. The main arguments to use KB is that the spent fuel stores less water molecules and is easier to handle, as it reacts less strongly with water [84]. KB reacts with water to form $KBO_2.4/3H_2O$, whereas SB usually has either 2 or 4 water molecules after hydrolysis [84]. When heated above 408 K the KBO_2 hydrate loses a water molecule, resulting in only $KBO_2.1/3\ H_2O$. At a similar temperature, SB still stores 1 water molecule. This means that the spent fuels have a very similar weight, with molar masses of 83 and 87u respectively. The regeneration process of KBO_2 back to KB is very similar to that of SB. However, depending on the process, KB has an advantage. If ball-milling is used, anhydrous borate is desired [31]. The energy required to get an anhydrous borate costs less energy and only comprises of two steps (compared to 4 steps for SB) and is thus advantageous [84]. Thus, KB has some advantages considering storage and perhaps regeneration as well, but the overall energy density of KB is much lower than that of SB.

$LiAlH_4$

Lithium aluminium hydride ($LiAlH_4$) has been mentioned as a promising storage material for hydrogen [92]. It stores up to 10.6 wt% of hydrogen [88, 92]. The dehydrogenation temperature depends on the way of storage and the catalysts used. Dehydrogenation of $LiAlH_4$ usually happens in three steps. During the first step 5.3 wt% of hydrogen is released at about 423 K, resulting in $3H_2$, Li_3AlH_6 and 2Al [88, 90]. During the second and third step 2.6 wt% per step are released, with in between reaction products LiH and Al. These react and form, as the final product (next to the hydrogen) LiAl [88]. The multiple steps occur because each step requires a higher temperature for the substance to decompose [88]. The dehydrogenation temperature can be reduced when using doping, however the main issue is that it also results in a much lower storage availability of hydrogen [88]. An example is doping the $LiAlH_4$ with TiN [119]. This results in a release of about 7.1 wt% at a temperature of 403 K [119]. Another way of lowering the dehydrogenation temperature is using nanoconfined $LiAlH_4$, which will decrease the temperature of the first step to about 408 K (instead of 423-473 K) and the complete dehydrogenation at 573 K (instead of 373-723 K) [92]. Using only the first step results in a residual product (Li_3AlH_6) which is practically impossible to regenerate [92]. Next to dehydrogenation, there are also rehydrogenation issues [88, 90, 92]. The current technology reaches the desired goal of 7.5wt% of hydrogen release, even though only the first two steps are practically applicable as the third step requires a too high temperature [92, 119]. However, the weak reversibility and bad desorption kinetics, make $LiAlH_4$ at this moment not a good candidate for hydrogen storage aboard a ship.

$NaAlH_4$

Sodium aluminium hydride ($NaAlH_4$) is closely related to lithium aluminium hydride. It has a lower hydrogen weight percentage of 7.41 wt% and a higher decomposition temperature (483 K) than $LiAlH_4$ [90]. Another issue for $NaAlH_4$ is the poor reversibility [93]. Similar to $LiAlH_4$ the hydrogen is released in three steps, all requiring higher temperatures for decomposition than the previous step [93]. The reaction products are also similar: after the first step Na_3AlH_6 and Al are created. Na_3AlH_6 decomposes at 533 K to NaH and Al, next to 1.9 wt% of hydrogen. Another 1.9 wt% of hydrogen is released in the third step, where NaH is decomposed into Na and hydrogen at 708

K [93]. So only the third step is significantly different from the process with lithium aluminium hydride [90]. Additionally, all three steps are slow [16, 52]. The dehydrogenation temperature can be lowered by using catalysts and doping [93]. Doping with TiN, for example, results in a lower dehydrogenation temperature for the first two steps, resulting in 5.2% release of hydrogen, as well as a faster release than without doping (5.2 wt% in 10h, instead of 2 wt%) [93]. The release is still at temperatures between 403 and 458 K [93]. According to [93] a lot of work still needs to be done before $NaAlH_4$ can be considered a realistic option for hydrogen storage. Keypoints are reducing operating temperatures and pressures, enhancing kinetics and understanding dopants [93].

2.3.5 AMMONIA

Ammonia is a key nutrient and recently also a much researched hydrogen carrier and is often thought to be one of the most promising new (marine) fuels [19, 20, 53, 120, 121]. Even though ammonia can be used in a direct SOFC fuel cell or directly burned in an engine, this chapter will only look at its use in a PEMFC, for reasons mentioned previously [20]. Ammonia is a chemical with a hydrogen content of 17.6 wt% [16]. It is gas at ambient pressure and temperature, but becomes liquid at slightly lower temperatures (263 K) or slightly elevated pressures (1000 kPa) [20]. It is usually stored that way. Ammonia is a well established substance, its production process is very well known and currently at industrial scale, due to its use as fertiliser [16, 20, 120]. This also makes it a relatively cheap solution [120]. Ammonia has good hydrogen carrier properties overall, except for its high toxicity and corrosiveness [20]. The toxicity is usually an issue; it was one of the reasons for the U.S. DoE to stop funding ammonia research [19, 53, 70, 120]. Another reason was the energy-consuming process of decomposing ammonia into hydrogen and nitrogen [70]. Since this research is focused exclusively on the PEMFC and not on other energy conversion technologies like internal combustion engines or SOFCs that can utilize ammonia, the process of cracking becomes indispensable [20]. Cracking of ammonia is energy-consuming due to its endothermic nature and high temperature (higher than 673K) requirements [21, 70, 120, 122]. Because ammonia has a high energy density, research focuses on lowering the energy consumption by using catalysts [70, 122]. The decomposition of ammonia is a well-known process and there is a lot of research into the catalysts used for this [122]. Cracking uses a lot of energy, depending on the source 13 to 26% of the total lower heating value of the hydrogen produced [21, 123]. The cracking process has to be done very well, as PEMFCs are very sensitive to ammonia poisoning [53]. Other fuel cells, such as SOFCs are more tolerant to hydrogen from ammonia [18]. So, even though ammonia has a high energy density and is widely available, due to the complex and energy consuming cracking (required for use in a PEMFC) and the high toxicity, it will not be taken into account further in this chapter.

2.4 EVALUATION OF HYDROGEN CARRIERS

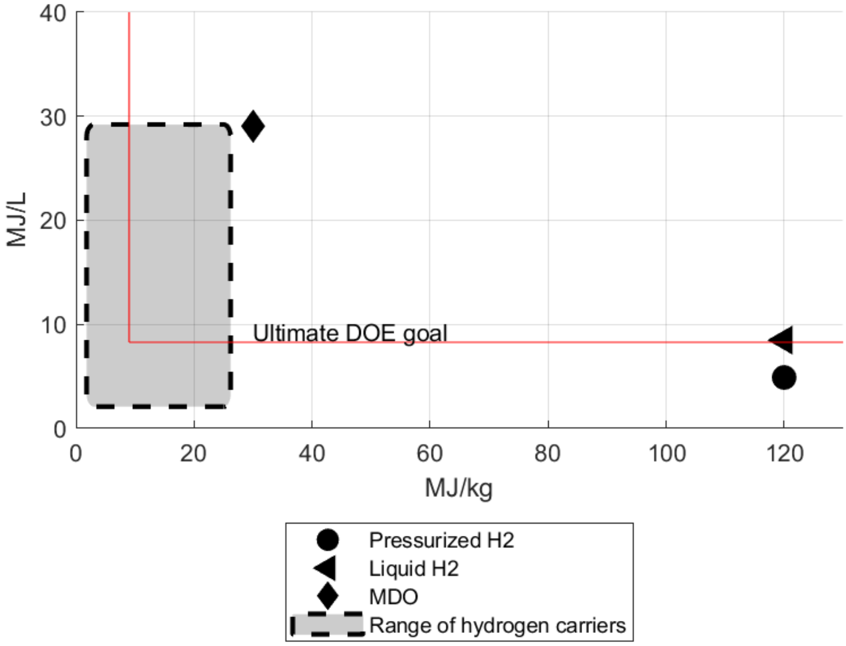

Figure 2.2: Theoretical gravimetric and volumetric energy density range of hydrogen carriers, liquid and pressurized hydrogen and diesel, with the red line representing the U.S. DoE target of 9MJ/kg and 8.28MJ/L for lightweight vehicles

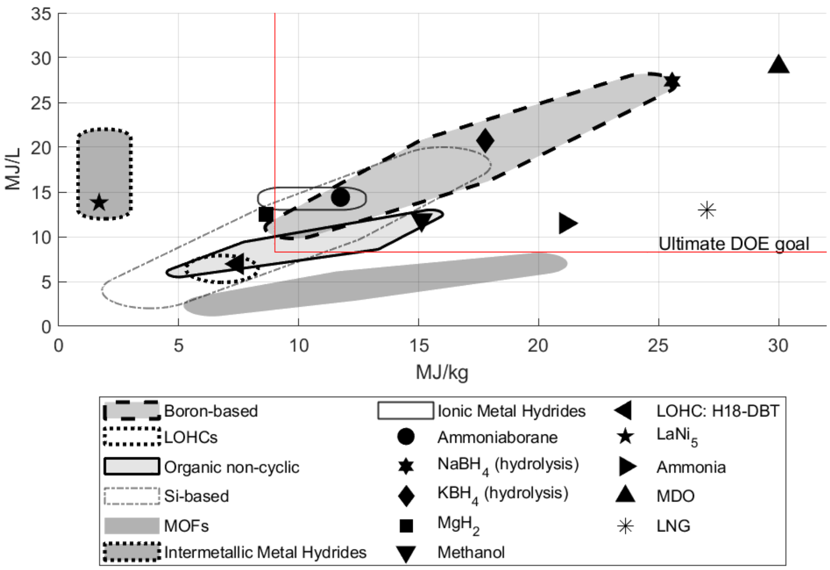

Figure 2.3: Theoretical gravimetric and volumetric energy density of different groups of hydrogen carriers, with the red line representing the U.S. DoE target of 9MJ/kg and 8.28MJ/L for lightweight vehicles. Physical-based hydrogen storage is left out because otherwise, details are not visible due to the high theoretical gravimetric energy density of liquid and pressurized hydrogen

This section aims to evaluate the hydrogen carriers on characteristics relevant for shipping purposes. It starts with the pure, theoretical energy densities, without packing factors or tanks, despite the lower limit of the U.S. DoE including these factors. If this lower limit is not reached without taking these factors into account, it will not be reached regardless, which is why only theoretical energy densities are taken into account here. Next other characteristics, such as TRL, dehydrogenation, safety and handling are evaluated.

2.4.1 ENERGY DENSITY

Figure 2.2 shows a graphical overview of the pure theoretical energy density of the discussed groups of hydrogen carriers. Only metal decorated structures (discussed in section 2.3.2) are not taken into account in this figure, as their volumetric energy density could not be found. As the red lines indicate the U.S. DoE targets, everything above and to the right of these lines can theoretically reach the targets. Figure 2.3 shows a zoomed in version of figure 2.2. As shown in figures 2.2 and 2.3, only a few hydrogen carriers have theoretical energy densities that are able to reach the goal set by the U.S.DoE. This figure shows only the theoretical (chemical) value, without packaging factors or tank weight. When packaging factors and tank weight are included, the volumetric and gravimetric densities only go down [56].

2.4.2 OVERVIEW OF REVELANT CHARACTERISTICS FOR SHIPPING PURPOSES

Next to the volumetric and energy densities of the carriers, there are several other criteria to evaluate the carriers. The main relevant parameters which are relevant for shipping purposes are given in Table 2.1, including reasoning and limits. For safety, handling and storage, flashpoints are taken into account, however low flashpoints do not necessary limit application onboard, as there are already guidelines for low flashpoint fuels.

Table 2.2 shows the hydrogen carriers and their main properties. From the table it can be seen that the TRL level at this moment and the safety, handling and storage are a main issue for many of the different hydrogen carriers. For a hydrogen carrier to be useful onboard, the safety, handling and storage of the carrier should be at reasonable temperatures and pressures to avoid phenomena such as boil-off. Additionally, having storage at near ambient conditions reduces the energy required for storage and thus enhances efficiency. Similar criteria can be used for the dehydrogenation process. When the dehydrogenation process requires (extremely) high temperatures and/or pressures, this greatly reduces the onboard efficiency, effectively reducing the energy density.

Table 2.1: Relevant characteristics to judge hydrogen carriers for shipping purposes

	Relevance for shipping purposes	**Limiting metrics**
Gravimetric and volumetric energy density	Define the required storage capacity	At least 9MJ/kg and 8.28MJ/L
Technology Readiness Level	Estimate the timeline for technology implementation	Higher than 4 (research stage only)
Safety, handling and storage	Defines the measurements needed for onboard application	No species that either combust spontaneously (very low flashpoint) or that react violently with substances that cannot be avoided onboard a ship, such as (humid) air. Toxic gasses are also unwanted, as in case of a leak, these may spread easily through the ship. Substances that require high pressures (>10MPa) for storage are also unwanted, because of additional explosion risks. Similarly, risk of freeze burns limits application of substances that need cryogenic temperatures (<77K).
Dehydrogenation	The dehydrogenation process onboard should be relatively fast, to enable load following and not release extremely high temperatures, as this will result in high energy requirements and thus reduction of energy density. Dehydrogenation should produce restproducts that can safely be stored on board and regenerated on land	Release temperatures lower than 620K. Possibility of 100% release
Recycling	Recycling should be possible and energy efficient	No metrics, usually mentioned as either possible, theoretically possible or not possible

In the end, there is a set of hydrogen carriers that may be interesting for usage on ships in general, likely without there being a single solution that fits all ship types and operations. All carriers with a low TRL level at this moment have been disregarded in this review, as there is insufficient research to be found on the implementation of these carriers. Additionally, substances that react violently with water or that have difficult dehydrogenation processes are not taken into account either. The (on-shore) rehydrogenation process for compounds such as borohydrides, which is considered difficult, is not seen as a deal-breaker due to the amount of research currently going on. In short, this leaves the LOHC DBT (despite the rather high temperature for dehydrogenation), the borohydrides SB and KB as well as AB for further investigation in this research.

Table 2.2: Overview of the chosen hydrogen carriers, their main properties and main problems. Due to the similarity in properties, $LaNi_5$ is chosen as an example for metal hydrides. Highlighted cells indicate inadequate values. Borohydrides indicated with a *, have theoretical values only, without added hydrogen from hydrolysis.

Carrier	**MJ/kg**	**MJ/L**	**TRL**	**Safety, handling and storage**	**Dehydrogenation**	**Recycling**
MOF	5.4	7.2	4–6	Low temperature (77 K), solid	Fast	Limited amount of cycles possible
MDS	2.4	5	<4	Low temperature (100 K), solid	293–373 K	Possible
Nanostructures	6.2–8.76	N.A.	<4	High pressure (>15 MPa), low temp. (77 K), solid	Slow, can self-collapse	Risk of self-collapse, complex recycling
Ice	6.6	5.5	<4	High pressure (>700 MPa), low temp. (approx. 114 K), solid	Fast, high quality	Possible

Continued on next page

Table 2.2 (continued)

Carrier	**MJ/kg**	**MJ/L**	**TRL**	**Safety, handling and storage**	**Dehydro-genation**	**Recycling**
Ammonia borane	23.5	14.4	4–6	Stable, store away from water, solid	By-product NH_3, exothermic, water required; only 7.8 wt % H_2, rest ammonia	Possible but energy-intensive
$NaBH_4$*	12.8	13.7	4–8	Store away from water, solid	Exothermic, water required, catalyst needed	Possible but energy-intensive
KBH_4*	8.9	10.4	4–8	Store away from water, solid	Exothermic, water required, catalyst needed	Possible but energy-intensive
$LiBH_4$	22.1	14.6	4–6	Store away from water, solid	Only 50 % release during hydrolysis	Possible
$LiAlH_4$	12.7	11.7	<4	Violent reaction with water or humid air, solid	486 K undoped, 408 K doped	Not possible under moderate conditions
$NaAlH_4$	6.7	8.4	3–6	Violent reaction with water or humid air, solid	High T (up to 708 K), 3-stage process, only 5 wt % release	Possible but energy-intensive

Continued on next page

Table 2.2 (continued)

Carrier	**MJ/kg**	**MJ/L**	**TRL**	**Safety, handling and storage**	**Dehydrogenation**	**Recycling**
LiH	15.1	13.2	3–6	Violent reaction with water or humid air, solid	High T required (>973 K)	Possible
LaNi$_5$	1.7	13.8	7–9	Generally considered safe, solid	Endothermic, ambient-to-moderate (293–353 K)	Possible
NEC	7.0	6.6	<4	Generally considered safe, liquid	Endothermic, 423–353 K	Possible
DBT	8.3	7	7–9	Generally considered safe, liquid	Endothermic, 573 K	Possible
Pentasilane	9.5	20	<4	Generally considered safe, liquid	Fast, high quality	Possible
NH$_3$	21.1	11.5	4–8	Toxic gas	Cracking required at 673 K	Not directly possible
Methanol	15.1	11.9	4–8	Low flash-point fuel	By-product CO$_2$	Not directly possible without on-board CO$_2$ capture

Continued on next page

Table 2.2 (continued)

Carrier	**MJ/kg**	**MJ/L**	**TRL**	**Safety, handling and storage**	**Dehydro-genation**	**Recycling**
Formic acid	5.3	6.4	3–6	Generally considered safe, liquid	Required product hard to get	Not directly possible without on-board CO_2 capture
Liquid hydrogen	120	N.A.	7–9	Gas at ambient conditions, flammable	Not applicable	Not possible

2.5 EFFECTIVE ENERGY DENSITY OF INTERESTING HYDROGEN CARRIERS

In the previous section, a set of promising hydrogen carriers have been identified based on their theoretical energy densities and other basic properties. These hydrogen carriers are SB, KB, AB and DBT. To thoroughly evaluate these hydrogen carriers, a switch has to be made from theoretical values to realistic energy density values. This is also what the U.S. DoE goal is based on: values including packing factor and required other materials [110]. The effective energy density is based on the following three parameters: the properties of the material itself, the tanks that are required, and the extra equipment required to release the hydrogen. The aim of this section is to give an overview of what is already known about the effective energy density of promising hydrogen carriers for each of the three parameters and to identify where additional research is required.

2.5.1 CHALLENGING MATERIAL PROPERTIES FOR APPLICATION

Material properties, such as the state of matter and the density of both the fuel and the spent fuel influence the energy density. As DBT is a liquid, the density and viscosity depend on temperature. Especially the viscosity is important for

DBT as it influences the pumping power. As DBT has a very high viscosity, pumping at normal temperatures may not be feasible and preheating of the tanks may be required. However, in the shipping industry, this is a common practice, as HFO needs to be preheated before pumping is possible [124]. However, preheating costs energy and thus lowers the overall energy density of the hydrogen carrier, by up to 7% as estimated by [21].

For the borohydrides and AB the exact composition of the solid defines the bulk packing density and thus the energy density. The rougher the particles, the less densely packed the substance becomes. The exact differences between the bulk density and the material density depend on the material but can be as low as 25 to 35 % of the material density [125]. Thus, the exact composition and state of the solids onboard will highly influence the overall energy density. This does not only apply to the fuel, but even more to the spent fuel. Equation 2.2 shows a potential dehydrogenation process of SB. The form of the spent fuel depends on the temperature and can be $NaBO_2$, $NaBO_2.2H_2O$ and $NaBO_2.4H_2O$. All these spent fuels are heavier and take up more volume compared to the original SB. For example, 1kg (0.93L) of SB produces 2.7kg and 1.4L if $NaBO_2.2H_2O$ is produced [115]. For KB a similar issue occurs. This is because during the reaction a metaborate hydrate is formed, which is always heavier than a borohydride.

For AB, there is an additional complication as ammonia is released during the hydrolysis. Ammonia cannot be used in its pure form in fuel cells, it has to be cracked first, which costs between 33 and 95% of the total energy inside ammonia [21]. However, ammonia can also be used as a fuel inside an internal combustion engine. There is a lot of research on use of ammonia as a power source, see for example [126]. Further research is needed to determine the optimal utilization of the released mixture from AB to evaluate the overall energy density onboard ships.

2.5.2 TANKS

The size and especially the shape and thickness of the walls of the tanks are determined by safety measures. The additional amount of material due to tanks is called the packing factor [56]. The packing factor of the hydrogen carriers is relatively easy to determine. DBT does not have a packing factor, as it is very similar to HFO and can thus be stored in standard HFO tanks. For the borohydrides and AB, it currently appears that they do not react with moisture in the air, as long as the temperature stays below approximately 30C [127, 128]. Additional research here is needed to see whether the air in the storage tanks of borohydrides stays below this threshold and whether no hydrogen is released at all because otherwise, countermeasures have to be taken to avoid preliminary release of hydrogen.

2.5.3 ADDITIONAL EQUIPMENT RELATED TO HYDROGEN CARRIERS

To release the hydrogen from hydrogen carriers, specialized equipment is necessary. The amount of components and their size depends on the process, which in its turn depends on the hydrogen carrier. As most of the promising hydrogen carriers are still in laboratory phase, upscaling to industrial size is required, which is difficult but necessary to be able to calculate both the energy but also the power density of the hydrogen carriers. The size of the equipment depends on the required power, the dehydrogenation process and possible pre- and post-treatment. Whether the dehydrogenation process is exothermic or endothermic determines whether cooling or heating is required. The exact amount of energy necessary or produced during the dehydrogenation and the heat integration also determines the size of the additional heating or cooling equipment. The possible pre- and post-treatment is closely related to the material properties of the hydrogen carrier.

As mentioned in the first subsection, DBT might need preheating as pre-treatment and purifying of the hydrogen as post-treatment. On the other hand, the borohydrides and AB likely require mixing with water as pre-treatment and crystallization of spent fuel as post-treatment. These additional treatments will require additional components, which will take up space and thus reduce the overall energy and power density of the system.

2.5.4 INITIAL CALCULATIONS OF EFFECTIVE ENERGY DENSITY

With the current knowledge, an initial attempt can be made to compute the effective energy density. For liquid hydrogen, this data is taken from literature [16].

For the hydrogen carriers, the calculations are based on the following assumptions. For SB and KB the spent fuel is taken into account. Depending on the operating conditions of the reactor and process this spent fuel is between 1.7 and 3.3 (SB) or 1.5 and 2 (KB) times heavier than the original fuel.

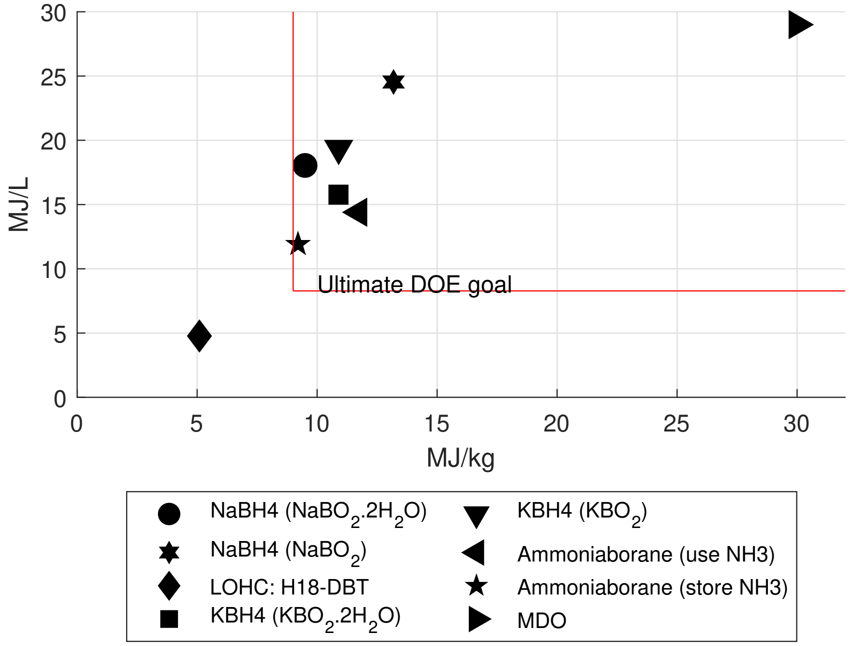

Figure 2.4: Effective gravimetric and volumetric energy density of selected hydrogen carriers including packing, spent fuel weight, dehydrogenation energy losses and other influencing factors

Thus, instead of using the weight and volume of the original fuel, the energy density of the spent fuel is calculated, as the weight and size of the spent fuel determine the amount of fuel that can be brought on the ship. Under the operating conditions on the ship, the spent fuels are most likely to be $NaBO_2.2H_2O$ and $KBO_2.1/3H_2O$. The hydrate (water) part can be removed at a cost of approximately 50kJ/mol H_2) that should be removed for SB [84], thus resulting in 100 kJ per mol SB energy loss. For KB this is a total of 59kJ/mol for the first mol and 19 kJ for the 0.3 H_2O that should be removed [84]. This energy cost is subtracted from the overal contained energy per molecule to calculate the energy density of the borohydrides with the non dehydrated spent fuel. Thus, an estimate on the effectiveness of removing the hydrate can be made, as there is discussion and research on the effect of the spent fuel composition on the regeneration process [129, 130, 131].

AB does not form a hydrated spent fuel, but it does produce additional ammonia. The spent fuel is calculated as either $B(OH)_3$ part with and without ammonia. With ammonia means that the ammonia is stored onboard as well, without ammonia means that ammonia is either cracked (and used in the PEMFC), or used for other onboard processes. In this 'use ammonia' case, however, the ammonia is assumed not to add to the overall energy density because of the large difference in estimation of the energy costs related to cracking of ammonia (ranging from 95% to 33% of total energy available) [21].

For DBT an average loss of 31% as calculated by [21] is used to calculate the overall energy density. Here the weight and volume of the spent fuel is not taken into account. The spent fuel is lighter than the fuel and the density does not differ much [25].

The calculated energy densities of the hydrogen carriers as well as of liquid hydrogen are visible in figure 2.4. Figure 2.4 shows clearly that the hydrogen carriers have much lower energy densities than diesel when the known factors such as the energy required for dehydrogenation or weight of spent fuel are taken into account, especially as additional things like packing factors have not been taken into account yet for the hydrogen carriers.

2.6 ASSESSMENT OF SUITABILITY OF HYDROGEN CARRIERS FOR DIFFERENT SHIP TYPES

This research proposes a framework to assess the suitability of hydrogen carriers for different ship types and ship operations. Table 2.3 gives an overview of this framework and the considered ship types.

The first of the different ship types considered are inland cargo ships, traveling up and down rivers, canals and other inland ship corridors, with intermediate bunkering facilities along the corridor. Because these are inland ships, they do not have a large amount of volume available for fuel. Due to the characteristics of inland ship corridors, inland ships are likely to travel through densely populated areas, resulting in the need for a fuel that is safe for the environment and the general public in the surrounding areas. As they do not always travel the same river or have the same destination, they are generally a bit flexible in their destination.

Ships that also travel parts across the sea, along the coastline, are short sea ships. These ships can travel large distances, from Africa to the Baltic Sea.

Table 2.3: Framework to evaluate the application of hydrogen carriers for ship types and ship operations

	Inland	Short sea	Seagoing	Dredging	Workboats (tugs)	Fishing vessels	Ferries	Naval
Required range	-	+	++	+	-	+	+	+++
Volume available for fuel and process plant	+	++	+++	-	—	o	o	+
Safety requirements relative to stakeholders and environment	+++	++	+	++	++	++	++++	+
Bunker flexibility requirement	++	++	++	++	–	–	—	+++

Because they are bigger and sail longer distances compared to inland ships, they require more propulsion power and energy storage. Therefore, they have a larger volume available for fuel. The safety requirements for detonation and toxicity are more manageable, as they are less likely to travel through densely populated areas and have a higher educated crew that is able to respond better to incidents. Finally, just like the inland ships, they do not always have the same destination, even though a lot of short sea (and inland) ships sail in line services with standard destinations.

The largest types of cargo ships are the ocean-going ships. They have the most volume available for fuel. Again, similar to short sea ships, detonation and toxicity risks are more manageable on these ships because of the size of the ship, the larger free area surrounding the ship and the higher level of education of the crew. However, as these ships stay at sea for longer periods of time, the risks have to be covered. Because of the distances they travel, which depend on the world trade, they have to be flexible in which harbours they go to.

Besides these types of cargo ships, there are special-purpose ships, such as dredgers, workboats, pushboats and fishing vessels. These ships generally do not have large volumes onboard available for fuel. Especially tugs and push boats have extremely little space, but dredgers and fishing vessels have less space than cargo ships. For dredgers, workboats and fishing vessels, similar reasoning for safety as for short sea ships is used, resulting in an 'in-between' level of safety required.

Another type of ship is ferries. These travel a broad distribution of distances, but all have in common that they transport people. This results in high safety requirements. Because of the number of people on board, they have less space for fuel than cargo ships. Ferries generally shuttle between ports and thus have very little flexibility in destinations.

Naval ships are the final type of ship considered. Even though they are generally at sea for long periods of time, they do not have a lot of excess volume available for fuel. Additional space is preferably used for weaponry and other systems, instead of fuel. Because of the presence of weapon systems and the possibility of attacks on the ship, the safety requirements for the fuel are considered different. Unsafe fuel should not give additional risks, but the crew has a high level of education and is trained to react adequately to possible threats, including fuel-related incidents. Thus, fuels that are not safe enough for ships with passengers, may be used on naval ships. Of course, naval vessels are extremely flexible in their destination, as they travel across the world.

2.7 SUITABILITY FOR DIFFERENT SHIP TYPES AND SHIP OPERATIONS

Based on table 2.3 the suitability of the identified hydrogen carriers can be evaluated for different ship types and ship operations. Additionally, recommendations for further development will be provided. Table 2.4 gives an overview of the relevant parameters required to evaluate the suitability of hydrogen carriers for the different ship types. For the hydrogen carriers, it is assumed that regeneration does not take place locally and definitely not onboard the ship. This assumption is made because of the uneven distribution of renewable energy resources [132] and the envisioned size and complexity of regeneration locations, which combines likely results in more centralised regeneration locations.

Table 2.4: Relevant parameters of promising hydrogen carriers and liquid hydrogen for application as storage of hydrogen fuel onboard ships

	Borohydrides	LOHCs	Ammoniaborane	Liquid H_2
Range	High	Low	High	Low
Onboard space needed for storage and dehydrogenation	Medium because of mixing tank. Requires specialized equipment for handling due to solid	Medium because of preheating. Onboard handling can use conventional equipment	Medium because of mixing tank. Requires specialized equipment for handling due to solid	Medium — large tank required, but no additional dehydrogenation equipment needed
Safety	Medium	High	Low	Low

2.7.1 BOROHYDRIDES

The borohydrides SB and KB have very similar properties. They have a high energy density and can thus provide a high range with a relatively small volume required for storage. However, the size of the reactor and pre/post-treatment equipment required is unclear. Assuming it depends on the power consumption required by the ship, this can make the borohydrides less favourable for ships with high power requirements and low onboard volume available, such as dredgers, push boats and other workboats. Thus, in order to assess whether borohydrides can be used as alternative fuel on these types of ships more research on reactor design is required. For many of the other ship types, such as inland, short sea and seagoing ships, as well as fishing vessels and ferries the borohydrides seem to be suitable to use. For ferries, safety is extremely important. Because of the slow reaction kinetics, especially at relatively low (≤ 303 K) temperatures [127, 128], no hydrogen gas is expected to be released outside of the controlled environment, making the borohydrides relatively safe. However, borohydrides remain corrosive to human skin [133]. For fishing vessels, volume is important with less power requirements than workboats or dredgers. This is why the borohydrides are considered for fishing vessels and less for workboats and dredgers, as the ratio between additional equipment (such as the fuel cell and dehydrogenation reactor) and fuel itself may become less favourable. As it is assumed that regeneration will take place at centralised locations, the borohydrides have to be transported to and from these locations, which is relatively easy due to their powdery structure. Thus, borohydrides can be used in a large variety of locations, providing a high bunkering flexibility. Naval ships are extremely flexible in their destination, but they also occasionally require large amounts of power, while not having large amount of volume available for the fuel and the reactor. This means that more research is required to assess whether borohydrides are suitable for naval vessels. So, additional research in reactor design and regeneration of borohydrides is considered important and generally speaking borohydrides are suitable for inland-, short sea- and seagoing cargo ships, as well as fishing vessels and ferries.

2.7.2 AMMONIABORANE

AB is very similar to the borohydrides, but it has a much higher energy density and is less safe due to ammonia gas released during dehydrogenation. However, AB does not react spontaneously with water, so it can still be used for vessels that sail in areas that are less densely populated [66, 111, 134]. The high energy density makes AB very suitable for naval and seagoing vessels as there range is important. However, before AB can be used on ships in general, further development is needed to make full use of the energy density of AB. For internal combustion engines and gas turbines, research on hydrogen and ammonia dual-fuel is needed, whereas for both SOFC and PEMFC ammonia cracking should be researched. Additionally, more research on both the dehydrogenation and hydrogenation of AB is needed, the former because of the uncertainty in current literature on the exact process and how much hydrogen is released. Hydrogenation, or regeneration of AB, faces similar issues as the borohydrides, as a by-product of regeneration of AB appears to be sodiumborohydride. However, because AB is a powder just as the borohydrides, it can be transported easily to different destinations and thus does not affect the flexibility of bunkering. For shipping applications besides naval and seagoing vessels, AB is not encouraged because of the generation of ammonia. Depending on the region, however, AB could be considered for short sea, dredgers, workboats or fishing vessels. These vessels should then have the majority of their operation far away from densely populated areas. For ferries and inland ships AB is not suitable as densely populated areas cannot be avoided for these ship types and ferries obviously carry passengers. So, AB is a prime interest for usage on naval and seagoing cargo ships, but research into the dehydrogenation, regeneration and conversion processes is required.

2.7.3 LOHCS

DBT, but also BT and NEC have generally low energy densities, but are easy to handle and extremely safe. This easy handling provides a high flexibility in bunkering locations, as again dehydrogenation is assumed to be a centralised process. This would mean that for ships with flexible destinations and a lower range, LOHCs would be ideal. This would fit with dredging vessels, but research is required on whether the limited available volume onboard is sufficient for the volume required by the LOHC to provide the power and energy the vessel needs. Furthermore, as the dehydrogenation reaction is endotherm, either waste heat or, when not enough waste heat is available, costly hydrogen is needed to release hydrogen from LOHCs. Additionally, the reactor size for LOHC dehydrogenation is unclear and should be researched further to see how the deliverable power and size relate, especially for use on dredging vessels. An advantage that LOHCs have here is that they are fluids and do not need special tanks or transport systems for storage. LOHCs can also be considered for inland shipping and short sea ships, depending on the range and bunkering locations available. Transport of LOHCs is easy and current oil distribution systems can be used for LOHCs as well, opening up the possibility of LOHCs becoming widely available. However, for ships whose operations require large sailing distances, such as seagoing ships and naval ships, or large amounts of power, such as workboats, LOHCs are not suitable as they do not contain enough energy. For ferries and fishing vessels it depends on the range and volume available onboard for the storage and dehydrogenation reactor. The safety of LOHCs is another advantage for use of LOHCs onboard of ferries. So LOHCs have limited suitability for different ship types because of their low energy density. Depending on the exact requirements, they may be suitable for inland, dredgers, short sea, ferries and fishing vessels. Just like with the borohydrides and AB, however, more research into the dehydrogenation reactor and specifically its power and size relation is required to assess where are LOHCs are suitable as fuel.

2.7.4 LIQUID HYDROGEN

Next to the liquid hydrogen carriers, liquid hydrogen is also considered. Liquid hydrogen has a low energy density and requires tanks with a set, suboptimal shape, but when using liquid hydrogen no reactor is used. The tanks make liquid hydrogen harder to transport, resulting in less bunkering flexibility. However, the absence of a reactor can be advantageous for applications with high power demands, relatively small range and small onboard volume. Thus, liquid hydrogen might be suitable for workboats such as tugs or dredging vessels. These are also the types of vessels where hydrogen carriers may not be suitable. For the other ship types, liquid hydrogen is not considered as an option because of the relatively low safety and many requirements to onboard storage. This makes liquid hydrogen a less attractive option for short sea, seagoing, fishing, naval vessels or ferries. For inland shipping liquid (or pressurized) hydrogen could be considered (and is, see the inland ship Antonie [135]), however, borohydrides or LOHCs are considered here as better options because of their higher safety levels.

2.8 CONCLUSION

This chapter aimed to evaluate hydrogen carriers as an alternative power source for ships. The first step was to categorize hydrogen carriers based on relevant characteristics such as the dehydrogenation process and reaction, phase of the hydrogen carrier, and temperature, pressure, and reactivity of the carrier. Next, several hydrogen carriers were investigated in more detail and discussed features important for circular use on ships, such as gravimetric and volumetric energy density, safety, storage and handling, technology readiness level and dehydrogenation and rehydrogenation process.

LOHCs and borohydrides offer good potential, due to their high energy densities, medium to high technology readiness levels, good safety and well-known dehydrogenation processes. These hydrogen carriers are viable to use on ships. LOHCs can most likely make use of the current infrastructure, whereas borohydrides show energy densities close to diesel.

The framework shows that these two types of hydrogen carriers are suitable for almost all types of ships, ranging from fishing vessels and ferries to naval and seagoing ships. This conclusion is further substantiated through an analysis of current state-of-the-art projects, ranging from canal boats to submarines, which shows that borohydrides and LOHCs are being considered as alternative power sources on ships in the industry as well.

So hydrogen carriers, especially borohydrides and LOHCs, are promising and viable options for alternative power sources on ships. However, practical implementation requires further research, particularly in the regeneration of borohydrides and heat integration of LOHCs. Nevertheless, our study highlights the potential of these regenerative, circular, high energy density, and zero-emission hydrogen carriers, contributing to the research for alternative power sources for shipping applications.

PART 2: POWER & ENERGY

> *"Short cuts make long delays"*
>
> — J.R.R. Tolkien, *The Fellowship of the Ring*

PART SUMMARY

Ships are limited by either volume and weight, so minimizing the space and mass of their propulsion systems and fuel storage is desired. Thus, alternative fuels and especially hydrogen carriers, low weight and volume are desirable, without risking operational performance. Evaluating such fuels therefore requires considering energy density (useful energy per unit mass or volume, in electrical or mechanical form) and power density (power output per unit mass or volume of the full power delivery system). Power density includes all components that scale with output, such as engines and dehydrogenation reactors, but not fuel tanks.

This part of the thesis investigates the energy and power densities of various hydrogen carriers and energy converters, to assess their suitability for different ship types. In this part, the following hydrogen carriers will be reviewed in detail:

1. Sodium borohydride ($NaBH_4$, SB)
2. Ammonia borane (NH_3BH_3, AB)
3. Dibenzyltoluene (DBT)
4. N-ethylcarbazole (NEC)

Details on the fuels discussed in this part can be found in appendix A.

POWER & ENERGY

3

ENERGY DENSITY

> *“Menneisyys on mielessä turvallinen mesta Mut ei se ikin palaa, Mikan faijalla on nyt Tesla”**
>
> — Arttu Wiskari feat. Pyhimys, *Mikan Faijan BMW*, adapted from Anssi Kela for Vain Elämää

* * *

CHAPTER SUMMARY

This chapter provides an overview of the energy density of different hydrogen carriers. The energy density is paramount to implementing hydrogen carriers; a high energy density is desired. The effective energy density depends on integrating heat and mass with energy converters. This combination defines the energy efficiency and, thus, the energy density of the system. This paper addresses the effective energy density of the hydrogen carriers, including the dehydrogenation process. Using a 0D model, the five carriers were paired with PEMFCs, SOFCs, an ICE and a GT. NEC and DBT offer medium energy densities, reaching almost 4 MJ/kg. However, the effective energy density of SB and AB is very high, up to 15 MJ/kg, including the energy converter. This is similar to the energy density of MDO combined with an ICE. Thus, hydrogen carriers are alternative fuels that deserve more attention because of their strong potential to make shipping zero-emission.

* * *

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*The past is a safe place in the mind, but it never comes back, Mika’s dad has a Tesla now

3.1 INTRODUCTION

In the previous chapter, several requirements were stated; one of which was the energy density. The U.S. DoE had set a goal to reach an energy density of 9MJ/kg and 8.4MJ/L for the entire system [16, 49]. However, this is for land transport; for the shipping sector the energy density should be as high as possible. Either space or weight is highly optimized in most cargo ships; the more space or weight the fuel takes up, the less cargo can be brought. Thus, a high energy density is required.

The energy density of hydrogen carriers is not necessarily trivial and can differ strongly from the theoretical value; for example LOHCs can lose 30% of their energy when not correctly integrated [21]. In this chapter five hydrogen carriers will be investigated. Next to the four mentioned already in the summary of Part 2, potassium borohydride is investigated as well. It is extremely similar to SB, but might have better storage and handling. The other four carriers are NEC, DBT, SB and AB. Two of these carriers, NEC and DBT, are LOHCs and release hydrogen endothermically. A good heat integration can reduce losses and enhance the overal energy density. The other three carriers, SB, AB and KB, release hydrogen exothermically. Yet, elevated temperatures are still required. Due to their solid nature, the spent fuels of SB, AB and KB can not easily be used for preheating; using heat from the energy converter is preferable. Additionally, they require pure water, which should be ideally be reused from the energy converter.

Most research regarding energy optimization of hydrogen carriers focuses only on LOHCs combined with fuel cells and is not in a maritime context, such as but not limited to [21, 23, 24, 25, 26]. Only very few studies looked at hydrogen carriers integrated as mentioned here (LOHCs, boron-based carriers, but also metal organic frameworks) on ships, not always including calculations [19, 27, 30, 31, 136]. None of these studies include thorough calculations on a multitude of hydrogen carriers on ships.

This study aims to obtain the effective energy density values of the previously identified hydrogen carriers, including the dehydrogenation process. Effective energy density is defined here as the amount of energy that can

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The content of this chapter is based on the following article:
E. S. van Rheenen, J. T. Padding, A. A. Kana, and K. Visser, “Comparative energy analysis of hydrogen carriers as energy source on ships,” J. Marine Engineering and Technology, 2025. doi:10.1080/20464177.2024.2448057

be transferred to a ship's propulsion system per unit weight of a hydrogen carrier. This definition takes into account the following factors:

- Additional tank weight (when applicable)
- The practical energy required for hydrogen release

In essence, the effective energy density represents how much energy 1 kg of a hydrogen carrier can deliver to the ship's propulsion. Therefore, it must include the weight of the storage tank and the energy needed for hydrogen release. The latter can be optimized by capturing and utilizing waste energy from the energy conversion system (such as an engine or fuel cell).

Thus, the choice of energy converter is not trivial; an energy converter with a high heat output may be less efficient overall, but enhance heat integration possibilities. The efficiency of the energy converter also influences the effective energy density. A higher efficiency means less fuel is required to fulfill the operational needs. Several energy converters exist, but in this study the following four are reviewed. These are the ICE, gas turbine (GT), PEMFC and SOFC.

3.2 METHOD

To assess the efficiency and, thus, the total energy density of the hydrogen carrier, a simplified 0D thermodynamic model was constructed. The electricity or mechanical energy produced in the energy converter is not converted to the same energy output to ensure a fair and balanced comparison. Each energy converter converts energy most efficiently. Additionally, the required mass of additional water for SB and KB are evaluated, as these might significantly influence the comparison of these fuels.

3.2.1 SPECIAL CONSIDERATIONS REGARDING SB AND KB

SB and KB are similar substances in almost all respects except for the theoretical energy density, spent fuel composition and water requirements. The theoretical energy density of KB is significantly worse than that of SB [137]. Storage and handling conditions are supposed to be easier for KB [31, 117]. Its spent fuel is also less susceptible to crystallisation than $NaBO_2$. Yet, the latter is not necessarily an advantage, as crystallisation is necessary to increase the energy density. Without crystallisation, the spent fuel would hold large amounts of water and thus be heavier and require more space than necessary. However, crystallization does cost additional heat and energy. Furthermore, a separate crystallizer has to be added onboard, increasing overall system size and complexity. Finally, drying the spent fuel changes the product and is likely to influence the handling of the product.

The dehydrogenation process of KB requires less water. Thus, with an imperfect water recovery system, KB may be superior to SB, as no extra water would be necessary. Therefore, this will be checked to see whether KB has a real advantage over SB or if it is worse or equal in all perspectives. As AB also requires water, it is also included in this small model.

Despite the easy access to water onboard ships, less water requirements during the dehydrogenation process may be an advantage. The water required for hydrolysis has to be pure water, which is usually acquired using reverse-osmosis pumps. A closed water loop would thus result in less pumping power being required.

The stoichiometric hydrolysis equations are used to calculate the water requirements of the boron-based hydrogen carriers. The stoichiometric equation for AB can be seen in equation 3.1.

$$NH_3BH_3 + 3H_2O \rightarrow 3H_2 + B(OH)_3 + NH_3 \tag{3.1}$$

The stochiometric relations for the SB and KB are as follows [117]:

$$NaBH_4 + 4H_2O \rightarrow 4H_2 + NaBO_2.2H_2O \tag{3.2}$$

$$KBH_4 + 10/3H_2O \rightarrow 4H_2 + KBO_2.4/3H_2O \tag{3.3}$$

Additionally, the water that becomes available after the energy converter is calculated according to the following equation:

$$2H_2 + O_2 \rightarrow 2H_2O \tag{3.4}$$

A small model compares the overall water required with the water available from the energy converters. As not all water may be usable, a range of usable water is set, ranging from 50% to 100%, with 100% meaning that all water acquired from the burning or reaction of hydrogen can be used.

Water recovery potential

The potential of water recovery from the outlet largely depends on whether the water is in fluid or in gas phase. If the water is in gas phase, as water vapour, a water separator is limited by the fact that it cannot tamper with the outlet. For example, a water separator behind a hydrogen internal combustion engine could recover at most 50% of the available water, to avoid tampering with the outlet [138]. As the gas turbine operates at higher temperatures, it is assumed that a water separator will have a similar efficiency.

SOFCs also have higher operating temperatures, resulting in an outlet of steam. However, SOFCs also have anode off-gas recirculation loops, where steam is condensed from the exhaust gas [139]. This helps maintain a stable hydrogen-to-steam ratio in the fuel cell and lowers the total gas flow through the system [139]. This in turn influences the system efficiency. Thus, removing this water from the SOFC system to use in other systems may influence the overall system efficiency of the SOFC.

PEMFCs have a much lower outlet temperature. Calculations by [140] show that efficiencies of up to 110% can be achieved with simple water recovery at slightly elevated pressures of 4 atm. With expanded water recovery, efficiencies of up to 180% (at 4 atm) can be reached, while at 1 atm, efficiencies over 100% can be achieved as well [140]. Thus, no additional water is required when using a PEMFC, but for the other three energy converters, the water recirculation rate is likely lower than 100% and comparing the additional water requirements is relevant.

3.2.2 0D THERMODYNAMIC MODEL

This research makes use of a 0D thermodynamic model. In this model, mass and heat are calculated and compared. Figure 3.1 gives an overview of the model. The model's input is formed by setting an energy requirement and choosing a hydrogen carrier and an energy converter. The model then estimates the mass of the hydrogen carrier based on previous calculations. This hydrogen carrier mass goes into the reactor, where it is split into spent fuel and hydrogen. The hydrogen goes to the energy converter. Next to the spent fuel and the mass, there will be a heating requirement for the reactor to operate. This heating requirement consists of the preheating and dehydrogenation

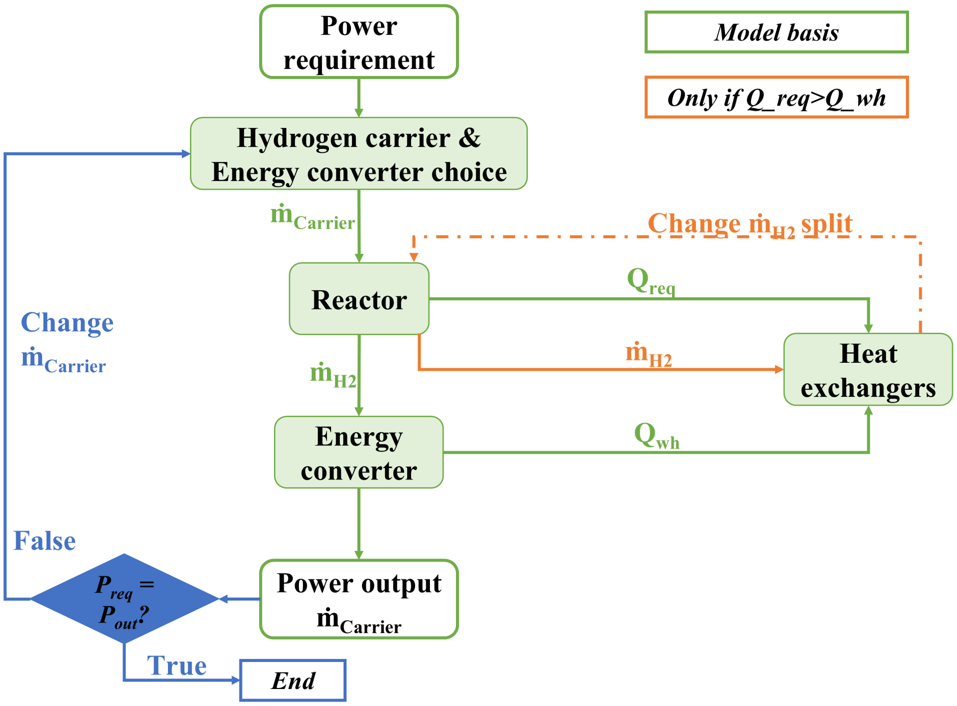

Figure 3.1: Representation of the 0D thermodynamic model

heat (the latter only if the heating requirement is positive). The preheating is calculated using the following equation:

$$Q = m \cdot c_{p,avg} \cdot \Delta T \tag{3.5}$$

with Q the heat required or released (if the temperature difference is negative) in kJ, m the complete mass of the hydrogen carrier (in the case of the borohydrides including the water) in kg, $c_{p,avg}$ the heat capacity of the overall fluid in kJ/kgK and ΔT the temperature difference in Kelvin. The heat requirement is sent to the heat exchangers, which are assumed to be 100% efficient.

The hydrogen carrier and energy converter choice also defines the resulting hydrogen mass. This hydrogen mass goes to the energy converter, where the parameters from table 3.1 are used to calculate the energy output (E_{out}), waste heat (Q_{wh}), and irrecoverable losses.

In the heat exchanger, the available waste heat and corresponding temperatures are compared to the required heat and its corresponding temperatures.

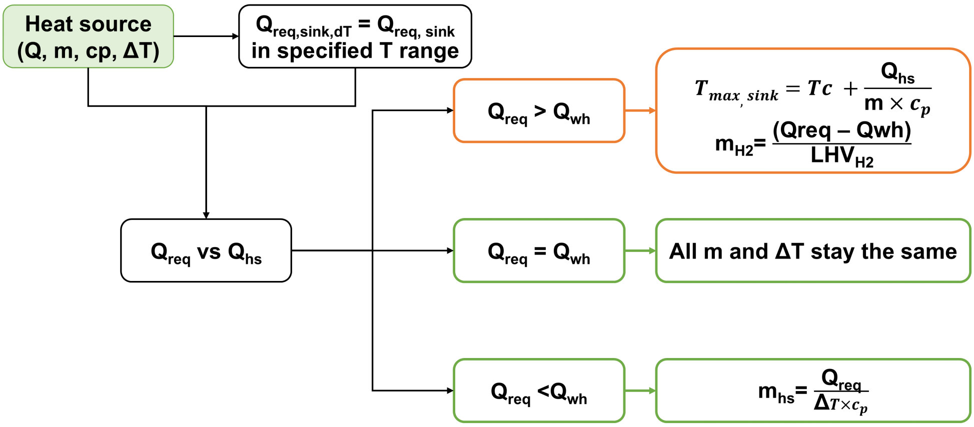

Figure 3.2: Representation of the heat exchangers inside the model

Figure 3.3 illustrates the heat flows calculated in the model. These heat flows correspond to different processes, but not all of them are applicable in every scenario. Each heat flow is associated with a specific heat exchanger (HEX), each of which is labelled (e.g., HEX1, HEX2, HEX3.1). The figure provides a detailed layout of the heat exchanger configuration and their roles. Additionally, terms such as dehydrox (for dehydrogenation), 'FG' (flue gas), and 'FG LT' (flue gas, low temperature), which will be referenced in subsequent sections, are linked to these heat flows and the corresponding HEX units. Figure 3.2 gives an overview of how the heat exchangers themselves operate. A heat source, based on the output of the energy converter, is matched with a heat requirement. In general, when available, the model uses the coolant to preheat the first part of the flow and then uses the spent fuel to preheat further. For the boron-based carriers, spent fuel and dehydrogenation heat from the reactor is not used for preheating. Not using this heat reduces complexity, prevents crystallisation in the spent fuel and removes a single point of failure. Flue gases are used to cover the final preheating and dehydrogenation heat. A minimum temperature difference between the heat source and heat sink of 10 K is assumed. If the heat sink and source differ, figure 3.2 shows how this is handled. The equations in figure 3.2 are all based on equation 3.5. In the case of a larger heat sink, the final temperature of the fluid is calculated. When the heat source is larger, the mass of the heat source fluid can be adjusted to avoid huge heat exchangers. The model saves the heat content and maximum

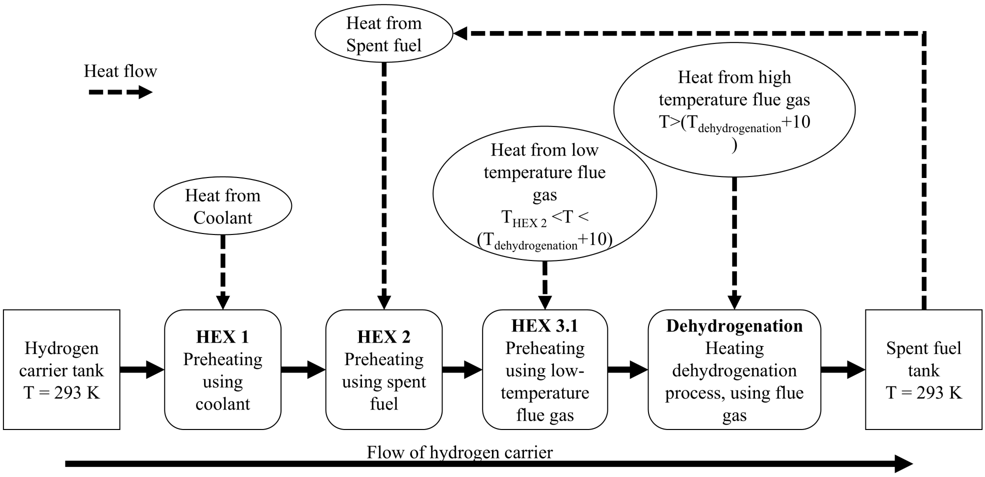

Figure 3.3: Heat flows and corresponding heat exchangers in the model

and minimum temperatures of a source or sink for detailed heat analyses. Whenever a source is insufficient to completely fill the need of a sink, an additional hydrogen burner will be used. This hydrogen burner reaches a temperature of 2480 K, the adiabatic flame temperature of hydrogen when combusted in air [141]. The efficiency of the burner is calculated by using an efficiency of 95% of the Carnot efficiency, with the cold sink being at the dehydrogenation temperature. The exact size of heat exchangers is part of chapter 4.

3.2.3 INPUT PARAMETERS

The model requires several parameters to function. First of all, there is the energy requirement. In this paper, it is set to be 2 MJ. The rest of the parameters are divided into energy converter parameters and hydrogen carrier parameters. Table 3.1 gives an overview of the parameters used in the energy converter section of the model, and table 3.2 the parameters for the hydrogen carriers. This data is based on literature.

Energy converter parameters

The energy converter is approached as a component that divides the total amount of energy inside the hydrogen over several possible allocations:

$$E_{tot} = m_{H2} \cdot \mathrm{LHV}_{H2} = E_{out} + Q_{coolant} + Q_{fg} + E_{loss} \tag{3.6}$$

Here, E_{tot} is the total energy available in the mass. m_{H2} is the mass of hydrogen, and the LHV of hydrogen is 120 MJ/kg. E_{out} is the output energy, $Q_{coolant}$ the energy going to the coolant, Q_{fg} the energy going to the flue gases and E_{loss} the energy that cannot be recovered, all in MJ. This equation must always be true in the model; if it is false, it will run again. The model only uses the heat in the flue gasses at temperatures above the required threshold (for example, the dehydrogenation temperature). Equation 3.7 gives an overview of how this local heat source is derived from the total heat source.

$$Q_{local} = \frac{Q_{fg}}{\Delta T_{max}} \cdot \Delta T_{local} \tag{3.7}$$

The energy below this temperature cannot be used for heating and is thus excluded, adjusting the available (at the correct temperatures) flue gas energy accordingly. The exact parameters defining the output values, as visible in table 3.1, must always sum up to 100%. These parameters are all based on literature. However, due to a lack of available data, engines were chosen based on the amount of data available, not on the output power of the engine. For example, the H2-ICE engine of [142] has a maximum output power of 54.9 kW, while the user can choose the output energy of this model. Additionally, this engine runs in lean conditions to reduce NO_x emissions. The flue gas temperature strongly depends on whether the engine runs in lean or rich mixtures. However, lean operation is encouraged as the overall aim of using hydrogen carriers in this case is to reduce all emissions.

Unfortunately, sources looking at ammonia-hydrogen dual-fuel options usually consider only a small amount of hydrogen and can thus not be directly used. However, no alterations are considered in terms of overall efficiencies or outlet temperatures for the mixture of ammonia and hydrogen compared to hydrogen only. This assumption is based on the substantial quantity of hydrogen present in the feed (75% mole fraction, which contributes approximately 70% of the total energy) and the similarity of the efficiencies of hydrogen only and ammonia only [143, 144].

The ammonia generated from AB cannot be used directly in a PEMFC; it first has to be reformed to hydrogen. This reforming process incurs an energy penalty of 19 to 26% (dependent on the cracking temperature) [21]. While one mole of ammonia yields 1.5 moles of hydrogen, the initial reaction (seen in equation 3.1) produces 3 moles of hydrogen. The associated energy penalty, combined with increased system complexity, the need for additional control mechanisms, and extra equipment, renders the use of ammonia from AB impractical. However, certain catalysts enable the selective release of hydrogen directly from AB [145]. Therefore, when utilizing AB with a PEMFC, in this study only the hydrogen produced from the initial reaction is used, while the ammonia is not utilized.

Table 3.1: Parameters of energy converters, including sources.

Parameter	SI-ICE	PEMFC	SOFC	GT
T coolant [K]	363	348	-	-
P coolant [%]	30	44.8	0	0
P effective [%]	35	42.9	48	37.5
T flue gas [K]	623*	-	1023	790
P flue gas [%]	25	0	42.1	53
P losses [%]	10	12.3	9.9	9.5
Sources	[142]	[146]	[143]	[147] [148]

P is the percentage of power distribution, mainly based on Sankey diagrams.

* Flue gas temperature of SI-ICE largely fluctuates depending on operating conditions and can range from 423 to 773K

For the PEMFC, relatively old data has been used [146]. More recent research shows that PEMFCs can reach efficiencies of up to 65% [149]. However, efficiency is not the only parameter required in this research. Even though a PEMFC is actively cooled, there will always be energy lost to the environment that cannot be recovered. The losses in this model also include losses due to saturated oxygen lean air and traces of (purged) hydrogen. Additionally, energy is lost in the balance of plant and electrical transformers [146]. These power losses accumulate to a total of 12.3%, but are likely to change with different efficiencies and types of PEMFCs. Thus, the data for PEMFCs in this research may be underestimated.

For the SOFC, data from [143] is used, even though [24] has already integrated a SOFC with a LOHC. As [143] reviews data from different papers and provides a detailed overview of mass and heat flows, the data from [143] is used in this study. The complementary information of [143] gives additional information needed to evaluate the parameters. The efficiency of the SOFC considers the fuel utilisation, and in this case, a fuel utilisation of 80% is considered. Most SOFCs in literature operate at this fuel utilisation [143] as higher fuel utilisations may lead to unbalanced gas flows, resulting in corrosion and damage to the cells [150]. The remainder of the gas is combusted in an afterburner and the heat is used to preheat the fuel and air [143]. As the SOFC is air-cooled at high temperatures, the coolant power and temperatures are set to zero and the output cooling of the SOFC is treated as a flue gas.

The parameters of the gas turbine were based on data from [147]. However, the mass and energy balance in this model seemed incorrect. Consequently, it was decided to adopt the provided efficiency value, assuming that it is accurate and consistent with similar systems. To make the energy balance feasible, reducing the mass flow of air going in the gas turbine was proposed, as this would result in a thermodynamic balance. Additionally, a thermal loss of 9.5% was approximated, which aligns with typical values observed in ICEs and SOFCs, both of which operate as heat engines. This estimate is slightly lower but remains within a reasonable range, reflecting the expected heat losses for this type of system.

Hydrogen carrier parameters

Table 3.2 gives the specific parameters for the hydrogen carriers. Of these parameters, several are factual, such as the molecular weight and hydrogen yield per molecule, the latter of which is the maximum possible yield of pure hydrogen. The dehydrogenation temperatures are chosen to optimise reaction rates without compromising the hydrogen carrier.

Table 3.2: Parameters of hydrogen carriers, all parameters derived from [21, 53, 96, 151, 152, 153, 154, 155, 156, 157, 158] and the Aspen database

Parameter	DBT	NEC	SB	PB	AB
Theoretical energy density [MJ/kg]	7.44	6.98	25.56	17.6	23.52
Theoretical energy density [MJ/L]	7.0	6.63	27.34	20.78	14.4
Hydrogen yield per molecule of hydrogen carrier [-]	9	6	4	4	3
Molecular weight [g/mol]	290.54	207	37.8	53.94	30.8
Heat capacity fuel [kJ/kgK]	1.96	2.04	4.54	3.48	4.54*
Heat capacity spent fuel [kJ/kgK]	1.82	1.56	N.R.	N.R.	N.R.
Dehydrogenation temperature [K]	573	503	353	353*	353*
Dehydrogenation energy [kJ/mol Fuel]	558	318	-210	-220	-156

Values denoted with * are estimated by the authors,
as no precise information was available.
N.R. stands for not relevant, this data is not required in the model

As for KB and AB, no exact dehydrogenation temperatures are available. It is estimated that these reactions occur at the same temperature as SB. The reaction processes are similar, even though the optimal temperature may differ depending on the catalyst. However, in this case, the same dehydrogenation temperatures were chosen. For the LOHCs, the heat capacity values of both the fuel and the spent fuel are calculated based on experimental values from [151], [152]. The heat capacity values are averages over 273K to the dehydrogenation temperature. The heat capacity of the boron-based hydrogen carriers is more complicated. Boron-based hydrogen carriers are completely dissolved in water to avoid crystallisation [159]. The heat capacity of the mixture is thus relevant. Due to the surplus water, the heat capacity of water is prevalent. The exact heat capacity of the mixture of 0.18 molar percentage SB is calculated using the Aspen database [160]. The same approach is used for KB. The average values are shown in table 3.2. For AB, the Aspen database was insufficient. However, the molecular heat capacities for SB and AB are very similar (86.8J/molK at 298K [161] versus 81.4J/molK at 323 K[162]. Additionally, the amount of water required to avoid crystallisation in the AB process is very similar, resulting in an estimated similar heat capacity of the fuel. The heat capacity of the spent fuel is not used to avoid crystallisation in the heat exchangers, which is likely to result in clogging.

3.3 RESULTS

This section provides an overview of the model's results. The results include the additional water requirements (subsection 3.3.1) and validation of results (subsection 3.3.2). The energy distribution (subsection 3.3.3) is also displayed. As a large amount of energy is lost through heat, subsection 3.3.4 gives an overview of the detailed uses of heat. This way, possibilities for using waste heat can be found. The Sankey diagrams in subsection 3.3.5 give a graphical representation of these heat flows, and additionally include the energy output. Finally, subsection 3.3.3 showcases the effective energy density.

3.3.1 ADDITIONAL WATER REQUIREMENTS

The hydrolysis dehydrogenation reaction requires water. Recycling this water from the outlet of the energy converter could completely satisfy the overall water requirements for all boron-based hydrogen carriers. However, as this recycling is most likely not 100%, the water required for different recycling rates was examined. Figure 3.4 shows the different recycling rates and resulting additional water requirements. An external pure water source is needed for SB if the recycling rate is not 100%. KB will need an external water source when the recirculated water is less than 85%. However, in the case of AB, this external water source is only necessary for less than 70% of water recycling. AB requires less water, and the conversion of ammonia and hydrogen also results in water.

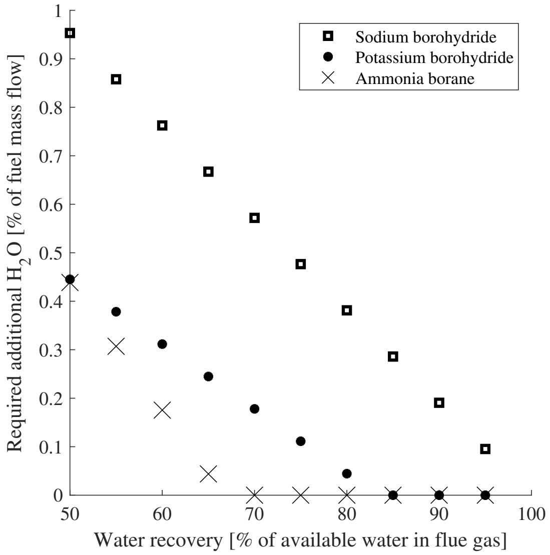

Figure 3.4: Effect of the water recirculation rate of water from exhaust gases on the amount of water that needs to be added to the system from an external source

3.3.2 VALIDATION OF RESULTS

Pinch analyses were performed on each total heat-exchanging system to verify whether the results were physically possible. A pinch diagram is a diagram in which each stream's temperatures and heat loads are plotted [163]. To have a thermodynamically possible heat exchange, the hot stream must always be hotter than the cold stream. Crossing lines indicates a disagreement with the second law of thermodynamics. Additionally, a pinch diagram shows where the design is most constrained, namely where the hot and cold lines are closest. This point is called a pinch. Pinch analyses were used for each of the configurations possible in the model. Figure 3.5 gives an example of a pinch analysis, in this case, of DBT and an ICE. The pinch analysis provides additional information, such as that the heat from the flue gases is insufficient in covering the dehydrogenation heat; additional heat from hydrogen burning is required.

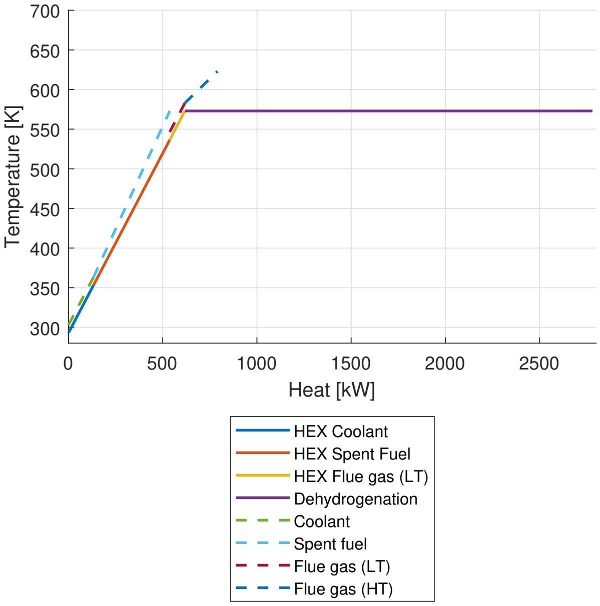

Figure 3.5: Pinch analysis of DBT combined with an internal combustion engine

3.3.3 ENERGY DISTRIBUTION

The energy distribution analysis, represented in figures 3.6 to 3.10, shows the energy distribution throughout the system, organised per hydrogen carrier. These figures show the delivered energy, energy in the coolant and the flue gases, additional energy added through a burner and absolute or irrecoverable losses. All combinations deliver the same output energy, in this case, 2 MJ. The mass of energy is also plotted in the figures.

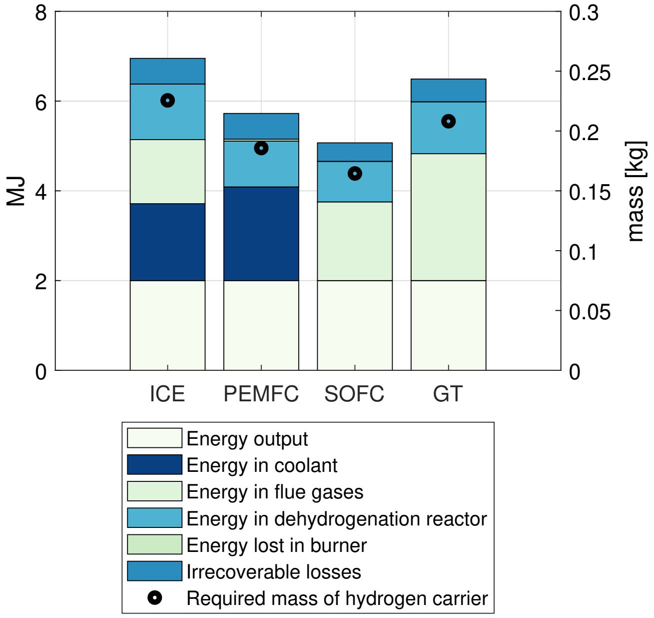

Figure 3.6: Energy distribution of SB

Figures 3.6 and 3.7 show the energy distribution of the borohydrides. KB (figure 3.7) has a very similar energy contribution as SB (figure 3.6), but does have an overall higher mass. Figure 3.6 shows the influence of the efficiency of the energy converter; a higher efficiency results in a lower mass of SB.

Figure 3.8 shows the energy distribution of AB. The heat produced in the reactor is much less for AB than the borohydrides' heat production. Additionally, this heat is less than the heat in the coolant and the flue gases. The combination of NH_3 and H_2 produces more power in an absolute sense, thus reducing the required mass. This is also clear when removing the NH_3, as done for the PEMFC. With only hydrogen, the mass required to deliver the same energy is much higher.

Figures 3.9 and 3.10 show the energy distribution of the LOHCs. Figure 3.9 shows that a hydrogen burner is always necessary for DBT, even though it only has to provide approximately 15 kW in the SOFC-coupled scenario. Figure 3.10 shows that both the SOFC and the GT give enough heat for NEC's preheating and dehydrogenation process, as the overall heating requirements are lower for NEC than for DBT.

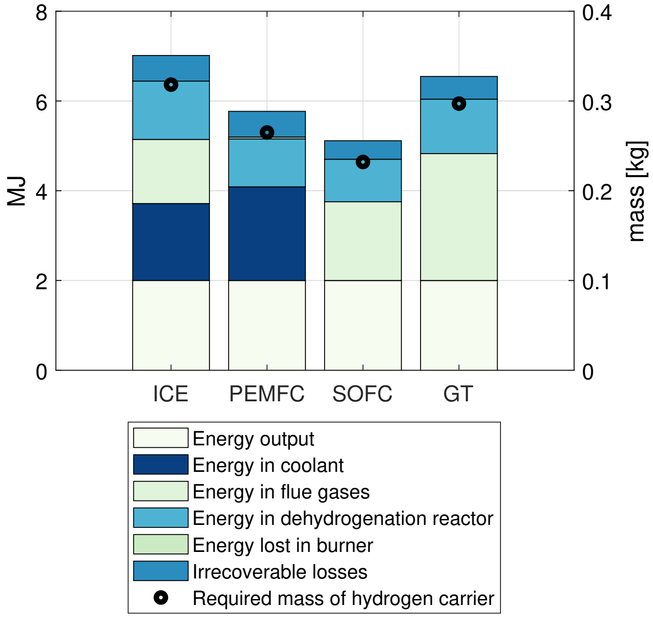

Figure 3.7: Energy distribution of KB

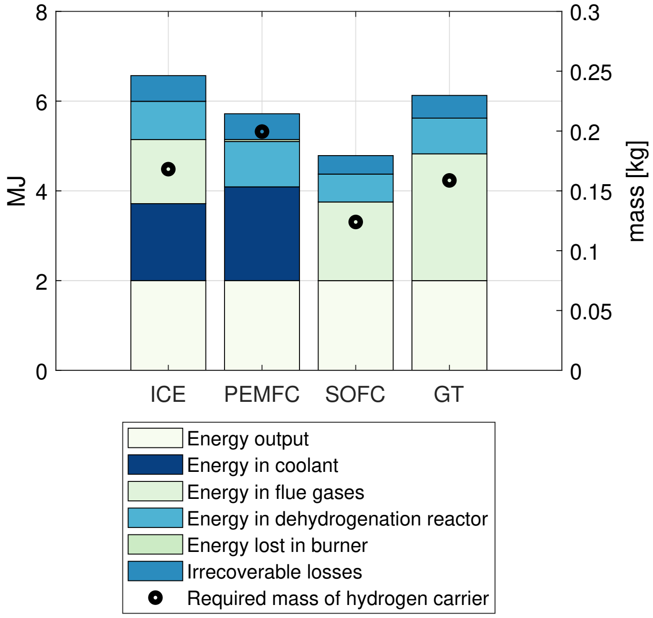

Figure 3.8: Energy distribution of AB

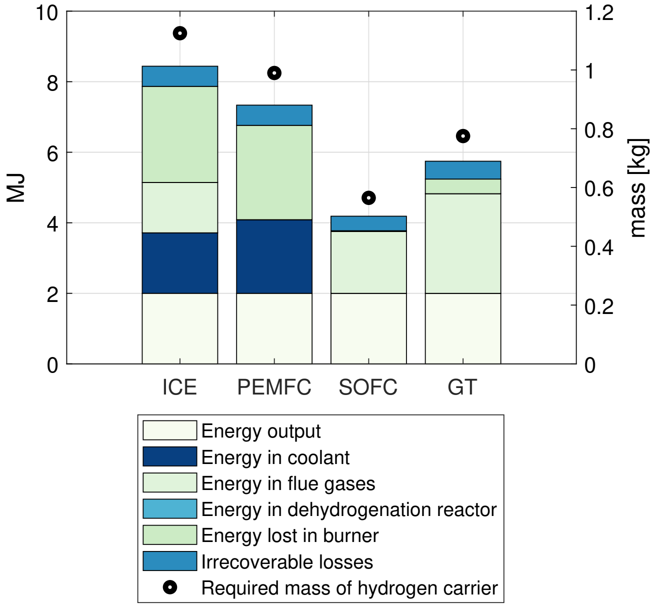

Figure 3.9: Energy distribution of DBT

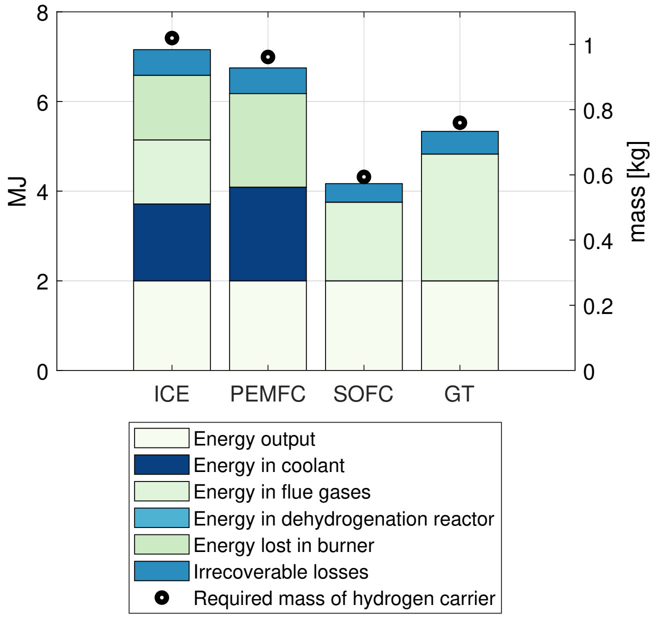

Figure 3.10: Energy distribution of NEC

3.3.4 DETAILED USE OF HEAT

The energy converters produce large amounts of heat, as only between 35 and 48% of hydrogen's total energy is converted to effective work. The rest of the energy becomes heat. Part of this heat is used for preheating fuel and dehydrogenation when necessary. In other cases, the dehydrogenation process produces more heat. A detailed analysis of the heat sinks and sources of the energy converter and the reactor offers insight into the quality of heat and the amount of heat left over. This gives insight into whether the heat can be used for other processes onboard. The detailed distributions of heat are visible in figures 3.11 to 3.15.

Boron-based carriers produce heat during the dehydrogenation process. Figures 3.11, 3.12 and 3.13 show these amounts of heat. AB produces less heat during dehydrogenation compared to the borohydrides, resulting in lower cooling requirements. A small amount of heat is required for preheating. Coolants and flue gases are used for preheating. Only for the combination of a PEMFC is a hydrogen burner required, as the average output temperatures of a PEMFC are too low to reach the desired temperature of the fuel.

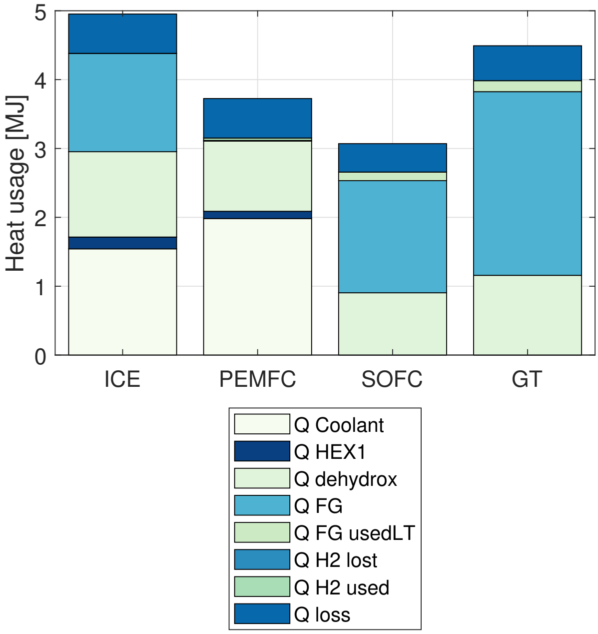

Figure 3.11: Distribution of heat for SB

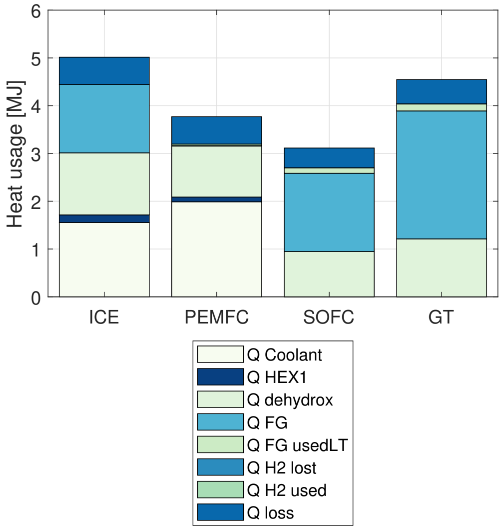

Figure 3.12: Distribution of heat for KB

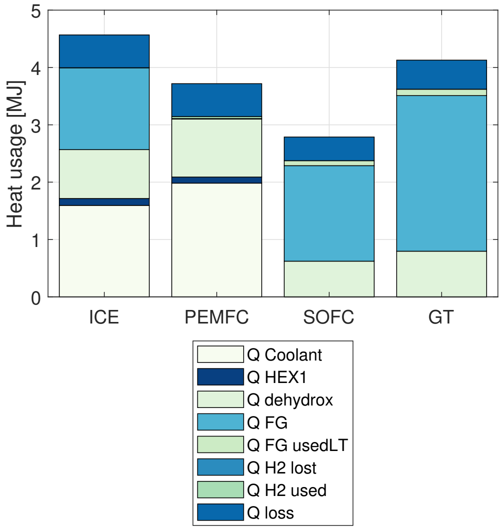

Figure 3.13: Distribution of heat for AB

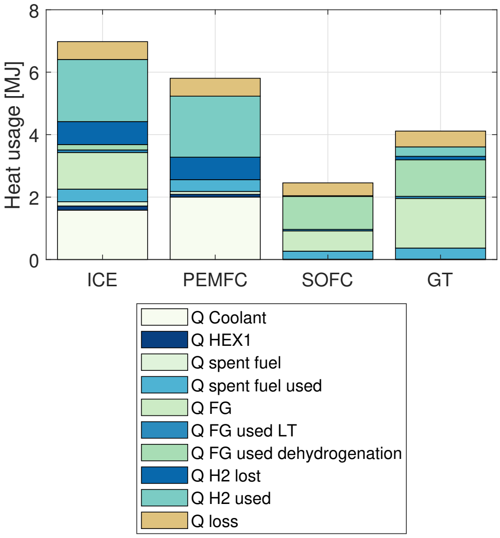

Figure 3.14: Distribution of heat for DBT

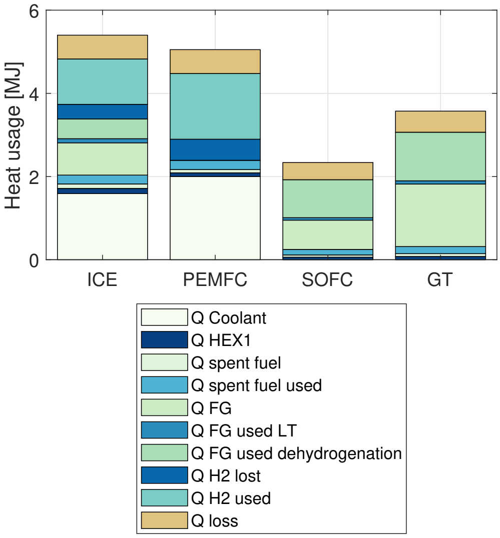

Figure 3.15: Distribution of heat for NEC

Figures 3.14 and 3.15 show the heat distribution of DBT and NEC, respectively. Despite the large amount of available heat, hydrogen burning is always required for DBT, as much of the heat is too low quality. High-temperature flue gas heat is the only heat available for dehydrogenation. Most of this high-quality heat is available in the SOFC and GT flue gases. As NEC has lower dehydrogenation requirements, its heat requirement can be covered when integrating with a SOFC and GT.

3.3.5 OVERVIEW OF ALL ENERGY FLOWS

Sankey diagrams can be used to get a graphical overview. A Sankey diagram provides an overview of all energy flows within a process. Sankey diagrams are presented for four combinations of energy converters and hydrogen carriers. These Sankey diagrams graphically represent cases with the same underlying data as provided in the previous subsection (subsection 3.3.4. The Sankey diagrams are meant to give an overview of the relevant processes in the integration of hydrogen carriers. To get correct Sankey diagrams, the enthalpy of all fluids has to be used. However, as these diagrams are meant to illustrate the process and its relevant energy flows, the lower heating value of hydrogen is used to calculate the energy flows.

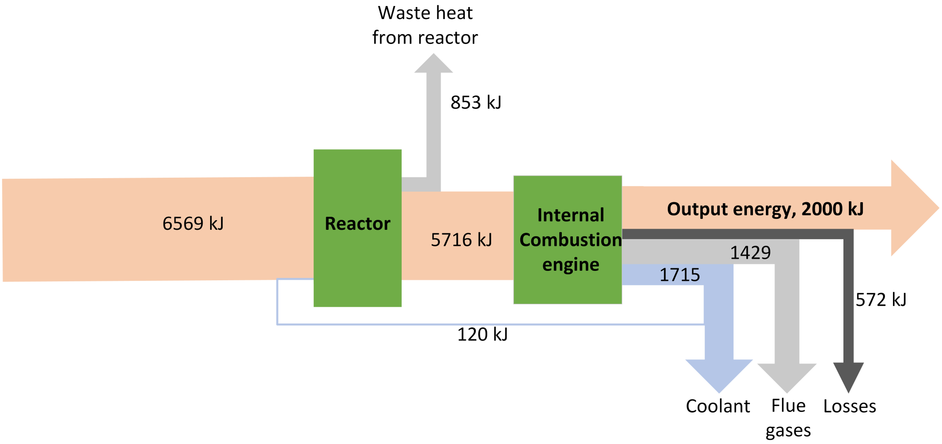

Figure 3.16: Sankey diagram of AB coupled with an internal combustion engine

We cover the combinations of DBT and a GT, which will require limited hydrogen heating and NEC and a SOFC, which requires no hydrogen heating. As AB in combination with a PEMFC is not practically possible, a Sankey diagram of AB with an ICE is made and the PEMFC and SB are visualised in another diagram. KB is not covered in the Sankey diagrams, as it is thermodynamically very similar to SB but has a lower energy density.

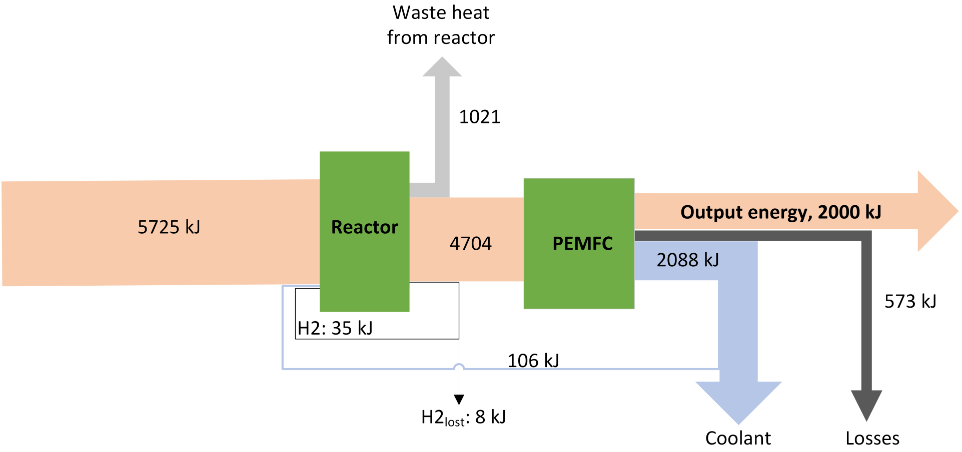

Figure 3.17: Sankey diagram of SB coupled with a PEMFC

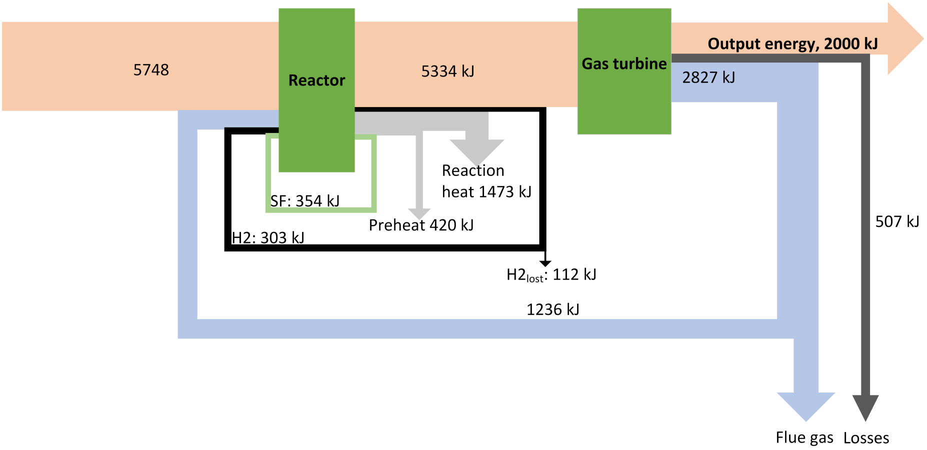

Figure 3.18: Sankey diagram of DBT coupled with a gas turbine

Figure 3.16 shows a Sankey diagram for AB coupled with an ICE. The waste heat of the reactor and the coolant form a large, low-quality heat sink, while the flue gasses form a significantly high-quality heat sink.

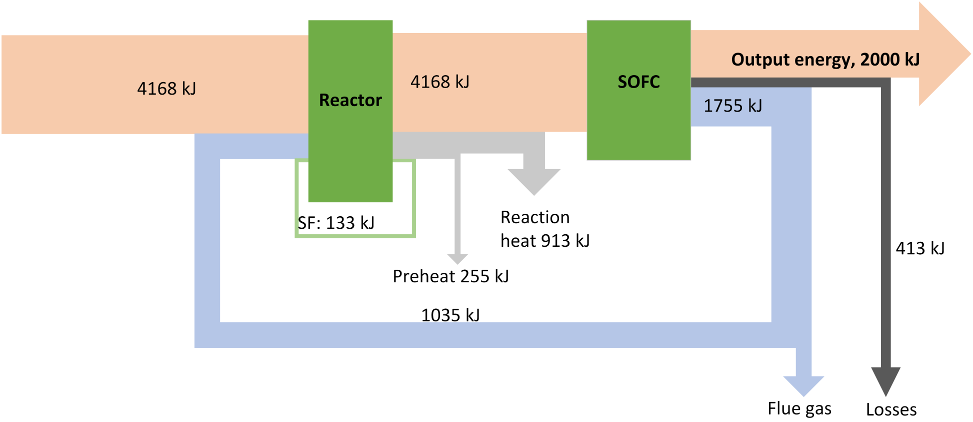

Figure 3.19: Sankey diagram of NEC coupled with a SOFC

Figure 3.17 shows SB coupled to a PEMFC. The heat provided by the PEMFC is of too low temperature to preheat the fluid fully. However, figure 3.17 clearly shows that the resulting hydrogen heating flow is minimal and is thus not a large energy loss.

Figures 3.18 and 3.19 give an overview of typical Sankey diagrams for LOHCs. Both Sankey diagrams show large heat flows returning to the reactor to provide sufficient heat for the dehydrogenation process. Figure 3.18 shows a small hydrogen flow required for preheating. This flow becomes larger when there are smaller high-temperature heat sinks. Figure 3.18 clearly shows that, in this case, the required hydrogen for dehydrogenation is minimal and only slightly influences the overall energy density. Figure 3.19 shows no additional heating is required for NEC coupled with a SOFC. The overall input energy is much less than the overall input energy of DBT combined with a gas turbine, indicating a much higher efficiency.

3.3.6 EFFECTIVE ENERGY DENSITY

Figure 3.20 shows the effective energy density of each fuel, as well as the effective energy density of MDO. Data for MDO is taken from [143, 147], while data for compressed hydrogen comes from [164]. The data from [164] reflect the ultimate goal of the U.S. DoE for the gravimetric energy density of compressed hydrogen. In this case, the effective energy density is the amount of mechanical or electrical energy that can be taken from 1 kg of fuel. This definition includes the energy converter, as heat and mass integration is necessary to use hydrogen carriers efficiently.

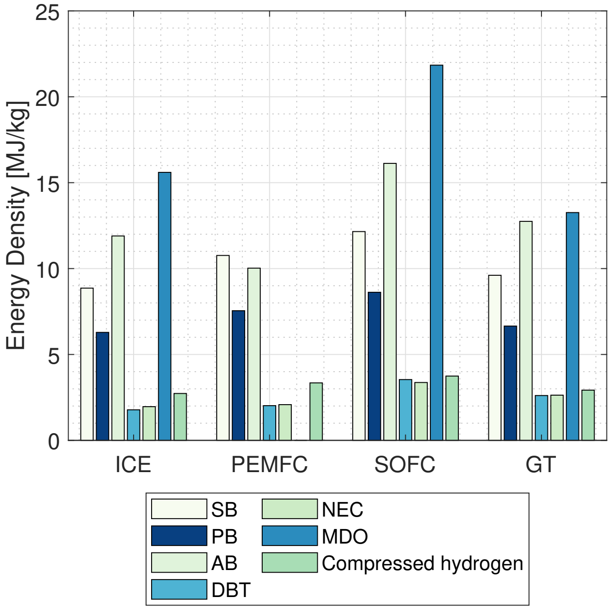

Figure 3.20: Effective energy density of the discussed hydrogen carriers, excluding the influence of the spent fuel

Table 3.3 gives an overview of the relevant masses of the hydrogen carrier and the pure hydrogen they carry. As SB and KB do not require hydrogen heating, their hydrogen mass is the same. This also applies to AB in combination with a PEMFC, as then only hydrogen is required. For the other energy converters, AB has less hydrogen content, as part of the energy is covered by ammonia. The table also clearly shows that both LOHCs not only have larger masses themselves, but the amount of hydrogen they require is often also more. As hydrogen is often required for preheating and dehydrogenation, more hydrogen is required to reach the same energy in total.

This hydrogen demand is governed by the maximum efficiency of the hydrogen burner, which in this study is modeled at 95% of the Carnot efficiency. This adjustment accounts for losses due to imperfect isolation, possible incomplete combustion and other practical inefficiencies. While the use of Carnot efficiency for a furnace is justified, Incorporating ambient temperature into the calculation has been suggested for a more accurate assessment [165]. In our current model, accounting for this different efficiency results in minimal output changes. For DBT, the mass of the hydrogen carrier is affected in all four cases: internal combustion engine (-0.06 kg), PEMFC (-0.07 kg), SOFC (-0.01 kg) and GT (-0.01 kg). For NEC, only the internal combustion engine (-0.02 kg) and PEMFC (-0.04 kg) were affected. Although these differences are relatively small, they demonstrate the flexibility of the model. The ability to accommodate variations in input parameters while producing consistent results underscores the robustness of the approach.

Table 3.3: Mass of hydrogen into the engine and mass of hydrogen carrier, to have an 2 MJ energy output.*For AB, only the hydrogen mass is shown in this table, the ammonia is not shown here, but does influence the overall energy density.

	SB	PB	AB*	DBT	NEC	
ICE	0.048	0.048	0.033	0.070	0.060	Hydrogen to engine
ICE	0.225	0.318	0.168	1.125	1.020	Hydrogen carrier
PEMFC	0.039	0.039	0.039	0.061	0.056	Hydrogen to engine
PEMFC	0.186	0.264	0.200	0.990	0.962	Hydrogen carrier
SOFC	0.035	0.035	0.024	0.035	0.035	Hydrogen to engine
SOFC	0.165	0.232	0.124	0.565	0.594	Hydrogen carrier
GT	0.044	0.044	0.031	0.048	0.044	Hydrogen to engine
GT	0.211	0.300	0.157	0.766	0.760	Hydrogen carrier

3.4 DISCUSSION

For hydrogen carriers to be relevant as future fuels, their energy density has to be identified. This discussion section will discuss the overall energy density and additional requirements for each of the hydrogen carriers.

3.4.1 SB, KB AND AB

SB and KB are very similar substances, while AB has similar chemical properties as both of them. A great advantage of KB as compared to SB would be the reduction of additional water, if not all water can be recycled. A recycling rate of 100%, however, is likely to be only practical when using a PEMFC [138]. Removing water from flue gases by cooling the flue gas to a water condensation temperature may influence the operating conditions and thus the efficiency of an internal combustion engine or a gas turbine, resulting in a limit of approximately 50% of water recycling. Anode off-gas recirculation, including water recycling and condensation, is often used in SOFCs [139]. The anode off-gas recirculation rate influences the efficiency of the system, extracting 100% of the produced water will likely result in a lower efficiency [139] . Thus, KB with a PEMFC has advantages if a closed loop is desired. Closed loops are less relevant onboard ships, where unlimited water is available.

The energy density of the boron-based carriers is influenced by their exothermic nature. Part of the overall energy available is lost to heat during dehydrogenation. As this is percentage-wise larger for KB than for SB, KB requires a significantly larger mass to reach the same energy output. It is the least for AB, which results in it requiring the lowest mass and, thus, reaching the highest energy density.

Although ammonia is produced by AB, pure ammonia is still excluded from this study, necessitating further explanation. First, the safety requirements for AB differ significantly from those for pure ammonia. While AB does release ammonia, it does so in much smaller quantities, and this ammonia is likely to be consumed immediately by the engine. If needed, a buffer could consist of pure hydrogen instead. Additionally, the amount of ammonia produced is lower than the hydrogen output and several liters of ammonia compared to storing the entire energy source as ammonia results in a critical safety distinction that should not be overlooked. Secondly, when considering ammonia as a hydrogen carrier, the cracking temperature required is notably higher than that of other carriers, such as DBT, which already poses challenges for integration with available heat sources, as demonstrated previously.

Generally, due to the exothermic nature of the hydrolysis process, a lot of high- and low-quality heat is available for other onboard systems. Low-quality heat is more challenging to use than high-quality heat.

3.4.2 LOHCS

DBT and NEC have similar energy densities, but there are still several differences. The mass of hydrogen carrier required to reach the energy output is lower for DBT, except when coupled to an internal combustion engine. Additional heating when combining DBT with an internal combustion engine causes this higher mass. However, especially for the ICE, a large percentage of the heat in the flue gas is at temperatures too low for dehydration. This is even stronger for DBT (see figure 3.14) than for NEC due to DBTs higher dehydrogenation temperature. As DBT has a higher hydrogen content, the overall mass is smaller with excellent heat integration. The SOFC scenarios endorse this, as very little additional heating is required when using DBT. The integration of dehydrogenation is more effective for NEC than for DBT. This suggests that the choice of LOHC may not be as important as the efficiency of the energy converter. However, as the LOHCs have such similar energy densities, other factors such as technology readiness levels, safety or handling, are likely to be the decisive factor in choice between LOHCs.

3.4.3 COMPARISON AND OVERALL ENERGY DENSITY

The effective energy densities of AB and SB are the highest, irrespective of the used energy converter. KB has a much lower energy density than SB on all accounts. Additionally, the highest energy efficiency for KB (when combined with an SOFC) still does not come close to the lowest effective energy density of SB (when combined with an ICE). Thus, KB is generally less energy dense.

Despite their different theoretical energy densities, figure 3.20 shows very little difference between the LOHCs. Both LOHCs have energy densities much lower than the other hydrogen carriers or MDO. Up to five times more LOHC is required to have a similar energy density as MDO. However, the LOHCs may be able to reach very similar energy densities as compressed hydrogen (which is here estimated to have a gravimetric energy density of 6.5 wt% of hydrogen, the ultimate U.S. DoE goal [164]). A large difference in effective energy density exists between the boron-based carriers and the LOHCs. There are two main reasons for this. Firstly, the endothermic nature of the LOHCs results in higher masses of the hydrogen carrier than the boron-based carriers. Secondly, the LOHCs store less hydrogen per kilogram, theoretically, than boron-based carriers.

The effective energy density is strongly influenced by the energy converter. An energy converter with a higher efficiency will result in a higher effective energy density. The energy density of AB when using a gas turbine differs only slightly from MDO combined with a gas turbine. The energy density of SB is lower than that of MDO for each of the combinations but does appear to be in a similar ballpark. On the other hand, the energy density of AB with an SOFC surpasses the combination of MDO with a GT and with an ICE. Thus, AB and SB have high energy densities, on par with or at least similar to current technologies.

3.5 CONCLUSION

This study aimed to evaluate the effective energy density of hydrogen carriers as alternative fuels. This goal was accomplished by examining the efficiency of the overall energy cycle when using alternative fuels. This model can calculate different efficiencies in a simple, yet accurate manner, enabling the calculation of the overall efficiency and, thus, the practicability of hydrogen carriers.

The model consists of two main types: the dehydrogenation process can be either endothermal or exothermal. However, this dehydrogenation process always requires either energy (in the form of heat) or mass (e.g. water). To determine the overall energy density of the system, a thermodynamic 0D model was built which integrates the heat and masses of the system. This model provided a first indication of the overall energy densities of five hydrogen carriers combined with four energy converters, which are as follows.

SB and AB have the highest energy densities of the hydrogen carriers. Without taking the spent fuel into account, these energy densities are close to (and may, in some cases, even surpass) the energy density of diesel. Although both LOHCs have lower energy densities, similar to that of compressed hydrogen, other characteristics may still make them relevant. KB, on the other hand, is not as favourable as SB.

This chapter highlights the importance of heat and mass integration of hydrogen carriers and energy converters for the overall energy density. Although the 0D model only provides estimates, it shows compelling findings, which should be investigated in more detail in future research. Hydrogen carriers can achieve overall energy efficiencies similar to conventional fuels, thereby considerably enhancing the attractiveness of more sustainable options.

3.6 FUTURE RESEARCH

The current model provides a simplified but well-founded overview of the effective energy efficiency and density of the different combinations of hydrogen carriers and energy converters.

In addition to the energy density, power density is important for all ships. To provide a more complete overview, the power density of each option should be evaluated. This is particularly important for hydrogen carriers, as their hydrogen-release systems require additional components that affect the effective power density. Chapter 4 discusses these additional components and their sizes.

The model currently calculates the gravimetric energy density. As some ships are volume-limited, the volumetric energy density is also interesting. Calculating this volumetric energy density can be easily done for the LOHCs. LOHCs are generally fluids in the hydrogenated and dehydrogenated states, and their density is clearly defined. The boron-based carriers, however, are powders. Powders have a bulk and particle density [166]. The differences between these densities can be large and are influenced by the moisture content and particle size [166]. Chapter 5 will also discuss the volumetric energy density.

POWER & ENERGY

4

POWER DENSITY

> *"More science happens through lucky accidents than you'd believe, Radiant Lopen," Rushu said. "It makes me wonder how many amazing innovations we've passed up because we were searching for something else, and didn't realize what we'd done."*
>
> — Brandon Sanderson, *Dawnshard*

CHAPTER SUMMARY

This chapter focuses on the power density and additional components required when using hydrogen carriers. Applying hydrogen carriers influences ship design significantly, as they require additional specialised equipment to remove hydrogen from the hydrogen carrier. This research estimates the size of the equipment. As this equipment will need to be stored and maintained on the ship, the exact sizing and sequence of the additional equipment will likely influence ship design. Results show that the reactor size is significant for all hydrogen carriers. Additionally, the size of respective energy converters is discussed here.

4.1 INTRODUCTION

Applying alternative power sources can have significant implications for ship design and is thus extensively researched, mainly focusing on using ammonia or methanol as alternative fuel [167], [168], [169]. Similarly, using hydrogen carriers will significantly influence the ship's power plant and, consequently, ship design, as additional components such as hydrogen release reactors are required. Additionally, these reactors cannot be placed everywhere on the ship, as they produce pure hydrogen and thus need to be in regulated and well-ventilated spaces. Besides the reactor, more components, such as heat exchangers, may be necessary. All these additional components that are required to release hydrogen from hydrogen carriers are components that are not necessary without hydrogen carriers. So, using hydrogen carriers may result in more components and, thus, more complexity.

As these additional components are of unknown size, it is unclear whether they are significantly sized to influence ship design. For other alternative fuels, such as methanol or LNG, it is clear that the additional components will influence ship design [168], [169]. Research focuses on resulting required design changes because of the space other components take up [168], [169]. However, the number of components explicitly needed for hydrogen carriers as power sources, and the size of these specific components are unknown. The sequence, size, and number of this specialised hydrogen carrier equipment are required to see how they influence and perhaps limit ship design.

This chapter will evaluate the same hydrogen carriers and energy converters as the previous chapter, namely the hydrogen carriers of SB ($NaBH_4$), AB (NH_3BH_3), NEC and DBT. Due to the small difference and limited energy density of KB as compared to SB, KB will not be regarded in this chapter, and the next. The investigated energy converters are a PEMFC, SOFC, hydrogen-powered ICE and GT.

This chapter aims to identify and size the relevant components when using the hydrogen carriers mentioned earlier as power sources onboard ships. First, all the required components for each hydrogen carrier must be known. Only the specifically relevant components for hydrogen carriers are

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E. S. van Rheenen, J. T. Padding, A. A. Kana, and K. Visser, "Ship system design changes for the transition to hydrogen carriers," in Proceedings of the 15th International Marine Design Conference (IMDC-2024), Delft: TU Delft OPEN Publishing, 2024.

considered; general equipment for hydrogen-fueled ships is not regarded. Each of these components will then be sized. This will form a first step in designing hydrogen carrier-powered ships.

4.2 BACKGROUND

SB, AB, DBT and NEC are considered in this chapter. As energy converters, same as in the previous model, the ICE, GT, PEMFC and SOFC are considered [29]. More information on these carriers and their chemical and physical properties, is given in appendix A.

4.2.1 REQUIRED COMPONENTS FOR HYDROGEN RELEASE

Figure 4.1 gives an overview of the specific components required for the LOHCs to release hydrogen. After the carrier is transported from the tank, heat exchangers are used to preheat the carrier up to the dehydrogenation temperature. Part of this heat exchange already has to occur in the tank, as DBT is highly viscous; thus, preheating is required to get it out of the tank. The dehydrogenation of AB produces hydrogen and ammonia. Ammonia gas can be burned in a heat engine, for example, in a dual-fuel ammonia-hydrogen internal combustion engine. For AB, only dual-fuel options of ammonia and hydrogen gas are considered. Only the PEMFC cannot run on the ammonia-hydrogen dual-fuel of the four investigated energy converters and is thus not considered for AB, similar as in chapter 3. Figure 4.2 gives an overview of the required components for AB and SB to release hydrogen.

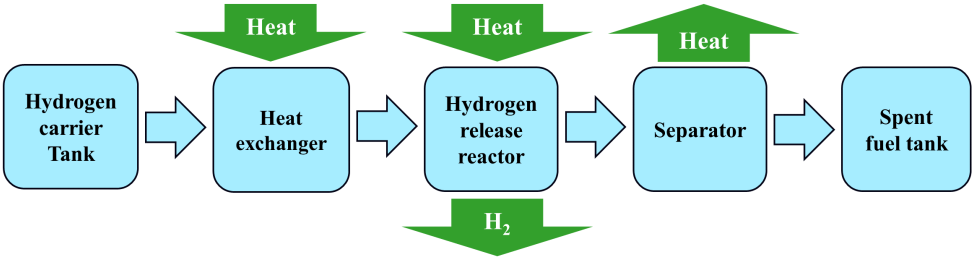


Figure 4.1: Simplified flow diagram with required components and main heat and mass flows for endothermic release hydrogen carriers

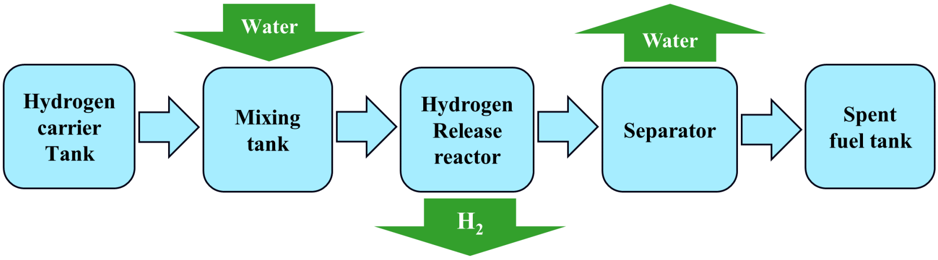


Figure 4.2: Simplified flow diagram with required components and main heat and mass flows for exothermic release hydrogen carriers

4.2.2 ENERGY CONVERTER

Energy converters convert the chemical energy inside hydrogen to electrical or mechanical energy. The model will simulate four different energy converters, namely a hydrogen spark ignition (SI) ICE, a PEMFC, SOFC and GT, as these are all considered possible alternatives within the shipping sector. At the moment, a compression ignition running on pure hydrogen is not feasible without a way to ignite the hydrogen and is thus not regarded [170]. Additionally, SI ICEs are more researched, and more data is available for these heat engines [142]. The output of both the SI ICE and GT is regarded as mechanical. Both are assumed to be able to run on pure hydrogen and a hydrogen-ammonia mixture [142], [147], [148].

4.3 METHOD

Using hydrogen carriers on ships results in additional components needed on board compared to using pure hydrogen or conventional fuels. Some of these components are specific to hydrogen carriers, whereas other components, such as the energy converter, may be different for hydrogen-based fuels in general. This research only covers the hydrogen carrier-specific components, not the hydrogen-specific components. These components are visible in figure 4.3, where the components that will be looked at in detail in this research are coloured green. The required input parameters, such as mass flows, compositions and temperatures, are calculated using the previously created 0D model (see also chapter 3). Figure 4.4 shows a simplified model outline based on [29]. The model is built so that each energy converter, regardless of the hydrogen carrier, will always have an output power of 2 MW, which is relevant for medium-sized vessels such as ferries and small cargo ships.

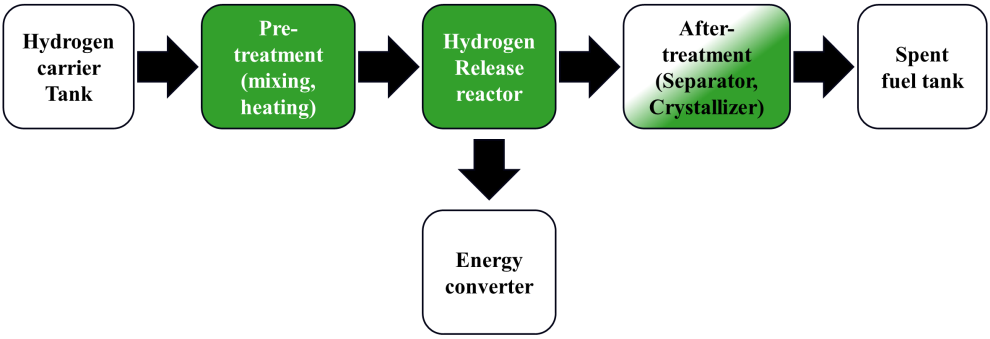


Figure 4.3: Overview of all components required on a ship when using hydrogen carriers as a power source. The components denoted in green are hydrogen carrier specific components and, thus, the main focus of this research

This section describes the necessary steps to upgrade them to get an overview of the sizing. A different approach is used for each component due to their significant difference in functionality. The parameters required for upgrading the components, such as mass flows and temperatures, are given by the 0D model. The following subsections will describe each critical component in detail and how they can be upgraded.

4.3.1 0D MODEL

Figure 4.4 gives an overview of the 0D thermodynamic model's layout, as implemented in Matlab Simulink. The power requirement, the hydrogen carrier and the energy converter can be chosen. These three parameters then define the mass flow of the hydrogen carrier. This mass flow, in its turn, defines the required energy for preheating and, if applicable, dehydrogenation. The model runs a complete iteration, including an energy balance check, and adjusts the mass flow accordingly if the required power and the output power do not match.

Tables 3.1 and3.2 give an overview of the used parameters and the resources from which they were derived. The thermodynamic model provides estimates and a simplified representation of reality. For example, the model does not

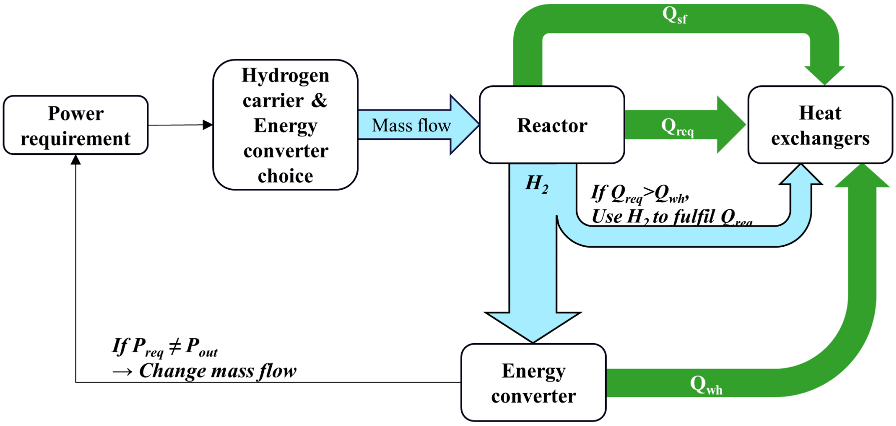


Figure 4.4: Simplified overview model. Flows that are used as a heat source can be turned on and turned off when necessary. Q_{wh} stands for waste heat, Q_{req} is the heat required for preheating and, if applicable, dehydrogenation and Q_{sf} stands for the heat inside the spent fuel

consider the preheating of air for a SOFC. In reality, this preheating, which is required, is a major, high-temperature heat sink [143]. When the heat needed for the dehydrogenation of the hydrogen carrier cannot be covered with waste heat from the energy converter, hydrogen will have to be burnt to cover the heat requirement. The heat required for preheating and dehydrogenation, Q_{req}, and the heat available inside the spent fuel, Q_{sf}, are calculated according to the following equation:

$$\dot{Q} = \dot{m} \cdot c_p \cdot \Delta T \tag{4.1}$$

With $\dot{Q}$ the heat in kW, $\dot{m}$ the mass flow in kg/s, c_p the heat capacity, in kJ/kgK and ΔT the temperature difference in Kelvin. In the Matlab model, c_p is considered constant, not temperature-dependent. Q_{wh} is defined by the percentage of heat going from the reactor to heat losses (denoted by P coolant and P flue gas in table 3.1). A fixed temperature difference is set for flue gasses and coolant, which is used to calculate the flue gas's or coolant's mass flow, using equation 4.1. The required mass flow of the flue gas or coolant to go into the heat exchanger is similarly calculated. However, if the heat (denoted by Q) is larger than required to heat the hydrogen carrier in that temperature window, the mass flow is adjusted, as equation 4.1 is always true [171].

4.3.2 PRETREATMENT: MIXING TANK

The boron-based hydrogen carriers are mixed with water in the mixing tank. This mixture is then further heated in heat exchangers before entering the reactor. The mixing tank uses a stirrer. The size of the mixing chamber depends on the required power and the selection of spent fuel. The hydrolysis reaction of the boron-based carriers is visible in equation 3.2 and 3.1. The hydrolysis requires a surplus of water. The amount of water, defined by the (2+x) term, is the minimum amount needed for the reaction to happen. Additionally, it defines the composition of the spent fuel. The (2+x) term depends on the temperature if enough water is available [159]. More important, however, is the solubility of the fuel and spent fuel in water. The amount of water should be sufficient to avoid spontaneous crystallisation, which may result in clogging. For both AB and SB, the spent fuel is less soluble in water than the fuel. As both the fuel and spent fuel are present in the reactor, the limiting substance defines the amount of water. For AB and its spent fuel product, boric acid, the limit at temperatures of 353K is about 19 wt% of AB in water [172]. For SB, this limit lies at around 44 wt% SB in water [159]. These limits thus define the minimum amount of water required in the mixing tank.

The size of the mixing tank is determined as follows. The amount of water required for the boron-based hydrogen carrier spent fuel to completely dissolve at 353K (the operating temperature of the reactor) is calculated. This amount of water is compared to the stoichiometric amount of water required for the reactions (as depicted in equations 3.2 and 3.1). The largest amount of water is taken. This amount should always be compared to the amount of boron-based hydrogen carrier that can be dissolved at room temperature (293K) without crystallisation [83], [173]. The spent fuel is the limiting factor for SB and AB. The largest amount of water (stoichiometric or dissolvent value) must be held in the mixing tank. As the boron-based hydrogen carriers will completely dissolve, their volume is negligible.

4.3.3 PRETREATMENT: HEAT EXCHANGERS

All hydrogen carriers need to be heated before entering the reactor. The amount and type of heat exchangers depend on the energy converter chosen and the hydrogen carrier.

A heat exchanger with a large heat transfer surface per unit volume is a compact heat exchanger. The ratio of heat transfer surface area to the volume of the heat exchanger is called the area density, denoted with β[171]. Generally speaking, heat exchangers with a β in excess of 700 m^2/m^3 are classified as compact, with heat exchangers in microreactors reaching area densities of over 15000 m^2/m^3 [171], [174]. However, these high-area density heat exchangers, which also include printed circuit heat exchangers, have high pressure drops, making them less suitable for the specific applications addressed in this paper due to the high viscosity of some of the fluids, such as LOHCs [171]. To have an efficient heat exchanger, the thermal conductance of both fluids should be similar [175]. This is more likely the case for liquids than for liquid-gas heat exchangers. Thus, liquid-liquid heat exchangers generally require different heat exchangers compared to liquid-gas heat exchangers [175].

The type of heat exchanger is defined by the fluids flowing through it. Generally, heat exchangers can differ depending on the fluid (gas or liquid), viscosity, fouling, pressure and temperature of the fluid [171], [175]. As the pressures are similar for all four hydrogen carriers (1-10bars), different heat exchangers are unlikely to be required based on pressures. Fluid types differ, and both liquid-liquid and gas-liquid heat exchangers are required. Similarly, the temperature ranges of the hydrogen carriers vary significantly, as dehydrogenation temperatures range from 353K to 573K. Finally, the viscosity of the different hydrogen carriers differs. The boron-based hydrogen carriers are mixed with water, and these mixtures have viscosities that are relatively similar to water. DBT is highly viscous at low temperatures, with viscosities of up to 4000 mPas [152].

Additionally, several other parameters must be known to evaluate the sizing of heat exchangers, namely, the mass flows, and in- and outlet temperatures of both the hot and cold sides. Thus, the 0D model should provide these mass flows. However, the 0D model uses a fixed heat capacity to calculate the mass flows of the hot side, which may result in small errors. The heat exchangers will all be designed in Aspen Exchanger Design & Rating (EDR), which will adjust the mass flow of the hot fluid when necessary. Aspen EDR can calculate the exact size and mass of heat exchangers and is widely used in industry and heat exchanger design research (K. Hooman, personal communication, November 27 2023). As a basis, the material properties from Aspen are incorporated. When a disagreement occurs between data obtained from any of the Aspen databases and experimental values from the literature, the data from the literature is taken. As the 0D model only incorporates a fixed, heat capacity value, the heat exchanged within a heat exchanger might differ between Aspen and the 0D model. In these cases, the mass flow of the heat source is adjusted accordingly while checking if the mass flow does not exceed the maximum mass flow according to equation 4.1.

Expected amount and sequence of heat exchangers

The 0D model can be used to estimate the amount and sequence of the heat exchangers (see chapter 3). The boron-based hydrogen carriers are mixed with water before entering the release reactor. This mixture has to be heated as well, and considering the difficulty of heating solid powders, the boron-based hydrogen carriers will be heated as a mixture. Heating the mixture will occur in a heat exchanger and requires only one heat exchanger, as they need to be heated to only 353K. No heat exchangers with spent fuel are used to avoid crystallisation inside heat exchangers. So, either flue gasses or coolant is used to preheat the exothermic-release hydrogen carriers, which are believed to contain enough heat to fulfil the requirements.

The endothermic-release hydrogen carriers, the LOHCs, will likely need more heat exchangers. When applicable, the LOHC will be heated in the first heat exchanger using the coolant from the energy converter. The second heat exchanger uses the spent fuel to heat the LOHC to almost the dehydrogenation temperature. A drawback for NEC here is that its spent fuel turns into a solid at temperatures lower than 343K. Thus, the fuel must be heated to at least 343K before entering the second heat exchanger. Finally, using flue gasses, a third heat exchanger will heat the LOHC until it reaches the dehydrogenation temperature.

4.3.4 AFTER TREATMENT: SEPARATOR AND CRYSTALLIZER

If the conversion rate of the LOHC is below 100%, a separator may be advantageous. The threshold below which a separator becomes worthwhile depends on the energy density, desired ship range, and volumetric fuel tank requirements. However, if a separator is larger than the additional fuel required to compensate for the lower conversion efficiency, it would not be worth using.

Next to the separator, a crystalliser can crystallise the spent fuel from the water to avoid storing large amounts of spent fuel. This water prevents the spent fuel from crystallising and thus clogging the system. The water required depends on the spent fuel, as the solubility of the spent fuel is lower than that of the fuel itself [159], [172], [176]. However, the water also adds a large amount of weight and volume to the spent fuel, reducing the energy density of the whole system. Thus, crystallising the spent fuel is essential, and a crystalliser has to be added to the system. For hydrogen carriers that exothermically release hydrogen, such as SB and AB, the crystalliser's size must be at least as big as the reactor's. In an emergency, the content of the reactor can then be dumped in the cooled crystalliser to stop or at least significantly slow down the hydrogen release reaction. This is unnecessary for hydrogen carriers that release endothermically as withholding heat will stop the reaction.

The sizing of the crystalliser and the separator highly depends on the conversion rate inside the reactor. In turn, this depends on the choice of catalyst, the amount of catalyst, the temperature, the throughput time of the reactor and, for boron-based carriers, the amount of additional water. Especially the catalyst choice is of significant influence and is thus well-researched [113]. Because of the depth of the studies on this subject, it was decided not to incorporate this.

4.3.5 RELEASE REACTOR

The hydrogen release reactor is where the hydrogen is released from the hydrogen carrier. In this reactor, the hydrogen carrier passes by the catalysts, upon which it reacts and releases hydrogen. Many researchers are studying this process. More detailed information on release reactors is provided in [177]. In this chapter, however, the release reactor will be modelled as a plug flow reactor, with a jacket around it to provide the necessary heat or cold. The plug flow reactor is assumed to have a membrane to remove the hydrogen. The hydrogen gas will expand vastly and thus significantly influence the reactor's working if not removed immediately.

The dehydrogenation of endothermic-release hydrogen carriers requires heat. A buffer fluid will be used when the heat has to be supplied to the reactor, and the heat source is not considered constant (such as flue gasses). This buffer fluid reduces the system's efficiency but controls the heating system. Using a buffer fluid can prevent overheating of the reactor, which can result in the decomposition of the hydrogen carrier and has to be avoided.

4.4 RESULTS AND DISCUSSION

This section discusses the main results. The model is first validated using pinch diagrams and a sensitivity analysis. The sizing of the mixing tank and reactor, as well as the type and sizing of the heat exchangers, is discussed next. It is important to realise that only the components from figure 4.3 are considered. The storage tanks, engines or fuel cells, and potential hydrogen burners are not considered, despite taking up significant amounts of space. The PEMFC is not considered in the case of AB. AB releases both hydrogen and ammonia. Cracking or storage of ammonia is not deemed feasible and the ammonia will be used as fuel, together with hydrogen [29]. This rules out a PEMFC, as ammonia is toxic to PEMFCs and strongly reduces the performance of the PEMFC [178]. Thus, the figures of AB will have only three results and the PEMFC is left out.

4.4.1 VALIDATION: INFLUENCE OF VISCOSITY

The viscosity of AB mixed with water is unknown. Thus, an estimation was made. The level of AB in the water (3mol/L, [172]) is much lower than the solubility limit. Therefore, low viscosity (1-2 mPas) is assumed. A sensitivity analysis was used to control the influence of small changes in the viscosity on the output of Aspen EDR. The viscosity was changed with a factor of 1.5 and 2, without any changes in the heat exchanger. Thus, such small changes in viscosity are insignificant.

4.4.2 MIXING TANK

To estimate the size of the mixing tank, the residence time and the mass flow of the mixture must be known. The residence time is defined by the dissolution time of the crystals, and is strongly influenced by the mixing equipment. The residence time should be sufficient to ensure sufficient mixing to avoid crystallisation. The residence time in mixing vessels for SB and AB is estimated to be relatively short (about 3 minutes), resulting in small mixing tanks. The mixing time is based on data from Aspen for SB. The same mixing time for AB is taken, as no additional data is available for AB. Experiments should be performed on the mixing time to estimate the mixing tank size better. Figure 4.5 gives an overview of the mixing tank size without considering a safety factor.

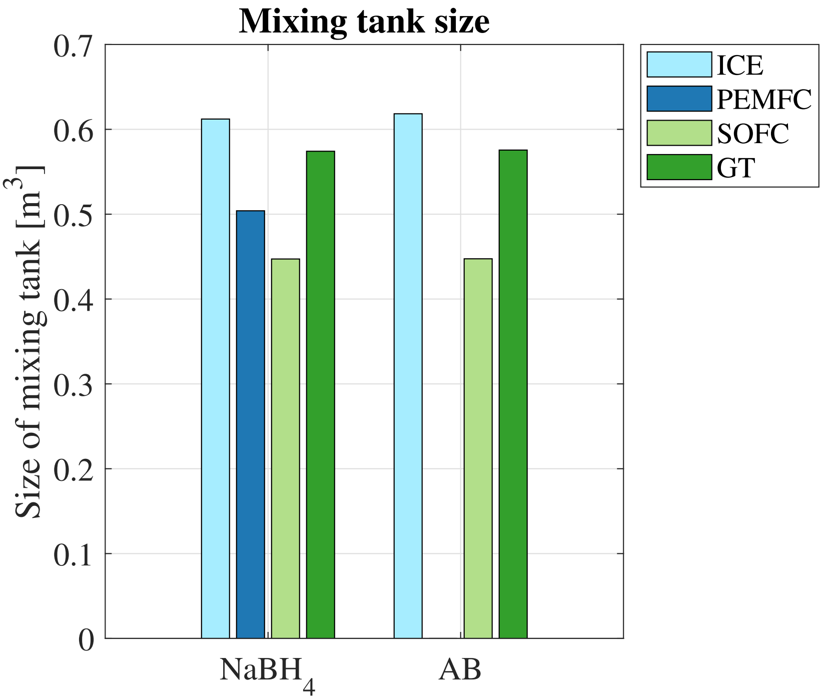


Figure 4.5: Size of mixing tanks, without safety factor

4.4.3 HEAT EXCHANGERS

This section will describe the choice and consequent size of heat exchangers. Table 4.1 gives an overview of the types of heat exchangers required for the different hydrogen carrier and energy converter combinations.

Choice of heat exchangers

Two main types of liquid-liquid heat exchangers exist: the shell-and-tube heat exchanger and the plate heat exchanger. The shell-and-tube heat exchanger is very common in industrial heat exchangers but is less suitable for the specific applications onboard ships, as they are relatively large and heavy

Cold medium	Hot medium	Mediums	Heat exchanger type	Sizing (Order of magnitude)
AB and SB	Coolant	Liquid-Liquid	Plate	$8 \cdot 10^{-3}$ m^3
AB and SB	Spent fuel	Liquid-Liquid	Avoided due to crystallisation resulting in possible clogging	N.A.
AB and SB	Flue gas	Liquid-gas	Plate with fins	$5 \cdot 10^{-3}$ m^3
LOHCs	Coolant	Liquid-Liquid	Plate	$5 \cdot 10^{-3}$ m^3
LOHCs	Spent fuel	Liquid-Liquid	Plate	$8 \cdot 10^{-3}$ m^3
LOHCs	Flue gas (Preheat)	Liquid-gas	Plate with fins	$1 \cdot 10^{-3}$ m^3
Heat transfer fluid	Flue gas	Liquid-gas	Plate with fins	1 m^3
LOHC (reactor)	Heat transfer fluid	Liquid-Liquid	Jacketed reactor	4 m^3

Table 4.1: Summary heat exchangers and reactor types and sizes

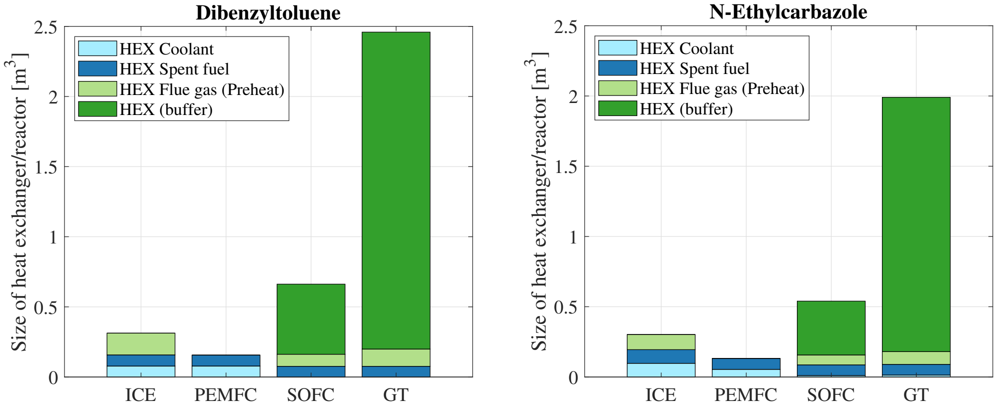
[171], [175]. This thus leaves plate heat exchangers, which are well suited for liquid-to-liquid heat exchange applications. The main limitation of plate heat exchangers is their unsuitability when large pressure or temperature differences between the hot and cold fluids occur [171], [175]. Neither occurs in any of the heat exchangers. Plate heat exchangers are generally cheaper, have less fouling and have shorter residence times than shell and tube heat exchangers [175]. As the dehydrogenation processes for all of the mentioned hydrogen carriers occur at only a few bars, and coolants are generally in a similar pressure range, this does not seem to be an issue. Thus, plate heat exchangers are the only type of heat exchangers considered in this research for liquid-to-liquid use.

The only exception to the plate heat exchangers is dehydrogenation reactors' heating (and cooling). The reactor design focuses on the reactor itself and less on the heating or cooling. For simplicity, a jacketed reactor is chosen. The jacket around the reactor can provide necessary heating or cooling. The reactors will be considered plug flow reactors, and the hydrogen is assumed to be immediately removed from the reactor. This latter is required as hydrogen is a gas and takes up a lot of volume. Removing hydrogen gas as soon as possible is essential for the reactor to keep working properly.

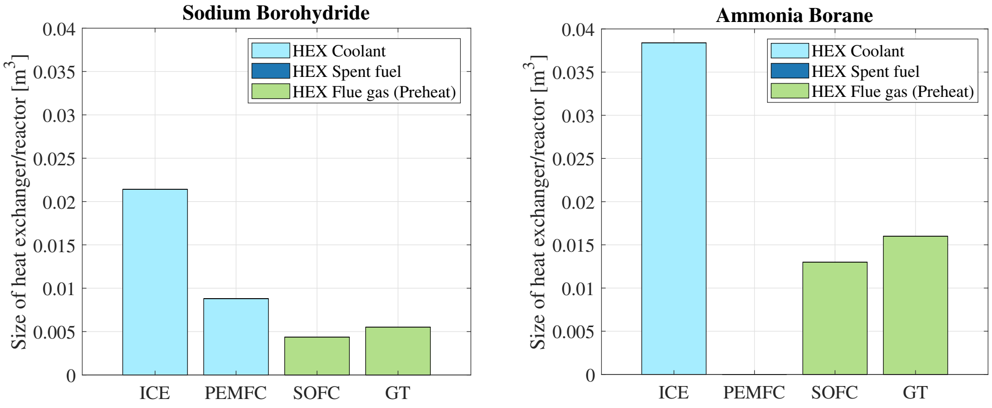
For liquid-gas use, plates with fins heat exchangers are used. A sensitivity analysis showed that plate heat exchangers would be significantly larger than plate-with-fins heat exchangers. Plate with fin heat exchangers are often used for liquid-gas heat exchangers, as they can have different surface areas for the gas and the liquid. Gasses usually require larger surface areas due to their lower heat capacities.

Sizing of heat exchangers

Figure 4.6 gives a more in-depth overview of the sizes of the different heat exchangers. Clear differences between the boron-based hydrogen carriers and the LOHCs can be seen. The LOHCs require several heat exchangers, which are significantly sized, while the boron-based hydrogen carriers require a single, small heat exchanger with a size of several litres.



(a) Sizing of heat exchangers of DBT (b) Sizing of heat exchangers of NEC



(c) Sizing of heat exchangers of SB (d) Sizing of heat exchangers of AB

Figure 4.6: Sizing of heat exchangers for different hydrogen carriers, additional possible hydrogen heaters are not taken into account

Between the boron-based carriers, the heat exchangers required for heating SB (represented in figure 4.6c) are smaller than those for AB (figure 4.6d). This difference is explained by the different amounts of water required for these carriers. Due to the higher solubility limits of the spent fuel of SB, less water is required in the process. More water is required in the process for AB, resulting in a larger overall mass flow, greater heat demand and thus, a larger heat exchanger. These figures also show that heat exchangers that use hot gasses as heat sources can be smaller than liquid-liquid heat exchangers. The internal area of the plate with fins heat exchanger is larger than that of the plate heat exchangers.

The results of the heat exchanger geometry for liquid organic hydrogen carriers differ greatly. The heat exchangers are generally tenfold larger than those of the boron-based hydrogen carriers. From figures 4.6a and 4.6b, it appears that the heat exchangers, when integrating with an ICE or PEMFC, are significantly smaller than those with a SOFC or GT. However, it should be noted here that the ICE and the PEMFC cannot cover the complete heat requirement of the preheating and dehydrogenation process of the LOHCs. An additional heat source, most likely hydrogen burning, is thus required. This reduces the energy density and efficiency of the system and requires an additional heater. This additional heater also needs to be sized. However, as this is a burner and not a heat exchanger, it is not considered here.

On the other hand, the complete system of heat exchangers required for the SOFC or GT integration can be simulated. Figure 4.6a shows that heating the buffer fluid results in an extremely large heat exchanger for this system. The large heat demand of the dehydrogenation process can explain this. The complete flue gas flow is required to heat the buffer fluid sufficiently. For both NEC and DBT, the differences between the gas turbine and the SOFC buffer-fluid heat exchanger are significant. These differences occur due to the mass flow of the flue gas of a gas turbine and SOFC. The mass flows are calculated using equation 4.1. As the SOFC has a larger temperature difference, the mass flow is consequently less than for the GT, with a smaller temperature difference. Additionally, the SOFC has a higher efficiency and, as visible in table 3.1, the overall component of the total available power going to heat is less for an SOFC than for a GT. Thus, combined, the mass flow of an SOFC is much lower than that of a GT, resulting in a smaller heat exchanger. However, figure 4.6a shows much larger heat exchangers in general, especially visible in the buffer, but also the other heat exchangers (for all energy converters) are larger. This difference occurs because dbt generally requires more heat, both for preheating and dehydrogenating. In figure 4.6b, a very small, additional heat exchanger is visible, which is required as the spent fuel of NEC should not be used to preheat the fuel at low temperatures. The spent fuel freezes at around 343K and should thus not be cooled down strongly. Thus, a heat exchanger must be added to do the first flue gas cooling step. These heat exchangers are generally very small, approximately 10L.

Knowing the size of the heat exchangers is not the only result of this study. The sequence and amount of heat exchangers is also an important input for ship design. As all the heat exchangers have to be connected to each other and different heat sources, they introduce limitations to the ship's design [168]. These limitations occur less when using fewer and smaller heat exchangers; the design freedom when incorporating boron-based hydrogen carriers is thus much higher compared to LOHCs.

4.4.4 REACTOR

Figure 4.7 gives an overview of the reactor sizes. The reactor size depends largely on the throughput time. In this case, a throughput time which results in a high conversion rate (>95%) is chosen. The throughput time can be shorter for lower conversion rates. The conversion rate depends on the temperature, catalyst, reaction rate, type of reactor, and more [113], [179]. Additionally, catalyst packing influences the volume size. In all of the cases, a packing factor of 0.5 is considered. The throughput time and conversion rate do not depend on the energy converter. The differences for each energy converter, as visible in figure 4.7, occur due to different mass flows. Higher mass flows with the same throughput time result in a larger reactor size.

Experiments are generally required to calculate conversion rates and throughput times. These conversion rates and throughput times strongly influence the reactor size and the hydrogen release rate. Literature shows this as well. SB, for example, was reported to have throughput times of 1 to 2 hours [180], whereas more recently, throughput times in the order of 20 minutes have been reported [181]. Thus, they form an area of very active research, as the hydrogen release rate influences the suitability and usability of a hydrogen carrier. As this area of research is very specialised, only known throughput times with a high conversion rate are considered [179], [181], [182]. Figure

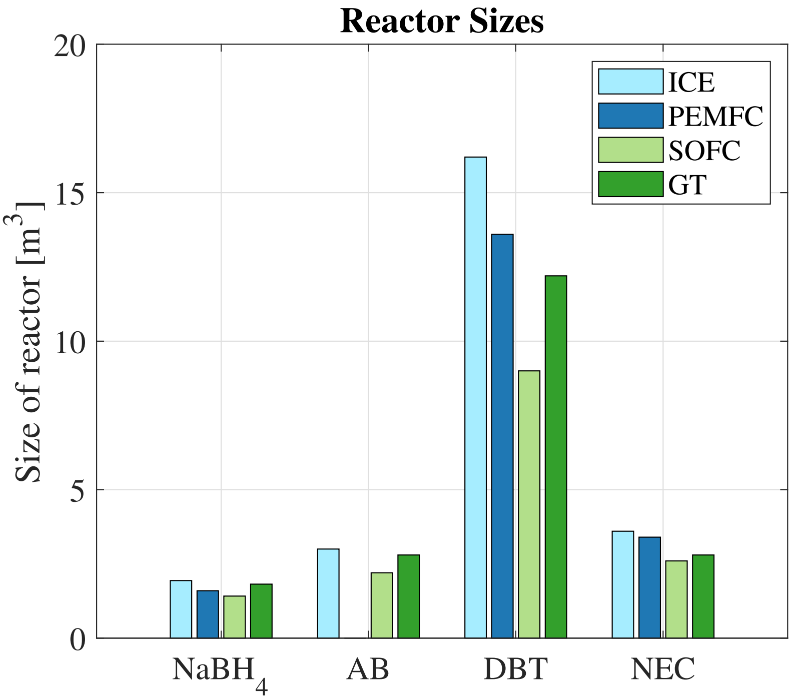


Figure 4.7: Estimated reactor sizes of different hydrogen carriers for different energy converters

4.7 clearly demonstrates the requirement for low throughput times, as the difference in reactor size is large.

4.4.5 OVERVIEW OF TOTAL REQUIRED COMPONENTS

Figure 4.8 gives an overview of the total sum of the size of the required components. Each of the specific components is influenced by several factors, each with its own levels of reliability. Thus, the resulting sum of the sizes is an indication. The reactor size is the main influence of the components' total sizing. This figure clearly shows that the equipment's total size does not differ too much if the throughput time of the reactor is low enough. The relatively large heat exchangers required for NEC and DBT are only relevant if the reactor size is similar to that of SB and AB. Even then, the overall sizing of the equipment is similar. The size of the mixing tank required for SB and

AB is similar to the heat exchangers required for DBT and NEC (except when combining these with a GT, in which case the heat exchangers are significantly larger).

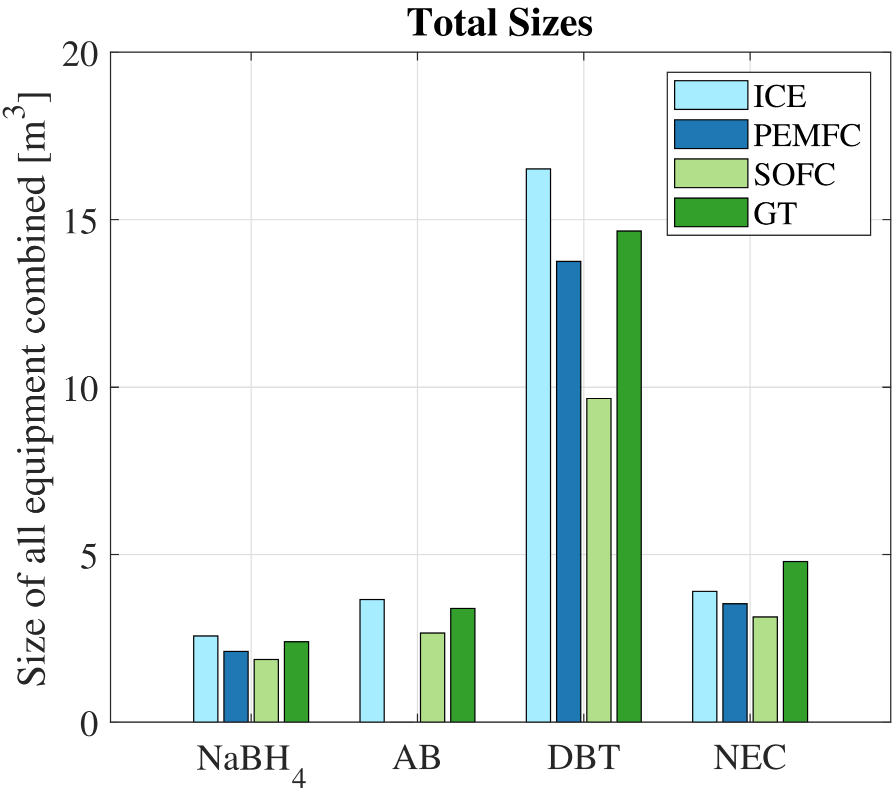


Figure 4.8: Overview of sizing of all components

4.5 CONCLUSION AND RECOMMENDATIONS

The sizing of all relevant components must be known to estimate the possible ship design changes required for incorporating hydrogen carriers as the power source. This research aims to give an overview of all the relevant components and their sizes.

The size of the release reactor is most significant for all hydrogen carriers. Further research on catalysts will hopefully result in shorter throughput times. This research clearly shows the benefit of shorter throughput times, as these strongly influence the reactor sizing. As this reactor has to be placed in a specialised room (due to the release of hydrogen), having an exact size is important. The reactors required for AB appear slightly larger than those for SB reactors. This size largely depends on the throughput time and dehydrogenation rate. The other components, such as heat exchangers and a mixing tank, are significantly smaller than the reactor. The heat exchangers are of such small size that it is unlikely they will influence ship design.

The sizing of heat exchangers is of importance only for LOHCs. The heat exchangers required to heat the buffer fluid are especially large. When no buffer fluid is required, and the main part of heating has to be done using hydrogen, no estimates on equipment size have been made. In general, the heat exchangers required to preheat and, when possible, provide enough heat for the dehydrogenation process of LOHCs are large and numerous. As these heat exchangers need to be in a fixed sequence and use waste heat, they create limitations on the ship design. Additionally, all of the equipment for DBT is larger than that for NEC.

All in all, the boron-based carriers pose fewer limitations to ship design. The required equipment is smaller and less numerous, even though it is still in a fixed sequence. In all cases except for the PEMFC, only three components are necessary: a mixing tank, a single heat exchanger and a reactor vessel. When a PEMFC is used, a small hydrogen burner is also required. For LOHCs, more and larger components are needed. The only setups in which no hydrogen burner is required need at least 3 (for DBT) or 4 (for NEC) heat exchangers. Besides these, a reactor is also required.

A clear understanding of the required components and their sizing is essential for designing ships using hydrogen carriers, and this chapter provides that foundation. The following chapter builds on this by evaluating the trade-off between the carriers' power density and energy density and assessing their applicability for maritime use.

Power & Energy

5

ENERGY DENSITY AND POWER DENSITY TRADE-OFF

> *"Change often starts with the smallest of whispers. Like-minded people building it up to a roar"*
>
> — TJ Klune, *The House in the Cerulean Sea*

CHAPTER SUMMARY

This chapter quantifies the power and energy trade-offs of four hydrogen carriers. Four reference cases (MeOH, ammonia, LH2 and MDO) are also examined. These case studies (carrier and converter combinations) are assessed using Ragone plots to compare their performance for several shipping applications. The results indicate that AB combined with ICE and SB combined with a PEMFC offer energy and power density profiles suitable for various vessel types, including inland ships and ocean-going vessels. These combinations also show strong potential for specialised vessels such as fishing boats, dredgers, tugs, and ferries, which operate under unique load profiles and duty cycles. Compared to other alternative fuels, such as ammonia, methanol, and liquid hydrogen, hydrogen carriers demonstrate higher energy and power densities. In specific applications, they may even outperform MDO paired with an ICE, highlighting their potential for zero-emission maritime propulsion.

5.1 INTRODUCTION

Some ships are limited by available volume, others by weight. Operational demands vary as well: some vessels experience high peak power requirements, while others operate under steady loads. Historically, MDO with ICEs satisfied most operational demands, but at a high environmental cost.

As the industry transitions to alternative fuels and converters, these once-reliable performance characteristics are no longer guaranteed. Different ship types will likely require tailored combinations because alternative fuels and energy converters differ significantly in power output, efficiency, and energy density. Understanding how these combinations perform in terms of power and energy density is therefore crucial to evaluating their suitability for different maritime applications.

Comparative studies that integrate system-level optimisation and evaluate both energy and power density of alternative marine fuels remain scarce. Several works have compared various more conventional alternative fuels (e.g., liquid hydrogen, methanol, ammonia) with different converters (ICE, gas turbine, PEMFC, SOFC). However, these focus mainly on fuel cells and omit hydrogen carriers (like LOHCs, SB or KB) or heat integration [18], [22]. Studies that incorporate hydrogen carriers do exist. Most of these studies concentrate on a single fuel family, such as liquid organic hydrogen carriers (LOHCs) [21], [23], [24], [25], [26]. Others provide limited multi-fuel comparisons [27], [28], [29], or only broad, high-level overviews [19], [30]. Finally, some single-fuel marine studies incorporate detailed integration, but without cross-fuel comparisons [31], [32]. To the authors' knowledge, no study has yet compared SB, AB, NEC and DBT on a system-level with their associated converters, including waste-heat integration and simultaneous evaluation of power and energy density. Moreover, these other studies often neglect hydrogen carriers, only regard specific fuels, or fail to optimise for system-level integration. Additionally, they do not sufficiently account for the wide variation in energy and power demands across different ship types. This chapter addresses these gaps by systematically evaluating fuel–converter

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The content of this chapter is based on the following articles:
E.S. van Rheenen, A.A. Kana, K. Visser, J.T. Padding, "Energy and Power Density as Key Metrics for Assessing Hydrogen Carriers as Alternative Fuels in Maritime Applications", under review at Energy Conversion and Management: X as of 2025

combinations in terms of their energy and power density, considering diverse vessel requirements. In particular, this study assesses the applicability of hydrogen carriers for maritime propulsion by explicitly linking power and energy density constraints to representative ship types. The key objectives of this chapter are to:

- Quantify the power and energy densities of selected hydrogen carriers and energy converters
- Evaluate hydrogen carrier–converter combinations for representative marine applications using Ragone plots
- Enable a consistent, system-based methodology to enable cross-carrier comparison

This chapter, thus, systematically evaluates alternative fuels and converters, focusing on hydrogen carriers. To cover both conventional and emerging options, this study evaluates eight fuels. Firstly, there are four hydrogen carriers: sodium borohydride (SB), ammonia borane (AB), dibenzyltoluene (DBT) and n-ethylcarbazole (NEC). Secondly, there are four reference fuels: marine diesel oil (MDO), ammonia, methanol (MeOH), and liquid hydrogen (LH2). These fuels are analysed in combination with different energy converters, including ICEs, gas turbines (GT), PEMFCs, and SOFCs. By comparing their energy and power densities using Ragone plots, this study provides new insights into the trade-offs of alternative fuel-converter systems and their suitability for different maritime applications.

A fundamental challenge in comparing hydrogen carriers lies in their distinct system integration requirements, which result in different combinations of reactors, heat integration schemes, and converters. These differences make comparison complicated. The contribution of this work is to establish a consistent, system-based methodology that enables cross-carrier comparison on equal terms, using power and energy density as unifying performance metrics.

5.2 METHOD

Figure 5.1 provides an overview of the entire process to deliver power to the ship's propeller, illustrating the various components that influence either

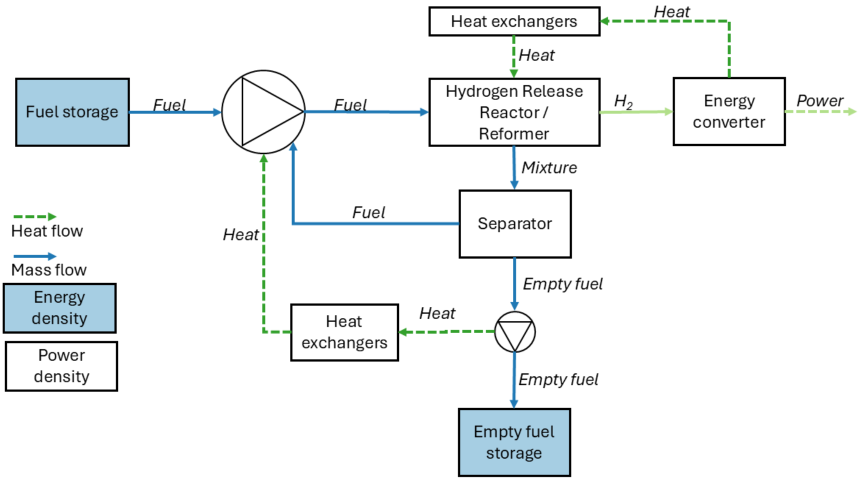


Figure 5.1: Schematic of mass and heat flows from fuel storage to propulsion, including optional storage of spent fuel and integration of heat exchangers

energy density or power density. This section starts by outlining the relationship between power and energy density. Section 5.2.2 goes into detail on the energy density of these fuels, describing what is relevant. Furthermore, subsection 5.2.3 describes the energy converters and other components relevant to calculating the overall power density. In subsection 5.2.4, the usefulness of waste heat integration and its influence on the energy density is briefly discussed. Subsection 5.2.5 discusses assumptions and system boundaries. Finally, subsection 5.2.6 describes how the 16 hydrogen carrier and energy converter combinations will be assessed.

5.2.1 RELATION POWER AND ENERGY DENSITY

Some components in figure 5.1, such as the fuel and empty fuel storage, influence the energy density; other components, like the hydrogen release reactor and heat exchangers, affect the power density. The power and energy density are closely related and can be visualised in a Ragone plot [18]. The Ragone plot requires an expression for the power density and the energy density, both of which require the following definitions:

- P is Power, delivered by a power converter, in [W]

- E is Energy in [J]
- η is the combined efficiency of the energy converter and reactors
- W is the energy density of the fuel, in [J/kg]
- P' is the power density of a single component (the power converter), in [W/kg]
- P'' is the power density of the whole system, in [W/kg]
- m_w is the mass of the fuel, including the tank, in [kg]
- m_p is the mass of the power converter, in [kg]
- t is the sailing time, in [s]

The required energy, E, to sail a certain distance can be expressed as follows [18]:

$$E = \frac{Pt}{\eta} \tag{5.1}$$

The amount of fuel required to fulfil this demand can be expressed with $m_w = E/W$, so:

$$m_w = \frac{Pt}{\eta W} \tag{5.2}$$

To calculate the power density, P'', we define it as follows: the power of the system, divided by the total mass of the system.

$$P'' = \frac{P}{m_p + m_w} = \frac{P}{m_p + \frac{Pt}{\eta W}} \tag{5.3}$$

If we then fill in the definition of the power density of the power converter, $P' = P/m_p$, we get the following equation for the power density of the whole system, also used by [18]:

$$P'' = \frac{P'm_p}{m_p + \frac{P'm_p t}{\eta W}} = \frac{P'}{1 + \frac{P't}{\eta W}} \tag{5.4}$$

Referring back to energy, equation 5.4 shows that, when t goes to infinity, P'' goes towards zero [18]. However, the effective energy density of the system, $W'' = P''t$, does not go towards zero but tends to ηW as t goes to infinity.

Equation 5.4 shows that there is a relation between the effective power and energy density of a system. This relation can be plotted to compare different energy systems, as previously done to compare fuel cell systems for example [18]. Each of the different systems has its own efficiencies and power densities. Equation 5.5 gives an example of how to combine the power densities [18].

$$P' = (\frac{1}{P'_{EC}} + \frac{1}{P'_{reactor}} + \frac{1}{P'_{HEX}})^{-1} \tag{5.5}$$

5.2.2 FUEL PROPERTIES AND ENERGY DENSITY

The traditional way of calculating the energy density of hydrogen carriers is to evaluate the amount of hydrogen inside the carrier, for example, by weight percentage. These energy densities can be seen in table 5.1 and give a relative objective overview of the energy density of these specific hydrogen carriers. However, this method has several flaws, including the omission of key factors such as specific reaction characteristics [83], bulk fuel densities [183], and tank weight [16]. So, it does not give an accurate overview of the amount of energy available inside each of the carriers.

	Gravimetric energy density [MJ/kg]	Volumetric Energy Density [MJ/L]
Sodium borohydride ($NaBH_4$)	12.8	13.7
Ammonia borane (NH_3BH_3)	23.5	14.4
Dibenzyltoluene ($C_{21}H_{38}$)	7.4	7.0
N-ethylcarbazole ($C_{14}H_{25}N$)	7.0	6.6

Table 5.1: Theoretical energy densities of hydrogen carriers, calculated based on the number of hydrogen atoms, which can be extracted from the carrier.

Hydrolysis Reaction

SB reacts with water to release hydrogen. This reaction with water is not useful in many settings, as the water often also needs to be brought along; however, ships have a distinct advantage here, as there is water all around. The reaction, visible in equation 5.6, shows that half of the hydrogen released stems from water. This means that the overall energy density can be doubled, especially as, theoretically, no (large) water storage is required. Hydrolysis of SB by direct use of seawater is chemically possible; however, in practice it leads to rapid fouling, chloride-induced corrosion, and contamination of the $NaBO_2{\cdot}xH_2O$ mixture, making regeneration extremely challenging. For this reason, it is foreseen that purified water, e.g. from a Reverse Osmosis (RO) unit, will be used on board of ships. Note that the size of this RO unit can be minimised in case water is recovered from the exit stream of the power converter (ICE, GT or fuel cell).

$$NaBH_4 + (2 + x)H_2O \rightarrow 4H_2 + NaBO_2.xH_2O + Heat \tag{5.6}$$

x ranges in this equation from 0 to 4, depending on the circumstances in which the reaction occurs.

Similarly, AB also reacts with water. Unlike SB, AB releases hydrogen and ammonia. The energy density of the fuel is easy to calculate when only the hydrogen is used. Ammonia also has to be used to use more of the available energy. However, this proves to be more difficult. Firstly, ammonia dissolves excellently in water [184]. The reaction from equation 5.7 has to occur in excess water to avoid the boron oxide's crystallisation. Because of this excess, most of the ammonia will dissolve in the available water and must be extracted before it can be used. It has been mentioned that not all ammonia will dissolve in water; some of it will be released in the gas phase [83]. There are several methods to extract ammonia from pure water, but the solution also entails boron oxide and, possibly, some unreacted AB. Luckily, extracting ammonia from contaminated water is a well-researched field, due to the many other applications this extraction process has [185]. If the ammonia is successfully removed, it can either be burned directly or decomposed into hydrogen and nitrogen. To avoid complicating the onboarding process, this chapter does not consider the latter option.

$$NH_3BH_3 + 3H_2O \rightarrow 3H_2 + B(OH)_3 + NH_3 + Heat \tag{5.7}$$

Bulk Density

Both SB and AB are powders. The particle density is often used to calculate the volumetric energy density, from the gravimetric energy density. However, powders have two types of densities: a particle density and a bulk density. Powders or granular materials are made of individual particles, and between these particles, there are voids, which lower the overall density of the material [183]. Generally, only the particle density (e.g, the density of one single grain) is provided. However, the bulk density is much lower than the particle density, due to the voids between particles [183]. For example, the particle density of SB is 1.07 g/cm^3, whilst the bulk density is much lower. For powder, it can be 0.550 g/cm^3, whilst granules have densities in the order of 0.510 g/cm^3 [183], [186]. Other sources assume a 60% reduction in density [187]. This large difference negatively influences the volumetric energy density of both SB and AB. In this research, the density of both SB is assumed to be 0.550 g/cm^3. Based on preliminary, unpublished, in-house laboratory measurements and handling observations conducted by the authors, the bulk density of AB is estimated at approximately 0.4 g/cm^3. This bulk density is used to calculate the volumetric energy and power density of AB. Given the preliminary nature of the estimate, further analysis is required to assess the exact bulk density; at the moment, it is an estimate regarding the order of magnitude.

Spent Fuel

Unlike traditional or conventional alternative fuels, hydrogen carriers are circular. This implies that the empty fuel, often called spent fuel and denoted by SF, must be returned to shore for regeneration. It has been hypothesised that the spent fuel can be stored in the same tanks as the fuel [19]. This requires only one empty tank to serve as a transfer buffer: you pump the spent fuel into it, and then pump new fuel into the now-empty tank, a process that avoids the need for dedicated spent fuel storage and saves weight and space. Careful tank design and mass distribution are essential to avoid potential sloshing and stability impacts [19]. However, this concept remains theoretical and has not yet been demonstrated in a maritime setting. A detailed assessment of tank stability and sloshing is beyond the scope of this study, but these concerns should be addressed in future design work.

Additionally, enhancing complexity, both SB and AB have spent fuels that are heavier than the original fuel. Equations 5.6 and 3.1 show the products of the hydrolysis reaction. The x in the equation for SB (equation 5.6) depends on the temperature and other circumstances, and ranges from 0 to 4 [159]. Usually, in the circumstances after the hydrolysis reactor, x equals 2 [159]. Practically, this means an increase in weight of 2.7 times the original weight of the fuel. This means that the substance in the fuel tanks is 2.7 times heavier when re-entering the harbour as compared to leaving (if all fuel is used). For AB, this difference is only 2 times. These differences are significant and greatly reduce the energy density of the fuel, but one should note that this only occurs during the voyage. Especially if not all fuel is used, the effect is mitigated. It is thus hard to estimate the exact result of this effect. In this paper, we will assume that x=2, as drying the fuel onboard the ship to enhance the energy density is not considered practical nor feasible.

The practical influence of the spent fuel on the overall space and weight the fuel requires is investigated in section 5.4.2. To assess the effect of the spent fuel, the pure fuel and a mixture are compared in this section. The mixture consists of 1/3 fuel and 2/3 spent fuel for two reasons: first, a ship is unlikely to use all its fuel; a safety margin is always maintained. Secondly, in a container ship case study, most trips would use only 2/3 of the maximum energy [20].

Dehydrogenation Energy Requirements

The LOHCs have different properties than the boron-based carriers, requiring energy during the dehydrogenation process. Thorough heat integration is extremely important to avoid energy losses. These energy losses can be significant; if the hydrogen from DBT has to be used to provide heat for the dehydrogenation process, this can result in a loss of up to 35% of the total energy available [21]. NEC requires less energy for dehydrogenation, and the dehydrogenation process occurs at lower temperatures. However, the losses can still be significant [29]. These losses can be reduced by using waste heat integration; however, this will also increase space requirements (e.g., for heat exchangers) and system complexity.

Handling Considerations

Both SB and AB are stored as dry powders and must remain completely isolated from moisture during handling to prevent deliquescence and premature hydrogen release [183]. This makes onboard transport and dosing technically challenging, as these solids cannot be pumped like liquids and are sensitive to ambient humidity. Developing moisture-isolated feeding systems for these materials is a substantial engineering challenge and forms part of separate, dedicated research [183]. As this paper focuses solely on the mass, volume, and energy/power density implications of the fuels, the detailed engineering of such handling systems is not considered here.

In contrast, LOHCs are liquids under typical operating conditions and exhibit handling characteristics similar to conventional marine fuels such as

MDO or HFO. Even NEC, which is solid at room temperature, becomes liquid at modest temperatures—comparable to the heating already required for HFO pumping [25]. Therefore, LOHC handling is assumed to be straightforward and falls outside the scope of this paper.

Tank Weights

The tank weight is mentioned often as well when regarding the difference between the theoretical and practical energy density [18]. This is critical for liquid or pressurised hydrogen, due to the major limitations imposed on the tanks [16]. Hydrogen carriers do have some limitations on tank type, as do almost all fuels. For example, SB is either corrosive or reacts (forming hydrogen) when it comes in contact with many other metals; storage in a metal tank should thus be avoided. A plastic liner will already solve this issue [188]. AB is not well-known enough to know how to store this exactly; however, suppliers do note that it should be stored in a fridge. This is likely because of the thermolysis reaction, which can occur at relatively low temperatures and can possibly have devastating results [189]. So, a climate-controlled tank may be required, although there is no consensus on whether this is actually needed [190], [191].

LOHCs do not have these issues, as they are not corrosive and do not easily react with other substances. All combined, for three of the four hydrogen carriers, the fuel tank does not appear to be a major consideration [25], [192].

5.2.3 POWER DENSITY

The power density consists of the power density of all relevant components to produce and use hydrogen on board the ship. The composition and quantity of components depend on the hydrogen carrier; a general overview is provided in Figure 5.1. Auxiliary components such as pumps, which are required for all fuels, are not considered here. The main components are heat exchangers (if necessary), a hydrogen release reactor (which can also be a reformer or cracking system), the separator and the energy converter. This data is all combined, using equation 5.5. Different efficiencies (e.g. reactor efficiency and energy converter efficiency) are calculated by multiplication to find the overall efficiency. Finding the data to calculate the power density is done differently for each of the components.

Heat Exchangers

Sizing of the heat exchangers is based on previous work [193]. First, complete heat integration is required to calculate the amount of heat each heat exchanger needs to transfer. Aspen Exchanger Design and Rating (EDR) is used to estimate the size and weight of each heat exchanger [160]. The materials from which the heat exchangers are constructed are not changed, which means that all similar-type heat exchangers are made from the same materials. It is also assumed that heat exchangers continuously scale with the power output; no discrete steps are expected.

Hydrogen Release Reactor and Separator

Calculating the size of the release reactor can be done in several ways. One way is to use the kinetics of the governing reactions. However, the actual reactions are shaped not only by kinetics but also by factors such as reactor geometry and catalyst morphology, which substantially affect the dehydrogenation process [194], [195]. Additionally, some hydrogen carriers release hydrogen in multiple steps, each with its own characteristic kinetics [194], while certain reactions can not be encompassed by 'simple' first, second or zero-order reactions. SB, for example, likely follows the Langmuir-Hinshelwood mechanism, where the reaction order is defined by, amongst others, the temperature [196]. In short, these reactions are difficult to capture in a theoretical framework.

Another way to estimate the reactor size is to calculate the required hydrogen output flow. Combined with a catalyst to estimate effectiveness, this can be used to calculate the required hydrogen carrier flow. The throughput time (again determined by the catalyst) can be used to estimate the size of the volumetric part of the reactor. The amount of catalyst depends on the type of reactor used [197]. The combined volume and mass of the catalyst and hydrogen carrier determine the volume and mass of the overall reactor.

The required output flow is calculated in the model. The throughput time comes from experimental data from different studies. For each of the hydrogen carriers, different studies are used to find average throughput times [181], [182], [198]. These experiments are conducted in a lab setting, with relatively low catalyst amounts, and are often in batch reactors. Intrinsic catalytic reaction rates (per unit catalyst) are independent of reactor scale provided the system remains reaction-controlled and transport limitations are avoided, while the required reactor size follows from the required catalyst inventory and bed properties [199]. When scaling up, a continuous reactor is preferred over a batch reactor. Because different reactor types require different amounts of catalyst, the catalyst-to-reactor-volume ratio may change. For heterogeneous (e.g. reactions with two phases) reactors, there are two basic types of two-phase reactors: packed bed (PBR) and fluidised bed reactors [200]. In PBRs, catalyst particles occupy a defined fraction of the reactor volume, while the remaining volume consists of void space through which the reactants flow [201] (the hydrogen carrier and hydrogen in this case). As PBRs are the most widely used reactors for heterogeneous catalytic processes [200], and they have already been considered for hydrogen carriers [202], they are assumed to be used for hydrogen carriers as well.

In this setting, a PBR with a void fraction (ϵ) of 0.5 is estimated. This estimate represents a typical balance between sufficient reactive area in and good flow properties through fixed-bed reactors. Typical packed-bed void fractions range from approximately 0.4 to 0.6, depending on catalyst particle geometry and packing, making $\epsilon = 0.50$ an appropriate assumption [195], [201]. So, reactor volume can be estimated from the fluid volume and void fraction (ϵ).

$$V_{reactor} = \frac{V_{fluid}}{\epsilon} \tag{5.8}$$

To estimate the reactor weight, two densities must be used: one for the hydrogen carrier (mixture) and one for the catalyst.

The current data are derived from laboratory-scale systems, whereas shipboard application requires reactors at significantly larger scale [203]. Reactor scale-up is not straightforward; certain critical parameters must remain constant during scaling [204]. At the same time, mass transfer, heat transfer, impulse transfer and mixing depend strongly on reactor design and scale [204].

Packed-bed reactors can be scaled in multiple ways. Two approaches are not fundamentally constrained for the application on ships. First, numbering-up can be applied by operating multiple identical reactors in parallel. In this case, each reactor retains the same geometry and operating conditions, and therefore the local mass transfer, heat transfer and impulse transfer characteristics remain unchanged. Second, a packed-bed reactor can be designed such that the relevant critical parameters (e.g., catalyst loading and residence time) are preserved during scale-up [204]. Since constant catalyst loading and catalyst activity per unit volume are assumed in this study, assuming the reactor performance stays similar to the one at larger scale is consistent with these established scale-up approaches.

The reactor volume scales directly with throughput times and required hydrogen throughput. For certain cases, the resulting reactor size may exceed practical shipboard spatial constraints. In such cases, the combination would be considered infeasible at system level. The present methodology therefore evaluates order-of-magnitude physical requirements rather than guaranteeing deployable configurations.

When designing the separator, two types of operation are considered in this study: normal and emergency. In normal operation, the aim of the separator is the splitting of fuel and spent fuel, or fuel, spent fuel and water. In an emergency operation, the separator is designed as an emergency dump vessel. In case of reactor malfunction (e.g., overheating), the reactor contents can be rapidly transferred to the separator to stop further hydrogen release and limit thermal decomposition of the hydrogen carrier. Because the detailed separation performance depends strongly on the specific carrier system and downstream unit operations (e.g., stripping/distillation for aqueous ammonia), separator sizing in this study is governed by the emergency dump requirement. The separator volume is therefore assumed to be 110% of the total reactor geometric volume, providing margin for level control, and minor additional hold up in piping and internals.

Energy Converters

Both manufacturers (such as [205], [206] for ICEs, [207], [208] for GT and [209], [210], [211] for PEMFC) and literature (e.g. [212], [213], [214]) have been consulted to estimate the power density of energy converters. The differences between these can be considerable. When literature has lower estimates than industry, it may be for three reasons: 1) literature using (slightly) outdated data, 2) industry slightly overestimating their data and 3) the inclusion or exclusion of the balance of plant. Higher estimates reported in the literature often reflect projections of future performance (e.g., authors anticipating that power density will increase beyond current levels). In this study, a large dataset was compiled from both literature and established manufacturers. These differences can be addressed through Ragone plots, which employ upper and lower bounds to capture the range of valid estimates. All data is compared, and significant outliers are removed, after which the upper and lower bounds are used. One piece of literature [215] was removed as the reported power densities were an order of magnitude higher than consistent ranges found in vendor data and other reviews.

5.2.4 WASTE HEAT INTEGRATION

Extracting hydrogen from hydrogen carriers commonly occurs at elevated temperatures, ranging from 70 to over 600 °C, depending on the hydrogen carrier. This results in a heat demand. During the process of converting hydrogen to either electrical or mechanical energy, heat is produced. This heat is, again, produced at very different temperatures, depending on the energy converter. To enhance not only the overall efficiency of the system, but also the energy density (energy which can be used for propulsion) of the hydrogen carriers, a proper waste heat integration is crucial. Waste heat integration is imperative for LOHCs [21], but also important for boron-based carriers. Figure 5.2 gives an overview of the various waste heat strategies that can be used to transfer heat towards the preheating and dehydrogenation processes. The approach is based on [29], where we previously calculated the effective energy density when optimal waste heat integration was used. Not all of these strategies can be applied to each hydrogen carrier or energy converter. To enhance readability and uniformity, we will always use the

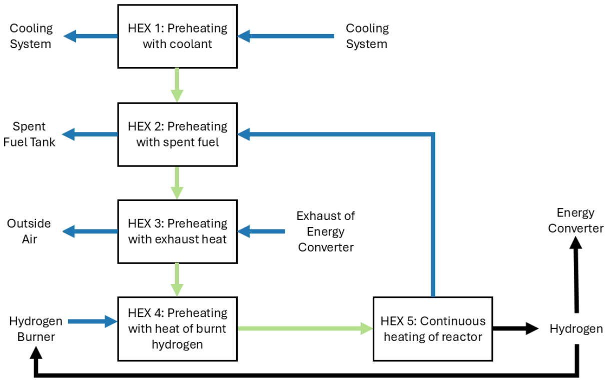


Figure 5.2: Waste heat strategies that can be incorporated, including numbering of heat exchangers. Heat exchangers are denoted by HEX. Not all strategies are applicable to each hydrogen carrier and energy converter. Approach based on [29]

same numbers to indicate the heat exchangers, as mentioned in Figure 5.2. This may result in combinations with, for example, only exchangers 2 and 3. Heat exchangers have a minimal temperature difference of 5 K. These heat exchangers are sized in Aspen EDR and accounted for in the power density. The upper bound of the energy density of the hydrogen carriers is assuming perfect waste heat integration, yet it still depends on the energy converter. For example, in a case where a PEMFC is used, the optimal strategy is determined with the PEMFC, not with a different energy converter. For large comparisons, such as in section 5.3.1, this optimised data is used, as this section only compares different energy converters for each hydrogen carrier separately. When comparing combinations, a lower bound is used, which is achievable with very minimal heat integration (the PEMFC case), as there is usually low-temperature waste heat available.

5.2.5 PRACTICAL ENERGY DENSITY AND SYSTEM BOUNDARIES

Having identified the limitations of the theoretical energy density, the following section derives a more practical formulation, along with the assumptions and system boundaries. Figure 5.1 shows the system; all that falls outside this figure (such as how the power is used exactly) falls outside of the system boundaries. Inside the system boundaries fall the fuel and empty fuel storage, the heat exchangers, the hydrogen release reactors, and the separators. Even though heat exchangers are less important (as shown previously [193]) for SB and AB, they will still be considered here. Components which are comparable across fuels, such as fuel tanks and auxiliary pumps, are excluded. Similarly, water purification systems are excluded, as these are required regardless of the fuel; only a small amount of water is required for the dehydrogenation process, most can be recycled [29]. Components specific to a fuel and that significantly affect system size or mass (such as cryogenic storage for liquid hydrogen and hydrogen release reactors for hydrogen carriers) are included. In a previous paper, we integrated the available waste heat to reduce the energy penalty common with LOHCs [21], [29]. A large part of the heat integration will be based on the results of that paper.

General Assumptions

Tank mass is not explicitly included in the present analysis. For the considered hydrogen carriers and most reference fuels, its contribution is expected to be limited. An exception is liquid hydrogen, for which tank mass is significant due to cryogenic storage requirements and is therefore taken into account [16]. For LOHCs, storage in conventional marine fuel tanks is generally envisaged [192]. DBT requires preheating prior to hydrogen release, similar to HFO handling. NEC must remain above a threshold temperature when entering the tank, which can be achieved by allowing it to cool down within the fuel tanks. SB and AB may require additional liners and adapted pumping systems; however, storage in conventional tanks with a thin liner is considered feasible. For both SB and AB, airtight containment is essential [183].

Although the mass of individual tanks is expected to be comparable to conventional marine fuel tanks, the lower energy density of several carriers implies larger total storage volumes and potentially additional tanks. A detailed assessment of tank sizing, arrangement, and structural implications depends on ship-specific design considerations and is therefore beyond the scope of this study, which focuses on comparative energy and power density.

Auxiliary power consumption is neglected, similar to a similar study [31].

An overall, combined efficiency of the reactor and separator is assumed to be between 95 and 99%, similar to the fuel treatment efficiencies reported by [18]. This efficiency represents the fraction of hydrogen recovered after reaction and separation. In practical applications, the separator separates unreacted fuel from spent fuel, enabling reuse within a circular fuel concept. Although the separator is explicitly modelled, it is not assumed to be perfect and minor losses may occur, which are reflected in the assumed efficiency range. For such a circular system, very high recovery is required to maintain viability; efficiencies close to 99% are therefore preferred. An efficiency of 95% is considered the practical lower limit and would only be acceptable if losses could be compensated by additional onshore separation, while lower values would compromise the feasibility of the system. Phase changes and vaporisation are not assumed to occur in the reactor, as these processes are energy-intensive and may damage the hydrogen carrier; operating temperatures are therefore assumed to remain sufficiently low to avoid vaporisation during hydrogen release [25].

Separators are included in the design and are conservatively sized at 110% of the release reactor volume, allowing full discharge of the reactor contents in the unlikely event of a runaway reaction.

Fuel Specific Assumptions

AB releases both ammonia and hydrogen. Hydrogen is fully present in the gas phase, together with a fraction of the ammonia [83]. The exact phase distribution remains uncertain due to the low TRL of AB, making precise system sizing difficult. Since a separator is already included in the design, no additional dedicated volume is assumed for ammonia separation. Approximately two-thirds of the usable energy originates from hydrogen and one-third from ammonia, yielding a combined energy density of approximately 34 MJ per kg. If only hydrogen is utilised, AB delivers approximately 23 MJ per kg; this case is taken as the lower boundary. The lower bound represents scenarios in which ammonia is not utilised due to separation, emissions, or system constraints. Separation of hydrogen and ammonia is not explicitly modelled but is assumed to occur within the separator.

Water mass is excluded for SB and AB. First of all, water produced in the energy converter is assumed to be reused where possible, particularly in fuel cell systems; while theoretically possible for ICE and GT systems, practical implementation remains limited. Additional purified water can be obtained using a reverse osmosis (RO) system. The RO system is assumed to supply water of sufficient quality for use in the hydrolysis reactor without fouling. Such systems are typically already available on board. The energy usage of an RO system is very limited and considered negligible here [31].

Energy density, including the volume and mass of spent fuel, is calculated separately, and the difference between fresh and spent fuel is reflected in the reported bounds. While fuel storage mass may increase over the course of a voyage due to seawater compensation effects, this has not proven problematic in practice, as demonstrated in submarine operations [216]. The spent fuel is analysed in more detail in sections 5.3.2 and 5.4.1, where its practical implications for ship operations are discussed.

Heat Flow Assumptions

LOHCs require additional heat, for preheating and releasing of hydrogen. Both of these heat requirements are included in the calculations, which may result in a lower energy density [21], [29]. For the upper bound of the energy density of LOHCs, an idealized waste heat integration is assumed for LOHCs upper bound (very limited waste heat integration assumed for lower bounds). The energy density of the LOHC is thus dependent on the energy converter used, as different energy converters have different waste heat streams, resulting in more or less heat integration possible [21], [29].

SB and AB release low-quality heat during the hydrogen release reaction. As this heat is at low temperatures, cooling of the reactor is not assumed. This is similar as a previous approach for a very similar process [31]. Preheating requirements are included.

Assumptions for Reference Fuels

The reference fuels are MDO, ammonia, methanol and liquid hydrogen. For the (more conventional) internal combustion engine, data from [18] are used. The energy density of MDO comes from [217].

Data for methanol and methanol engines are obtained from [218] and [219]. Due to regulatory requirements such as cofferdam spacing and filling limits [220], the effective onboard energy density may be lower than the theoretical maximum. Therefore, both the theoretical value and a conservative estimate of 90% are considered.

Data for ammonia are taken from [16]. In line with interim safety guidelines for tank arrangement, a conservative lower bound of 90% of the theoretical energy density is assumed. The SOFC efficiency is based on [221] and [143], and system sizing follows [18].

Data for LH2 are obtained from [16] and explicitly include tank mass and volume, as these are highly relevant for cryogenic storage. The PEMFC data are identical to those used for the other hydrogen-based cases.

5.2.6 SELECTION OF CASES

With four different hydrogen carriers and four energy converters, we end up with 16 combinations. Reference cases will be included next to these cases. These reference cases give an overview of the current situation and can be used to evaluate the carriers as compared to current technology. Comparing the full set of 20 cases (16 hydrogen carrier cases and 4 reference fuel cases) would be impractical and difficult to present in a clear manner. Therefore, a selection of cases will be reviewed.

First, all 16 combinations will be shown. For each hydrogen carrier, its four associated energy converters will be presented together in a Ragone plot. These plots provide an initial overview of the performance range within each carrier. Based on these results, the most promising combinations will be selected for further comparison, both with one another and with the reference cases.

Reference fuels to consider are MDO, ammonia, methanol and liquid hydrogen. The first is a conventional fuel, while the other three are alternative fuels that are on the rise in the maritime sector. As not all fuels are compatible with every energy converter, they cannot all be included in every combination.

5.2.7 DATA FOR RAGONE CHARTS

Table 5.2 gives an overview of all data required for the Ragone plots. For SB and AB bulk density and particle density are taken into account. The effective power density is calculated using equation 5.5 and includes the energy densities of the energy converter, reactor, separator, and heat exchangers. The latter is the least influential and is generally relatively small as compared to the reactor size [193].

5.3 RESULTS

This section presents the Ragone plots of the 16 studies. Subsection 5.3.1 gives an overview of the average predictions for the 16 hydrogen carrier and energy converter combinations. The choice of specific case studies of hydrogen carrier and energy converter combinations is motivated in this subsection as well. The results of these case studies are shown in subsection 5.3.2. This subsection also displays the upper and lower bounds for each combination, indicating their relative uncertainty. Subsection 5.3.3 shows the reference cases of MDO_ICE, LH2_PEM, NH3_SOFC and MeOH_ICE. Finally, subsection 5.3.4 shows the case studies and reference cases to enable comparison.

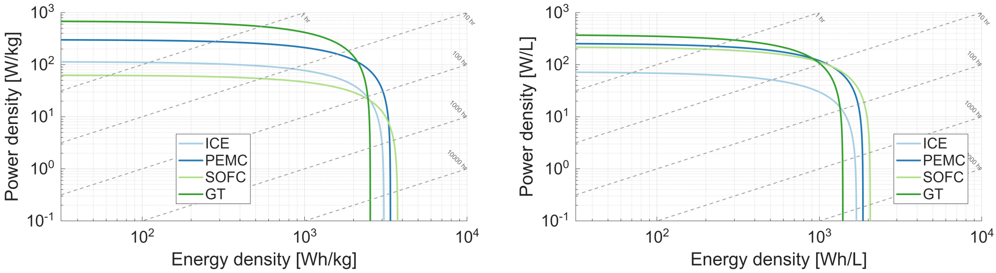
	Gravimetric Density [kW/kg]	Volumetric Density [kW/L]	LHV Efficiency [%]
Energy Converters			
PEMFC	0.042-0.85	0.015-1.6	45-55
ICE (H_2)	0.10-0.21	0.07-0.09	35-55
SOFC (H_2)	0.001-0.1	0.003-0.04	50-60
GT (H_2)	1.2-1.9	0.46-0.74	32-42.5
ICE (MDO/MeOH)	0.045-0.072	0.033-0.055	35-45
SOFC (NH_3)	0.025-0.035	0.05-0.08	45-55
Effective Power Density, including reactor and heat exchangers			Efficiency Reactor [%]
SB (PEMFC)	0.029-0.51	0.012-0.65	95-99
AB (ICE)	0.077-0.11	0.048-0.064	95-99
NEC (SOFC)	0.006-0.081	0.003-0.19	95-99
DBT (SOFC)	0.006-0.054	0.003-0.081	95-99
DBT (GT)	0.048-0.075	0.040-0.065	95-99
Energy Density	[kWh/kg]	[kWh/L]	
SB	6.3-7.0	3.4-3.8	
SB (SF)	2.3-2.6	2.7-4.9	
AB	6.5-9.4	2.6-3.8	
AB (SF)	3.3-4.7	4.7-6.8	
NEC	1.3-1.9	1.3-1.8	
DBT	1.3-2.0	1.2-1.9	

Table 5.2: Data for the Ragone charts: volumetric and gravimetric power and energy densities of different hydrogen carriers and energy converters, including reactor and heat exchanger sizes required for the case studies, which depend on the overall system power and efficiency. For hydrogen carriers where the mass of the spent fuel differs significantly from the fuel itself, an additional energy density is reported and denoted (SF).

5.3.1 RAGONE PLOTS FOR ALL FUEL-CONVERTER COMBINATIONS

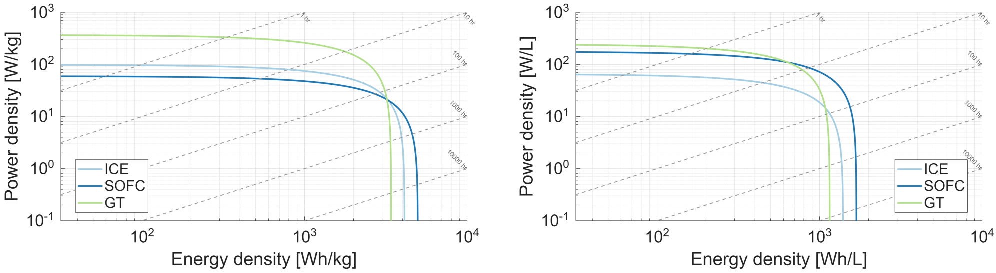
Figure 5.3 gives an overview of the different combinations for SB. SB can be integrated with an ICE, PEMFC, SOFC or GT. The figure shows that SB combined with a GT has a high power density, while combining SB with a SOFC results in a high energy density; this directly correlates with the high power density of the gas turbine and the high efficiency of the SOFC. In the gravimetric case, shown in figure 5.3a, the PEMFC shows a high energy and power density. In the volumetric case (figure 5.3b), the SOFC is very similar to the PEMFC. Thus, in the next subsections, SB will be combined with a PEMFC.

Figure 5.4 shows the different energy converters possible for AB. As AB produces ammonia, the PEMFC is not incorporated. The gravimetric Ragone



(a) Gravimetric Ragone plot (b) Volumetric Ragone plot

Figure 5.3: Ragone plots of Sodium borohydride

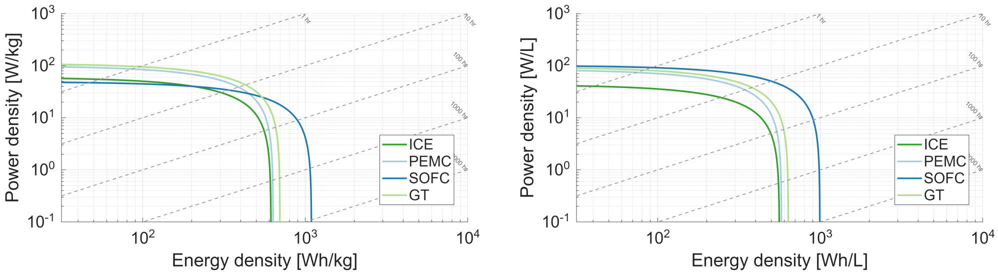


(a) Gravimetric Ragone plot (b) Volumetric Ragone plot

Figure 5.4: Ragone plots of Ammonia borane

plot (figure 5.4a) shows that all three options have their own advantages; the GT has a higher power density, the SOFC will result in a higher energy density, and the ICE is always in the middle of these two. Regarding the volumetric Ragone plot, visible in figure 5.4b, the GT and SOFC have higher power densities, while the SOFC results in a higher energy density. The ICE has a lower power density compared to both other options, but results in an energy density that lies between. The ICE does not outperform the GT or SOFC in either power density or energy density, but it occupies the middle range between the two. Because it provides a stable, balanced performance across both metrics and no single converter clearly dominates for AB, the ICE is selected as the representative case for the remainder of this study.

The Ragone plots of NEC are shown in figure 5.5. Figure 5.5a shows the gravimetric Ragone plot, where both the PEMFC and ICE perform worse than the SOFC and GT; likely due to the amount of heat available for waste heat integration. More waste heat integration is beneficial for NEC, due to



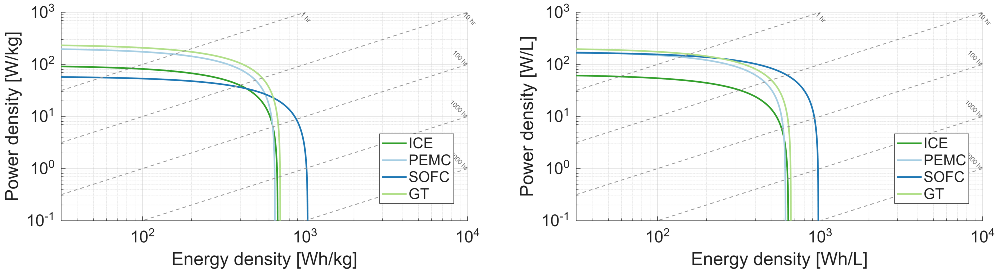
(a) Gravimetric Ragone plot

(b) Volumetric Ragone plot

Figure 5.5: Ragone plots of NEC

its endothermic dehydrogenation process. The SOFC shows a higher energy density, while the GT shows a higher power density. The volumetric Ragone plot (figure 5.5b) is different. The SOFC has the highest power and energy density. As the SOFC is clearly the best performer based on the volumetric Ragone plot, and also scores relatively well on the gravimetric Ragone plot, it is chosen to be the representative case for NEC in the remainder of this study.

Finally, figure 5.6 shows the Ragone plots of DBT. Similarly as to NEC, the gravimetric Ragone plot (figure 5.6a) shows a trade-off between power and energy density. The GT achieves a higher power density, while the SOFC achieves a (significantly) higher energy density. The volumetric case (figure 5.6b) shows similar results; however, the difference in power density between the SOFC and GT is significantly smaller than their respective difference in energy density. So, the SOFC overall outperforms the GT, and the DBT_SOFC combination will be regarded from now on. Table 5.3 gives an overview of all casestudies that will be considered.



(a) Gravimetric Ragone plot

(b) Volumetric Ragone plot

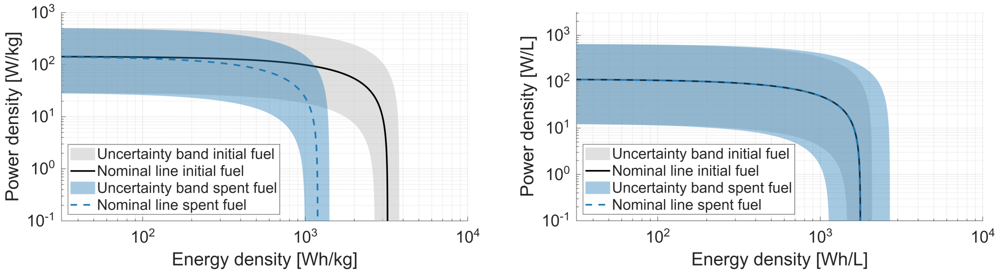
Figure 5.6: Ragone plots of DBT

Case name	Hydrogen Carrier	Energy converter
SB_PEM	Sodium borohydride	PEMFC
AB_ICE	Ammonia Borane	ICE
NEC_SOFC	N-Ethylcarbazole	SOFC
DBT_SOFC	Dibenzyltoluene	SOFC
MDO_ICE	Marine Diesel Oil	ICE
LH2_PEM	Liquid Hydrogen	PEMFC
NH3_SOFC	Ammonia	SOFC
MeOH_ICE	Methanol	ICE

Table 5.3: Case studies and names.

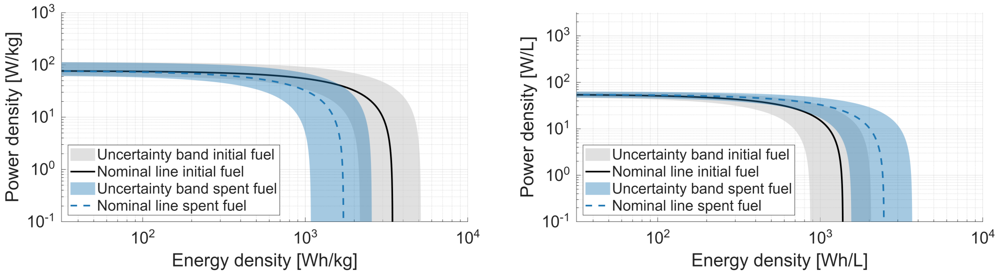
5.3.2 SPECIFIC CASE STUDIES AND THEIR UNCERTAINTY

This section presents the case studies for each hydrogen carrier, examining how data availability and consistency influence the results. In addition to the cases specified in subsection 5.3.1, a fifth case of DBT combined with a GT is chosen to be represented here; this way, the uncertainty of the GT and its influence on the results is visible as well. The GT is combined with DBT because this combination (visible in figure 5.6) showed better compatibility than the GT with NEC (figure 5.5). Figures 5.7 and 5.8 display the gravimetric and volumetric energy densities of SB and AB, respectively, with uncertainty bands representing the range of available data. These figures also illustrate the impact of spent fuel by including additional plots showing energy density calculations based solely on spent fuel mass.



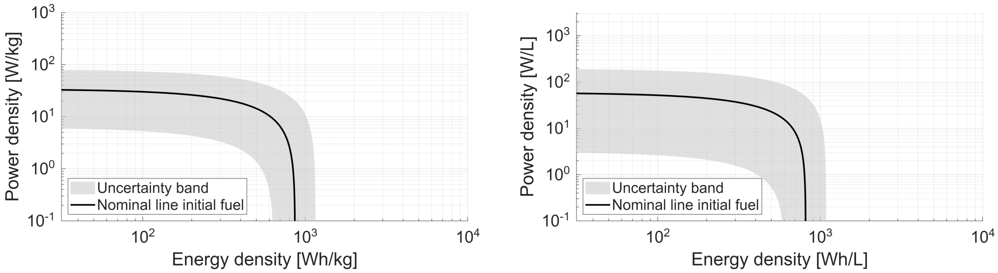
(a) Gravimetric Ragone plot (b) Volumetric Ragone plot

Figure 5.7: Ragone plots of SB combined with a PEMFC



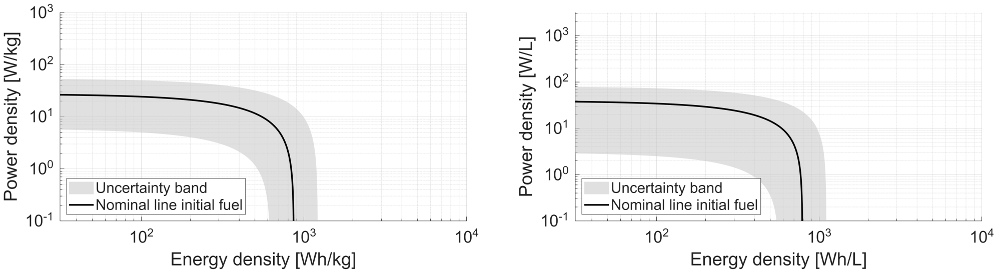
(a) Gravimetric Ragone plot (b) Volumetric Ragone plot

Figure 5.8: Ragone plots of AB combined with ICE



(a) Gravimetric Ragone plot (b) Volumetric Ragone plot

Figure 5.9: Ragone plots of NEC combined with an SOFC



(a) Gravimetric Ragone plot

(b) Volumetric Ragone plot

Figure 5.10: Ragone plots of DBT combined with a SOFC

Figure 5.7 shows the gravimetric and volumetric energy densities of SB and its spent fuel in combination with a PEMFC. The gravimetric range (Figure 5.7a) exhibits substantial variation in fuel-cell power density, spanning from 30 W/kg to around 500 W/kg, with values distributed relatively symmetrically around an average of approximately 140 W/kg. The gravimetric energy densities highlight the mass penalty associated with the spent fuel: the spent fuel-to-fuel ratio is roughly 2.7, reflected in average energy densities of about 1200 Wh/kg for the spent fuel and 3200 Wh/kg for the fuel.

The volumetric plots (Figure 5.7b) reveal a different pattern. Owing to the low bulk density of SB itself and the considerably higher density of the spent fuel, the volumetric energy densities of fuel and spent fuel partially overlap. The spent fuel density may be lower than shown, as it is unclear whether this density is the bulk or particle density. Both fuel and spent fuel cluster around approximately 1800 Wh/L, though the spent fuel range is noticeably wider due to greater uncertainty in the underlying data. The volumetric power density also spans a broader interval than its gravimetric counterpart, ranging from 12 W/L to 645 W/L.

Figure 5.8 presents the case of AB combined with an ICE. Here, the lower bound of the energy density assumes hydrogen-only utilisation and PEMFC waste heat integration, representing a conservative operation. The gravimetric power density exhibits considerable variability, as indicated by the broad uncertainty band in Figure 5.8a (60–115 W/kg). This reflects the strong sensitivity of the gravimetric metric to variations in reported engine mass. The gravimetric energy density also reveals the mass penalty associated with spent fuel; however, both fuel and spent fuel ranges are wider and partially overlap, reflecting the higher data uncertainty for AB compared with SB.

The volumetric power density displays a much narrower uncertainty interval (47-63 W/L), consistent with lower variability in reported volumetric parameters. For the volumetric energy density, the spent fuel exhibits higher values than the fuel. This follows from the relatively low spent-to-fuel mass ratio (around 2) combined with the substantial difference in material densities (approximately 400 kg/m^3 for the fuel and 1435 kg/m^3 for the spent fuel), which shifts the volumetric metric in favour of the spent fuel.

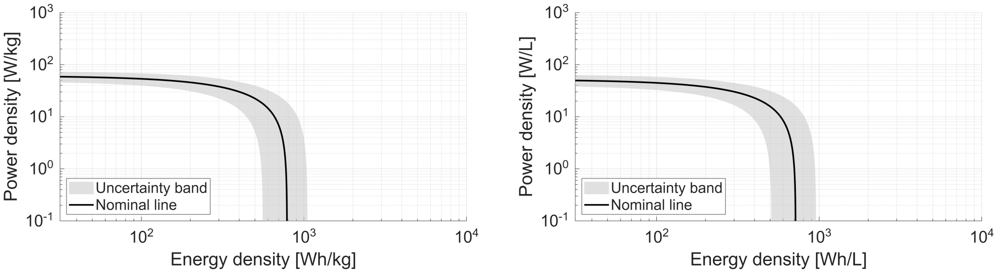
Figure 5.9 presents the power and energy density characteristics of NEC combined with an SOFC. The gravimetric power density exhibits a wide uncertainty band, ranging from 6 to 80 W/kg, with a skewed distribution that favours lower values, around 33 W/kg. The gravimetric energy density is centred around approximately 900 Wh/kg, and the associated uncertainty band is relatively broad.

The volumetric power density (Figure 5.9b) covers an even wider range than the gravimetric case, extending from 3 to 190 W/L, again with a clear concentration of values (midline being around 56 W/L) near the lower boundary. The volumetric and gravimetric energy densities are similar, reflecting the high material density of NEC (approximately 940 kg/m^3).

Figure 5.10 provides an overview of the performance of DBT when coupled with an SOFC. The gravimetric power density (Figure 5.10a) exhibits a slightly narrower uncertainty range (6 to 50 W/kg) compared with NEC. This likely reflects the larger and heavier reactor and heat-exchanger components required for DBT, which shift the system toward lower gravimetric power densities and reduce variability. The gravimetric energy density shows a broader spread than in the NEC case, ranging from approximately 400 to nearly 900 Wh/kg.

The volumetric plot (figure 5.10b displays a similar pattern: while the uncertainty range remains substantial (3-80 W/L), it is smaller than that of NEC yet still wider than the gravimetric equivalent. This again stems from the system-level mass and volume contributions of the reactor and ancillary components associated with DBT processing. Similar to NEC, the volumetric and gravimetric energy densities lie close to each other; DBT also has a density of approximately 910 kg/m^3.

Figure 5.11 shows the performance of DBT in combination with a gas turbine. The gravimetric and volumetric power-density bands (Figures 5.11a and 5.11b) are very narrow, ranging from 45 to 75 W/kg and 40 to 65 W/L, respectively. Both the magnitude and the limited spread reflect the small number of data sources available for GT systems and the fact that the reported values lie within a constrained region. This case is included primarily to illustrate the comparatively low uncertainty associated with the GT data relative to the fuel-cell cases discussed elsewhere in the paper.



(a) Gravimetric Ragone plot

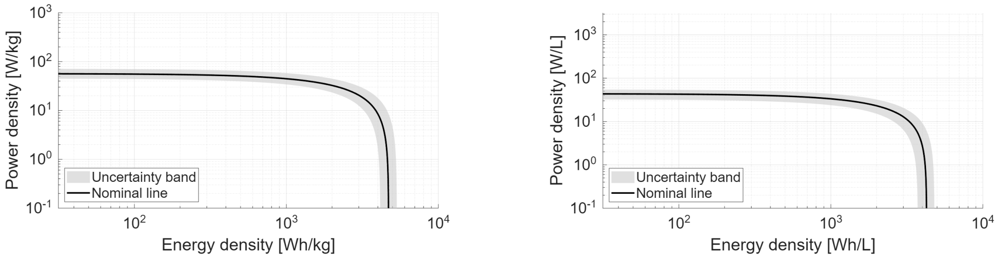
(b) Volumetric Ragone plot

Figure 5.11: Ragone plots of DBT combined with a gas turbine

5.3.3 REFERENCE CASES

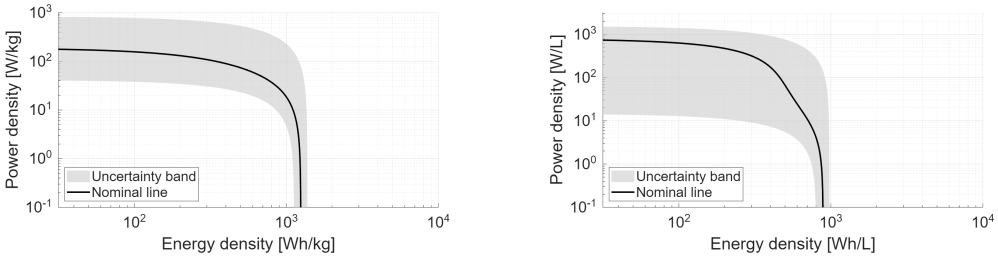
Figure 5.12 provides a comparison of all reference cases, with each case presented through both gravimetric and volumetric analyses. The liquid hydrogen case (Figure 5.12c and 5.12d) exhibits the only significant uncertainty band for the power density. The bandwidth of the power density is slightly different from that of SB. For the LH2 case, it ranges from 40 W/kg up to 820 W/kg, and from 15 W/L up to 1500 W/L. The energy density of liquid hydrogen shows narrow uncertainty bands. Because the midline is the geometric mean of the bounds, the apparent kink arises from the logarithmic scaling and does not reflect a physical discontinuity.

All other reference cases demonstrate very narrow uncertainty bands. For marine diesel oil shown in Figures 5.12a and 5.12b, the uncertainty bands range from 45 W/kg up to 71.5 W/kg, for example. The methanol and ICE cases exhibit the same narrow uncertainty bands, as these have the same background data for the internal combustion engine. The NH3_SOFC case study (Figures 5.12e and 5.12f) also shows narrow uncertainty bands, from 25 W/kg up to 35 W/kg, and from 50 W/L up to 77 W/L.



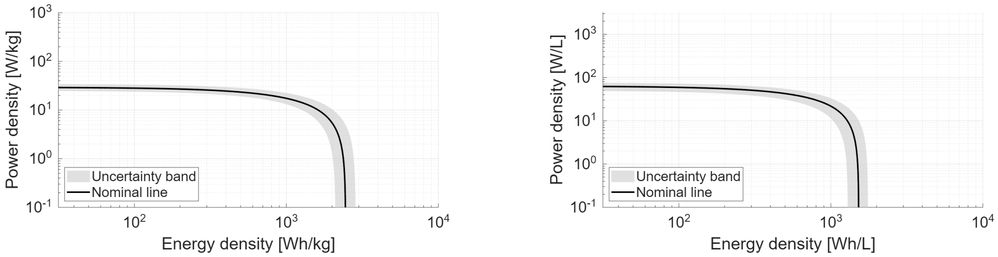
(a) MDO_ICE Gravimetric

(b) MDO_ICE Volumetric



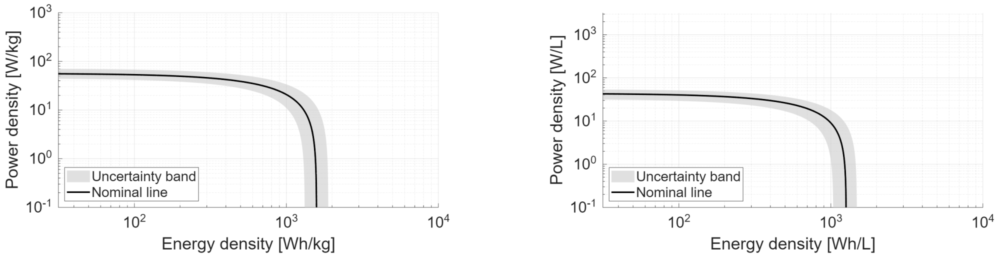
(c) LH2_PEM Gravimetric

(d) LH2_PEM Volumetric



(e) NH3_SOFC Gravimetric

(f) NH3_SOFC Volumetric



(g) MeOH_ICE Gravimetric

(h) MeOH_ICE Volumetric

Figure 5.12: Ragone plots of reference cases

5.3.4 COMPARISON OF CASE STUDIES

To enable comparison across all fuel systems despite varying data quality and availability, the midlines of the uncertainty bands are used for each technology combination. These midlines represent the geometric mean of the upper and lower bounds established in the preceding analysis. Figures 5.13 and 5.14 show all hydrogen carrier and reference cases in gravimetric and volumetric form, respectively. Solid lines denote the hydrogen carrier case studies, while dashed lines represent the reference cases.

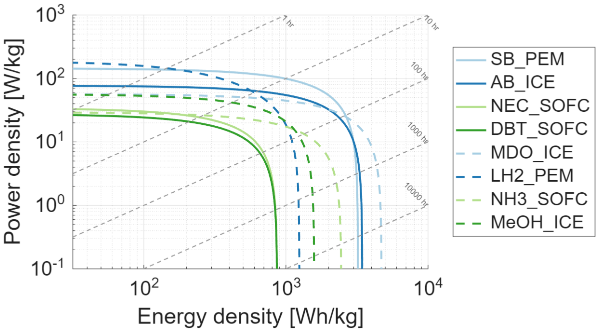


Figure 5.13: Gravimetric Ragone plot of all cases

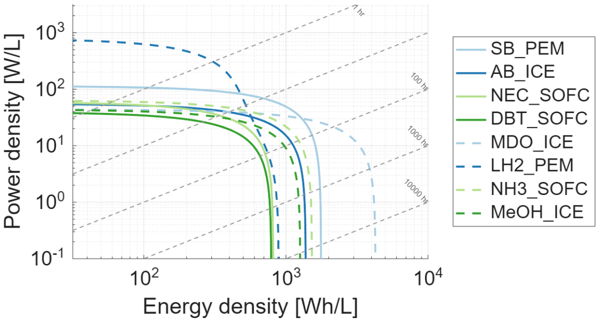


Figure 5.14: Volumetric Ragone plot of all cases

Figure 5.13 gives an overview of the gravimetric energy and power density of all cases; hydrogen carrier and reference cases. The plot shows the high power density of PEMFCs. The power density of a PEMFC with only liquid hydrogen is higher than that when combining it with SB, as SB requires heat exchangers and, most significantly, a release reactor and separator system to provide the hydrogen, thereby reducing the overall system's power density. However, the energy density of SB is considerably higher than that of LH2. SB_PEM may therefore be advantageous in applications where energy density is the primary constraint. AB_ICE demonstrates a significantly higher power density than most alternative fuels, including NH3 and MeOH, except for LH2_PEM and SB_PEM. The power densities of MeOH_ICE and MDO_ICE are essentially equivalent, with the power density of ammonia borane surpassing them both. When considering energy density, AB_ICE and SB_PEM are the alternative fuels that come closest to MDO, however the difference is still large; around 3200 Wh/kg for the hydrogen carriers and almost 4700 Wh/kg for MDO. When both energy and power density matter, SB_PEM might potentially, if the stated assumptions are correct, surpass MDO.

In figure 5.14, all three ICE cases show nearly identical volumetric power densities. The main differences therefore appear in the volumetric energy density, where the ordering is clear: MDO_ICE has the highest values, followed by AB_ICE, with MeOH_ICE lowest. These differences are substantial and reflect the underlying fuel volumetric energy densities rather than differences in converter performance.

When examining the SOFC-based systems, the ammonia case shows slightly higher power densities than the hydrogen carrier cases with NEC or DBT, mainly due to the large amount of additional equipment the latter require. In terms of energy density, ammonia remains much higher than both NEC and DBT. Compared with SB and AB, NEC and DBT both exhibit relatively low energy densities. In the LOHC cases, DBT has lower power density and slightly lower energy density than NEC in both gravimetric and volumetric terms. Although DBT_SOFC is the lowest-performing in the SOFC group, it still represents a functioning hydrogen carrier option in the overall comparison.

5.4 RESEARCH IMPLICATIONS

The analysis presented in the preceding section demonstrates that all hydrogen carrier case studies exhibit performance metrics within a similar order of magnitude as the reference cases. Each case study remains relevant for further interpretation, as shown in subsection 5.4.1. Their possible practical implications are discussed in subsection 5.4.2. However, the results should be interpreted with caution. The many assumptions necessary to do the calculations will influence the overall outcome. The influence of these assumptions is discussed in section 5.4.3.

5.4.1 INTERPRETATION OF RESULTS

Analyses and interpretation of the Ragone plots reveal several recurring patterns across the different fuel–converter combinations. These patterns provide insight into the relative maturity of technologies, the influence of system integration, and the key drivers behind the observed performance ranges.

First, several cases show a skew towards a lower or higher power-density values within their uncertainty ranges. This is particularly visible for the PEMFC-based cases (SB_PEM and LH2_PEM) and for the SOFC-based hydrogen cases (NEC_SOFC and DBT_SOFC). In these cases, most reported values cluster toward one end of the gravimetric and volumetric power-density ranges, with fewer data points broadening the uncertainty band. Despite appearing to make data less reliable, a large distribution with a skew towards higher estimates indicates a certain maturity to the technology. First of all, there is sufficient data to form such a wide band; secondly, there is even enough data to have a distinct skewer; finally, the technology is likely to be researched, with continuous improvements regarding the power density.

A second observation concerns the shape of the midlines. In some cases, especially visible in figure 5.12d, the upper and lower bounds have markedly different curvatures, resulting in midlines that show mild non-monotonic behaviour. This effect arises from the averaging procedure: when power-density bounds diverge strongly while energy density bounds converge to similar magnitudes, the midline reflects the mathematical interpolation between two distinct performance envelopes. The phenomenon is most evident in cases where the underlying datasets differ widely in system inclusion (e.g., balance-of-plant assumptions), but it does not indicate physical discontinuities in the underlying technology.

By contrast, the internal combustion engine results exhibit consistently narrow uncertainty bands. In the MDO_ICE case, this is explained by the high maturity of the technology. It is assumed that methanol engines do not differ greatly from MDO engines, resulting in the same narrow band. Hydrogen ICEs do differ from MDO engines, as compression ignition is not an option for hydrogen. Hydrogen ICEs also exhibit relatively narrow ranges: although their combustion characteristics differ from those of diesel engines, commercially available hydrogen engines have similar volumetric power densities, while gravimetric values differ only modestly.

The gas turbine case likewise shows a narrow uncertainty band, but for a different reason. Publicly available data for hydrogen-fuelled GTs remain limited, and the existing values cluster tightly. As a result, the DBT_GT case displays consistent but data-sparse performance envelopes.

The energy density behaviour differs across the hydrogen carriers and reflects their underlying chemistry. For AB, the fuel releases both hydrogen and ammonia; if both species can be utilised in the energy converter, the effective energy density is substantially higher than when only hydrogen is used. However, the use of ammonia is not straightforward, as it readily dissolves in water and may require additional separation steps before it can be supplied to the converter. Both AB and SB also require significant amounts of water for hydrolysis, although this can be largely mitigated by recycling the water produced when hydrogen is converted to useful energy. This reduces the net amount of additional water that must be supplied. In the case of SB, some studies report energy densities that include the mass of the required water; however, in this work, the energy density based solely on the hydrogen content of SB is used to represent the lower bound, allowing for consistent comparison across all carriers.

For LOHCs (NEC and DBT), the energy density is more strongly influenced by the degree of heat integration, as their endothermic dehydrogenation requires substantial thermal input. When heat can be integrated effectively from the energy converter, the usable energy density increases accordingly. This explains the broader energy density bands observed for NEC and DBT in figures 5.9 and 5.10.

Together, these findings underline the importance of evaluating complete fuel–converter value chains rather than isolated components. Although the hydrogen carriers differ substantially in chemistry, handling requirements, and heat-integration demands, the system-level Ragone framework provides a consistent basis for comparing their effective gravimetric and volumetric power and energy densities. This system-integrated perspective is essential for assessing the suitability of alternative fuels for maritime applications, where the converter, reactor, heat exchangers, and storage all contribute to the overall performance.

5.4.2 PRACTICAL IMPLICATIONS FOR MARITIME VESSELS

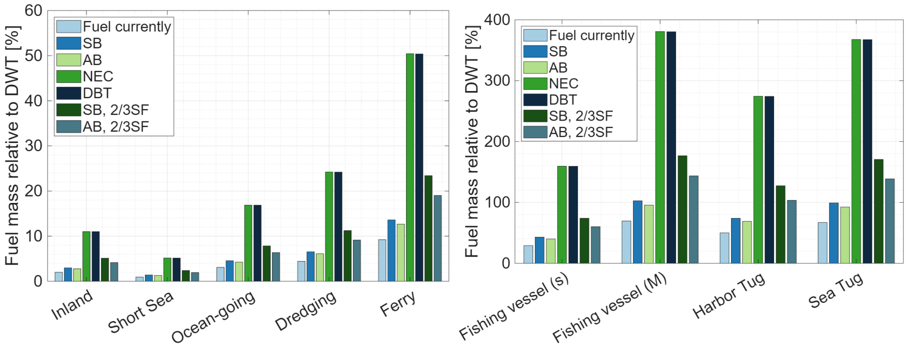
The respective energy and power densities of hydrogen carriers vary from each other and from other reference fuels, as visible in Figures 5.13 and 5.14. Combined with the well-known notion that there will likely not be a one-size-fits-all solution for alternative fuels and energy converters on ships [222], it is interesting to look at different ship types, their relevant power requirements and range or days of autonomy, and see which fuel-converter combination would be fitting for each ship type. Table 5.4 gives an overview of the typical ship types used in this study. The power, required energy or size of the fuel tanks, size and volume of each of a typical example of these vessels has been estimated. The space and weight current fuels (MDO) as well as a standard ICE take up (thus, not the size of the engine room), is then compared to each of the case studies. The results of the energy density are in figure 5.15 (gravimetric) and 5.16 (volumetric). Figures 5.17 and 5.18 give an overview of the minimum required engine weight and space compared to the overall ship weight (DWT) and (cargo) volume, respectively.

	Power	Time of autonomy	Notes	Source
Inland ship	250-840 kW	5-15 days	Trade off bunker frequency and space or weight requirements	[223]
Coaster	700-3000 kW	around 10 days	Trade off bunker frequency and space or weight requirements	[222]
Ocean-going	2.5-10 MW	over 30 days	Space requirements to have sufficient energy	[222]
Short-range fishing vessel	300-600 kW	5-6 days	Relatively small for the amount of energy required	[224], [225]
Dredger	8-15 MW	15 days	Relatively large amount of power and energy required	[222]
Tug	2-5 MW	2 days	Relatively small for the amount of power required	[222]
Short-range ferry	1-3 MW	50-180 minutes	Volume limited, safety important	[226]

Table 5.4: Typical ship types, power and days of autonomy

Inland Ships

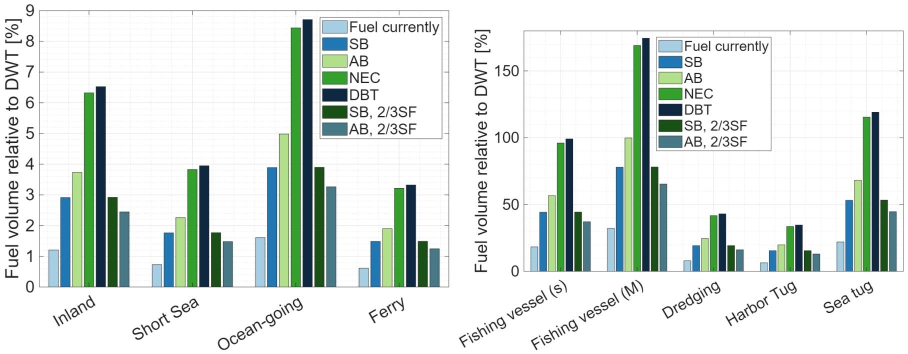
Inland ships require relatively little power but operate with medium to long autonomy. The choice of hydrogen carrier, therefore, has a strong impact on their bunkering arrangements. Although frequent refuelling is considered a feasible business case [227], it is generally undesirable. For these vessels, energy density becomes particularly relevant. Depending on the cargo, inland ships may be weight- or volume-limited: light cargo typically leads to volume limitations, while dense cargo results in weight restrictions. In figure 5.15a and 5.16a an inland container barge is taken as the example vessel; this vessel is likely volume-limited. SB_PEM and AB_ICE are both suitable options,



(a) Gravimetric percentages of fuel relative to deadweight tonnage of example vessels, low weight percentage

(b) Gravimetric percentages of fuel relative to deadweight tonnage of example vessels, high weight percentage

Figure 5.15: Gravimetric percentages of fuel relative to deadweight tonnage of example vessels

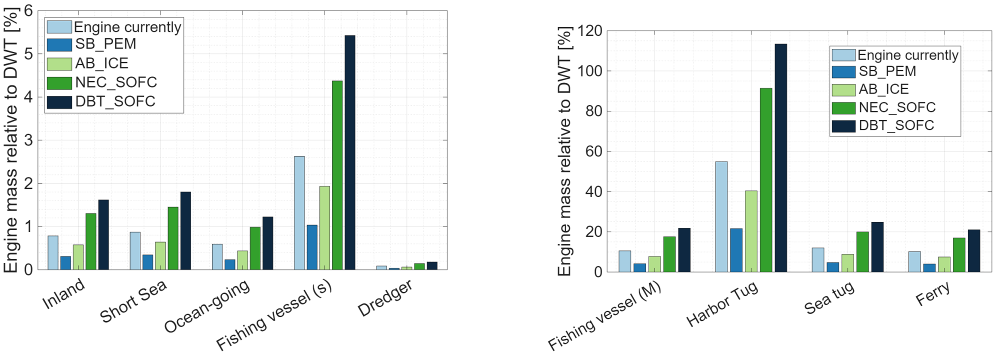


(a) Volumetric percentage of total available volume of example vessels versus required fuel, low volumetric percentage

(b) Volumetric percentage of total available volume of example vessels, versus required fuel high volumetric percentage

Figure 5.16: Volumetric percentage of total available volume of example vessels, versus required fuel

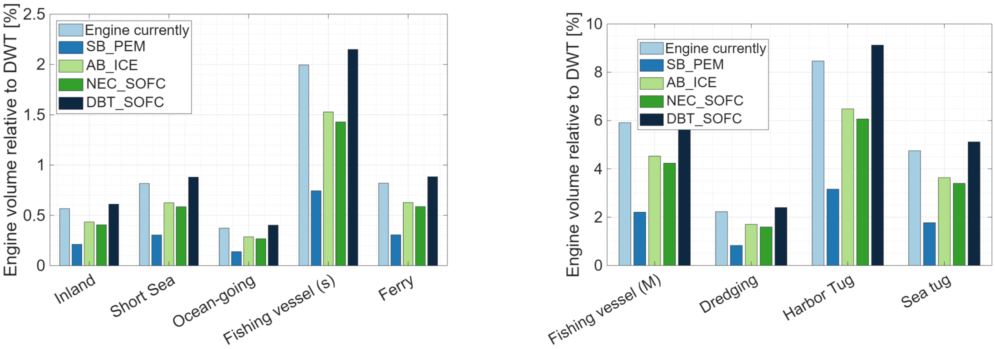
with SB_PEM being more attractive if volumetric energy density is extremely important. For weight-limited ships, it may be possible that no change in operational patterns can be achieved, while for volume-limited ships, some operational changes would have to be made. Regarding engine size and weight (figures 5.17a and 5.18a), it appears that SB_PEM and AB_ICE are



(a) Gravimetric percentages of deadweight tonnage of example vessels versus weight of energy converter, low weight percentage

(b) Gravimetric percentages of deadweight tonnage of example vessels versus weight of energy converter, high weight percentage

Figure 5.17: Gravimetric percentages of deadweight tonnage of example vessels versus weight of energy converter



(a) Volumetric percentage of total available volume of example vessels versus required energy converter space, low volumetric percentage

(b) Volumetric percentage of total available volume of example vessels versus required energy converter space, high volumetric percentage

Figure 5.18: Volumetric percentage of total available volume of example vessels versus required energy converter space

likely to fit in the current engine rooms, because of their high efficiencies and high power densities.

Coasters

Coasters, or short sea vessels, have medium power requirements and similar autonomy to inland ships. Bunkering frequency directly influences the required onboard storage volume; while more frequent bunkering reduces storage needs, it is generally avoided for operational convenience. These vessels, like inland ships, may be either weight- or volume-limited depending on their cargo. The reference coaster vessel currently has a very small amount of space and weight dedicated to its fuels (figures 5.15a and 5.16a). Similarly to inland vessels, both SB_PEM and AB_ICE emerge as relevant options. If the vessel is unlikely to refuel often and is volume limited, AB_ICE might be a better option than SB_PEM, due to the lower volume its spent fuel occupies. When looking at power, again, it is estimated that both options will possibly fit in the current engine room. So, SB_PEM and AB_ICE again emerge as relevant options, providing high power density while supporting operationally meaningful ranges.

Ocean-going Vessels

Ocean-going vessels require substantial power and very large autonomy, frequently exceeding 30 days [222]. Depending on the type of cargo and vessel layout, they may be either volume- or weight-limited. The reference vessel, an LNG tanker, often uses at most 2/3 of its maximum energy usage [20]. For weight-limited applications, figure 5.15a shows that AB_ICE is slightly favourable over SB_PEM, due to its higher energy density, combined with a gravimetric power density sufficient to sustain large propulsion loads over long periods. Additionally, its spent fuel is lighter, which becomes increasingly relevant as storage capacity increases. For volume-limited vessels, figure 5.16a shows that SB_PEM offers a higher energy density and a similar spent fuel density as AB_ICE. Thus, both AB_ICE and SB_PEM could be suitable options for ocean-going vessels.

Fishing Vessels

Fishing vessels vary widely in size and operational profile. This study focuses on shorter-voyage vessels operating for 5 to 6 days, which typically require modest power but have very limited space onboard. There are two reference vessels: a small Dutch vessel and a slightly larger Norwegian fishing vessel.

The fuel energy density percentage of both are depicted in figure 5.15b and 5.16b. A major issue with these fishing vessels is the very limited space and weight available for fuel. Current fuel already accounts for a large share of their DWT and volume. Of all hydrogen carriers, only SB_PEM and AB_ICE could possibly fit on both fishing vessels. However, a major issue of these fishing vessels is that they cannot currently contain both fuel and fish at the same time; heavier spent fuel is thus problematic and operational parameters need to be changed. However, using SB_PEM and AB_ICE may enable fishing vessels to continue operating within ecologically protected areas without causing environmental harm, even if they have to refuel more often. The engine room appears to not be the limiting factor.

Dredging Vessels

Dredging vessels exist in two types: long-range vessels with an autonomy of around 15 days, and shorter-range vessels with an autonomy of 3 to 7 days. Here, the focus is on the long-range vessels. These vessels have greater autonomy than most ship types in this study; yet, their power requirements are extremely high, making it essential to achieve a high power density. However, the overall size and weight of the current engine (estimated), does not appear to be limiting for the example vessel. Depending on the vessel's specific power demand, range, and weight- or volume-related constraints, SB_PEM, AB_ICE, and NEC_SOFC can all be viable options. SB_PEM offers the highest gravimetric power density. NEC_SOFC and AB_ICE exhibit high volumetric power densities as well. For the example vessel, the total fuel volume appears to be more limiting than the weight for the fuel. The gravimetric percentage the fuel takes up (figure 5.15a) is significantly smaller than the volumetric one (figure 5.16b). As a dredging vessel gets heavier over time, AB_ICE would likely be the best option for the example vessel; its spent fuel takes up less space than SB's and is also lighter. However, SB_ICE would also be possible, as well as NEC_SOFC. The latter would be less desirable due its higher volumetric energy density. It additionally appears all would fit in the current engine room.

Tugs

Tugs have relatively high power requirements for their size, but typically limited onboard space and relatively short autonomy. As tugs do not carry cargo, the concept of weight or volume limitated is less relevant; instead, volumetric power density and endurance are the key constraints. In this paper, two tugs are regarded: a harbour tug (lower endurance and higher power density) and a sea tug (higher endurance and lower power density). Especially for the harbour tug, the gravimetric power density appears to be limiting (figure 5.17b). This can be improved by using LH2. However, the amount of fuel both tugs need to bring, given their own weight and size, is relatively high. For both tugs, it appears that none of the hydrogen carriers can be used without compromising operational demands. The spent fuels, specifically, are too heavy for the tugs (figure 5.15b); the volume appears to be less limiting (figure 5.16b). For the sea tug, it is slightly worse than for the harbour tug.

Ferries

Ferries exist in many configurations, with operational profiles ranging from extremely short river crossings to medium-range sea routes. This study focuses on short-range ferries, such as those serving the Dutch islands [226], with an example ferry also operating between the Dutch coast and the island of Ameland. Ferries generally require high energy densities and are typically volume-limited. Quiet operation is also desirable, and the fuel needs to be safe for the passengers. AB_ICE is not considered, due to the presence of (toxic) ammonia. SB_PEM, NEC_SOFC and DBT_SOFC appear to be good fits for these vessels, offering a balance of power, energy density, and silent operation. These options would theoretically fit on the ferry, although the weight of DBT and NEC would likely influence the operational profile of the ferry, as seen in figure 5.15a. The latter becomes especially evident when taking into account the estimated size of the engine; a larger engine room is possibly required, especially for DBT_SOFC. As with all other ship types, the optimal choice ultimately depends on the vessel's detailed operational profile.

Broader Applicability

Table 5.5 summarises the relevant power and energy requirements and the case study combinations capable of meeting them. Although this analysis focuses on maritime applications, the underlying characteristics of hydrogen carriers, including high energy density, high power density, silent operation, and zero emissions, may also be beneficial in other sectors such as road transport, construction, and aviation. However, the results cannot be transferred directly to these sectors. Both AB and SB require large amounts of water during hydrolysis, which is not an issue for maritime applications but may be problematic elsewhere unless water is readily available.

	Inland	Short Sea	Ocean-going	Fishing	Dredging	Tug	Ferry
Power Requirement	Small	Medium	High	Small	High	Medium	Medium
Autonomy	Medium	Medium	Long	Medium	Long	Medium	Short
Case Study	SB, AB	SB, AB	SB, AB	SB, AB	SB, AB, NEC	LH2, SB, AB	SB, NEC, DBT
Operational Changes likely necessary	No	No	No	Yes	Maybe	Yes	Maybe

Table 5.5: Overview of possible hydrogen carrier and energy converter combinations suitable for different ship types and operations

5.4.3 REFLECTION ON MODELLING ASSUMPTIONS

The apparent consistency of certain technology combinations masks underlying assumptions that may not reflect real-world performance variability. This subsection examines how key assumptions in data treatment, system boundaries, and technology projections influence the results and their interpretation and how future research can improve the overall results.

From the energy density perspective, the bulk density, the treatment of fuel and spent fuel, and the heat requirements of each carrier strongly influence the outcome. The bulk densities of SB and AB used in this research are based on experimental data, yet they remain sensitive to the measurement method. SB exists as both powder and granulate, while AB is available only as a powder. These materials can be compressed to some degree, which increases bulk density, but excessive compression may hinder flowability and is therefore not always desirable. Bulk density can deviate significantly from particle density, with reported values as low as half of the true material density. In this research, the bulk density of SB is regarded as 65% of the particle density of SB, namely 550 kg/m^3. For AB, no data is available on bulk density. After in-house, unpublished testing by the authors, the bulk density appears to be less than SB and is estimated to be around 400 kg/m^3, although this value depends strongly on the packing state (e.g., loose or compressed). Because volumetric energy density scales directly with bulk density, this assumption introduces uncertainty into the volumetric performance of AB. The reported volumetric energy density values should therefore be interpreted as estimates within a realistic range rather than precise values. The gravimetric energy density is not influenced by this. Further research on the bulk density and a sensitivity study on how it influences the volumetric energy density is still advisable.

The distinction between fuel and spent fuel is also important. Figures 5.7 and 5.8 clearly show this, as well as figures 5.15 and 5.16. For safety reasons, ships are not operated with empty tanks, so energy density estimates based solely on spent fuel are not representative. That is why the specific mixture is chosen when evaluating the feasibility for different ship types. For gravimetric energy density, the effect of the spent fuel may be significant for weight-limited ships. These distinctions, while important at the ship-integration level, are not shown directly in the Ragone plots.

Heat integration assumptions further affect the energy density of LOHC systems. Proper waste-heat recovery can improve the overall energy density by up to about 30 % [21], and this has been included by using the average expected improvement in the comparison figures. However, the practical achievable degree of heat integration depends strongly on system layout, operational profiles, and thermal-management constraints.

Beyond energy density considerations, several assumptions regarding power density calculations influence the comparative results. The technology to convert hydrogen into useful power (e.g. electrical or mechanical) is in various stages of maturity. The PEMFC are the most mature. Substantial data is available for PEM, yet the range of these technologies may be improved. The other converters are less mature, yet have much smaller data bandwidths. In this research, all the data is assumed to be of a comparable level of performance characterisation. This assumption may make less-developed technologies appear more consistent than they are in practice, potentially underestimating their future improvement potential as well as their present uncertainty. This affects comparative conclusions, as emerging technologies may seem either more predictable or less promising than their true developmental trajectory suggests.

The reactor, separator and heat exchangers influence the power density as well. Because the separator size is determined by the reactor, reducing the reactor size significantly affects the power density. The reactor itself is strongly influenced by the choice of catalyst and type of reactor, but the throughput time also plays an important role. In this research, experimental data is taken as a basis, and it is assumed that these experiments can be easily scaled up. However, scaling up a reactor may influence its power density. Additionally, as these are emerging technologies, the throughput time of the reactor may still be reduced, which strongly influences its size and thus the power density. This scaling assumption is particularly significant given that most experimental data comes from laboratory-scale systems, while marine applications require industrial-scale reactors. Furthermore, as especially the DBT reactor is operated at temperatures very close to DBTs degradation temperature, intermediate heat exchangers were added to avoid overheating of the reactor of DBT and of NEC. These heat exchangers are of considerable size and strongly influence the power density of the overall system. Even though these intermediate heat exchangers were assumed necessary based on thermal limits, alternative reactor designs, improved thermal management, or improved overall energy management could potentially remove this requirement.

Mass-flow and heat-flow integration are also critical. In this work, ideal mass-flow matching is assumed, meaning that flow rates between components are perfectly aligned without practical constraints such as control limitations or pressure-drop penalties. Real systems will experience such constraints, potentially lowering power density. Similarly, waste-heat utilisation improves energy density, but may influence power density depending on the level of integration. Without heat integration, a hydrogen burner is required, which simplifies the system but increases hydrogen demand. This reduces both the energy density and, by increasing reactor throughput requirements, the power density. In this research, the net effect of heat-integration assumptions on power density is assumed negligible, although deviations from ideal integration could alter this balance.

Finally, more advanced integration strategies could further improve system performance. Internal reforming of NEC or DBT within an SOFC could reduce heat-exchanger requirements substantially. Likewise, the use of liquid cooling could reduce heat-exchanger size because liquid–liquid units are typically more compact than liquid–gas systems. These options were not considered here due to limited research availability, meaning the current approach may overestimate system size and underestimate power-density potential for future integrated designs.

The assumptions discussed above influence different performance metrics to varying degrees. Power density is dominated by converter data and reactor sizing assumptions, with heat-integration choices playing a comparatively minor role. Energy density, on the other hand, is more sensitive to heat-integration assumptions and spent fuel effects, and these factors may alter comparative outcomes significantly.

The potential for future optimisation varies significantly as limitations may be physical or technological in nature. Certain energy converter efficiencies, such as those for ICE and GT, are fundamentally limited by thermodynamics, specifically by the Carnot efficiency. On the other hand, reactor technologies and catalyst selections are largely technologically limited, resulting in possible optimisation as emerging technologies mature.

Finally, the logarithmic scaling used in the plots inherently reduces the visual impact of small performance differences. This results in emphasis on meaningful performance differences, while minor variations are not emphasised. In turn, small data discrepancies or measurement uncertainties are rightfully minimised, ensuring the focus lies on substantial performance distinctions, rather than small differences which will not likely influence practical design decisions.

5.5 CONCLUSION

Alternative fuels, particularly hydrogen carriers, represent a promising approach for reducing greenhouse gas emissions from ships. Given that alternative fuels vary significantly in power and energy density, no single solution is likely to work universally across all maritime applications. This study compared several alternative fuels and energy converters using Ragone plots and evaluated their suitability for seven distinct ship types. The analysis revealed that AB paired with an ICE and SB combined with PEMFC showed potential for most types of vessels, including inland, short sea, and ocean-going ships. For fishing vessels specifically, AB with ICE emerged as the only viable option among those considered.

Dredging vessels presented unique opportunities, with all four case studies deemed feasible due to their distinct operational characteristics and the high power requirements typical of dredging operations. Space-constrained vessels such as tugs required more specialised solutions: liquid hydrogen with PEMFC, SB with PEMFC, and NEC with SOFC were identified as suitable options. The latter two combinations also showed promise for ferry applications.

These findings demonstrate the value of Ragone plots in providing a clear visualisation of power and energy density trade-offs across different fuel-converter systems. The results confirm that no universal solution exists while simultaneously showing that hydrogen carriers can serve as effective alternatives for many ship types and can be on par with current systems (such as MDO) and other alternative fuels (such as ammonia, methanol and liquid hydrogen).

While this analysis focused primarily on power and energy density considerations, other critical factors such as safety and sustainability require further evaluation. Nevertheless, the study establishes the technical feasibility of hydrogen carriers for maritime applications, demonstrating that ships can operate for extended periods on hydrogen-based fuels while achieving zero emissions and protecting the marine environment from harmful pollutants.

PART 3: SAFETY & SUSTAINABILITY

> *“The major difference between a thing that might go wrong and a thing that cannot possibly go wrong, is that when a thing that cannot possibly go wrong goes wrong it usually turns out to be impossible to get at or repair”*
>
> — Douglas Adams, *Mostly Harmless*

PART SUMMARY

Safety is of utmost importance when using alternative fuels. Nobody wants to sail on a dangerous ship, and nobody would like such a ship in their harbour. When transitioning from the well-known fuels as MDO towards more unfamiliar fuels, safety is one of the major values used to assess these alternatives. Next to safety, long-term viability (sustainability) of these fuels is important as well. To avoid long-term harm, a sustainable alternative fuel is required; otherwise, MDO would still be sufficient. This part discusses safety of alternative fuels in a general and maritime contexts, as well as the importance for safety on ships, during design and afterwards. Finally, a framework is proposed with which alternative fuels, even in very premature stages of development, can be assessed on safety and sustainability.

Safety & Sustainability

6

GENERAL SAFETY HAZARDS

> *“For the sea has a lobsterpot full of tricks*
> *and illusions to confuse and beguile even the*
> *most rational 21st century sailor.”*
>
> — Nic Compton, *Off the Deep End: A*
> *History of Madness at Sea*

CHAPTER SUMMARY

Hydrogen carriers are often considered as safe alternative fuels; however, the definition of what safety entails is often lacking, both for hydrogen carriers as well as for ship safety. The aim of this chapter is to review the safety of hydrogen carriers from two perspectives, investigating potential connections between the chemical and maritime approaches to safety. This enables a reasoned consideration between safety aspects and other design drivers in ship design and operation. The hydrogen carriers AB, SB, KB and two LOHCs (NEC and DBT) are taken into consideration, together with four reference fuels (ammonia, methanol, pressurised hydrogen and MDO). After the evaluation of chemical properties related to safety and the scope of the current IMO safety framework, it can be concluded that safety remains a vague and non-explicit concept from both perspectives. Therefore, further research is required to prove the safe application of hydrogen carriers onboard ships.

6.1 INTRODUCTION

Hydrogen carriers are often considered to be safe alternative fuels [19], [20], [21], [47], [48], [53], [83]. Such claims imply that they can be safely integrated into the power and propulsion systems onboard ships. However, the exact definition of what safety entails is often lacking, both for hydrogen carriers as well as for ship safety. Occasionally, literature takes hydrogen carrier safety into account but the application of safety on ships is missing or not specified with sufficient detail [25], [228]. On the other side, the maritime safety committee (MSC) of the IMO is involved in defining overarching safety requirements for ships and their fuels [229]. However, these safety prescriptions are currently limited to conventional fuels and an explicit design philosophy for safety is lacking. Therefore, this study aims to review the safety of hydrogen and investigate potential connections between the chemical and maritime approach to safety.

This chapter starts with an identification of the hazards of the main hydrogen carriers in section 6.2. The second viewpoint, the maritime perspective and approach of safety, is summarised in section 6.3. The last two sections integrate the first three sections by matching chemical properties of hydrogen to maritime safety aspects and by providing a conclusion, respectively section 6.4 and 6.5.

6.2 HAZARD IDENTIFICATION

The discussed hydrogen carriers are considered to have potential for maritime usage based on their energy densities and TRL. This section only describes the potentially hazardous consequences as retrieved in the GHS (Globally Harmonized System of Classification and Labelling of Chemicals) and the more detailed safety data sheets. It does not aim to provide a hazard analysis, as this asks for a probabilistic representation of the likeliness of each hazard, which is strongly dependent on the specific context. The properties of substances in certain environments, such as flammability, toxicity and reaction

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The content of this chapter is based on the following articles:
E. S. van Rheenen, E. Scheffers, J. Zwaginga, and K. Visser, "Hazard Identification of Hydrogen-Based Alternative Fuels Onboard Ships," Sustainability, vol. 15, no. 24, 2023, Art. no. 16818. doi:10.3390/su152416818

to water, are established through so-called hazard assessments [230]. These provide the background for the GHS labels and the safety data sheets. Both the hydrogenated and hydrogenated forms of hydrogen carriers have to be taken into account.

Additionally, some of the hydrogen carriers react with water, splitting up into different substances. The hazards of these substances are also taken into account here, as it can be expected that, in a spill, alternative fuels come into contact with water. The hazards of thermolysed substances are considered as well because of the temperature of hydrogen fires (2400K) [231].

This chapter provides a comprised hazard identification of the hydrogen carriers mentioned in the previous section, starting with two LOHCs and followed by the borohydrides, ammonia and methanol. For each carrier, the relevant classes out of six applicable GHS classification categories are covered in the following order; flammable, acute toxic, health hazard, corrosive, irritant and environmental hazard. Of these, flammable represents a physical hazard that can cause physical damage, environmental hazards are hazardous to the aquatic environment, and the other four present dangers to human health [232]. Section 6.2.7 summarises the results, followed by section 6.2.8 with two hazards that are applicable to all hydrogen carriers.

6.2.1 GHS CLASSIFICATION AND QUALITATIVE RESEARCH

It should be noted that the following work is completely qualitative. This is mainly because the GHS only has a limited way of defining the hazards associated to each category. There are a total of nine pictograms, which all can be classified as either warning or danger [232]. Additionally, two pictograms, those of 'irritation' and 'environment' are always only classified as 'warning' [232]. This thus results in only 16 ways of categorisation of the dangers associated to substances. Within these major categories, there are subcategories, but these do not quantify the hazard, only specify it, e.g. 'flammable solid' [233]. The GHS also does not give exact values, such as toxicity potential indicator or lethal doses [232].

Similarly, for corrosivity, the GHS identifies two hazards under corrosion hazards: H290 (corrosive to metals) and H314 (causes severe skin burns and eye damage), but refrains from examining other forms of material corrosion since they are not classified by the GHS. This means that possible hazard propagation due to material corrosion is also not covered. All materials that are mentioned here as corrosive are accompanied by code H314, thus being corrosive to the skin and eyes. Consequently, it is acknowledged that substances may still possess the ability to corrode other materials or exhibit mild corrosivity that falls below the prescribed threshold value. However, this is generally not considered hazardous by the GHS, thereby falling outside the scope of this chapter.

It should be noted, however, that GHS statements are not static and are prone to modifications with the advent of new information. For example, hazard classifications have not been done for all hydrogen carriers. For some of the hydrogen carriers or substances that are a result of reactions that happen with these carriers, there is no classification at all; it is unknown how dangerous these substances are. On the other hand, some hydrogen carriers such as NEC have been thoroughly assessed using a hazard assessment [25], [234]. This adds to the uncertainty of the already relatively blunt form of qualifying hazards using the GHS symbols. So, the assessment of hazards, including the influence of alternative fuels on other materials, is paramount for the integration of alternative fuels in general, including ammonia, methanol and pure hydrogen.

All in all, current available knowledge and use of GHS classification results in a very broad division of detail of the hazards of hydrogen carriers. This is why the categorisation here in this chapter is done in a qualitative way. Because of the lack of quantification, it should be noted that comparison between two different e.g. hydrogen carriers is extremely difficult, even though they may have the same GHS pictograms, there can still be a lot of difference in the exact qualitative outcome of the comparison.

6.2.2 HAZARD IDENTIFICATION OF LOHC: DBT

DBT is commonly thought of as a promising LOHC. For safety purposes it has as its main advantage that there is no significant byproduct produced during dehydrogenation [25]. This means that when DBT is on board, only the hydrogenated and dehydrogenated versions of DBT itself have to be taken into account. DBT is a rather safe substance, as it has low volatility [21], low flammability [47] and is not carcinogenic [21]. Despite it being generally categorized as safe by authors [21], [25], [47], DBT forms a health hazard as it can be deadly if it is swallowed and reaches the airways, and because it may damage the unborn child [235]. Also, as DBT is a polycyclic aromatic hydrogen carbon, there is evidence that it can cause breast cancer [236].

Even though it is biodegradable [237], it is a possible environmental hazard [25] and is a long-term hazard toxic to aquatic life [235]. More exactly, there have been studies that show that DBT is very toxic to aquatic life on the long term, but not acutely toxic on the short term [238]. Of the hydrogenated version of DBT, so-called perhydrodibenzyltoluene, there is little data available [25]. No safety sheet could be found for this substance. This is mainly because DBT itself has been used as a heat transfer oil for technical applications already, thus being mature and requiring safety data sheets [234]. Safety measurements are thus still required. Therefore, DBT is a safe substance to use on ships, as long as it does not leak, as it is an environmental hazard to aquatic life.

6.2.3 HAZARD IDENTIFICATION OF LOHC: NEC

Contrary to DBT, when NEC is dehydrogenated, small byproducts are produced [25]. However, these are not discussed as only 2% of NEC degenerates and there are multiple economic and technological reasons to further limit the production of byproducts. NEC is less toxic than DBT or MDO [25], [239]. Consequently, NEC falls into the lowest toxicology level possible [239]. Nevertheless, it is classified according to GHS as a strong irritant as well as a long-term hazard toxic for aquatic life and the environment [240], [241]. The hazard assessment of [239], shows that it is not easily biodegradable (dehydrogenated NEC) to poorly biodegradable (hydrogenated NEC). There is limited information on the hydrogenated version of NEC, known as either perhydro-n-ethylcarbazole or 9-Ethyldodecahydro-1H-carbazole [242]. According to a vendor, it has to be stored in a closed container in a dry and cool place and it is an irritant [243], just like the dehydrogenated version [240]. If further hazard assessment confirms this, NEC is mainly hazardous due to its irritant, corrosive and pollutant properties, and leakage should be prevented.

6.2.4 HAZARD IDENTIFICATION OF BOROHYDRIDES

SB is considered as flammable, corrosive, acute toxic, irritant and health hazard according to the GHS symbols [133]. It is categorized as flammable due to the release of hydrogen when in contact with water, while the substance is not very flammable itself. According to the safety data sheet it is combustible but hard to ignite [244]. SB is corrosive to skin, causing severe burns [133]. However, it is not necessarily corrosive to metals. KB has a similar safety data sheet, but is in general less dangerous than SB. It is corrosive to skin, flammable (when in contact with water) and toxic for people [245]. Just like SB, it causes severe skin burns. Therefore, both the borohydrides should be stored away from people and the environment.

Spent fuel

The spent fuel of the borohydrides consists of several products [84], [246]. For SB, mainly $NaBO_2$ and $NaB(OH)_4$ remain, both of which are classified as irritant and health hazard, but only on the warning level [247], [248]. For KB, mainly KBO_2 and $KBO_2 \cdot 1/3H_2O$. KBO_2 has very similar properties to NaBO2, as it is an irritant and health hazard on the warning level [249]. Both $KBO_2 \cdot 1/3H_2O$ and $NaB(OH)_4$ split up in water, as they are salts, with the restproducts being sodium and potassium ions and $B(OH)_4^-(aq)$ (Tetrahydroxyboranuide) [246]. Tetrahydroxyburanuide, or tetrahydroxoborate, does not have a safetysheet of its own, however it has very similar properties to borax [250], which is a health hazard and is categorized as a danger in the reproductive category [251].

Thermolysis

Next to the hydrolysis of the borohydrides, they can also be thermolysed. This happens at elevated temperatures, such as temperatures occuring in a hydrogen fire. At these elevated temperatures, the borohydrides decompose in the following products [87]: sodium, boron, borol and sodium hydride. Elemental sodium, the major component, is extremely dangerous, as it is flammable and may ignite spontaneously when coming into contact with water [252]. Additionally, sodium is corrosive to human skin, causing severe burns and damage. Both pictograms are classed as 'danger' [252]. Boron, on the other hand, is only toxic if swallowed [253]. Other substances, such as sodium hydride (flammable, spontaneous ignition when contact with water) and borol (flammable, toxic, health hazard) are dangerous as well [254], [255]. The decomposition temperature of KB is 700K and that of SB is 693K [117]. Thermolysis of KBH_4 forms similar products as those of $NaBH_4$, such as potassium, boron and potassium hydride [117]. Potassium is flammable and corrosive to skin, and can, just like sodium, ignite when it comes into contact with water [256]. Potassium hydride is again very similar to sodium hydride, being flammable, ignites when in contact with water and corrosive to the skin [257].

6.2.5 HAZARD IDENTIFICATION OF AB

AB is a flammable solid (danger level) and an irritant for skin, eye and respiratory tract [258]. Hydrogen release from AB can be done in two ways, thermolysis and hydrolysis [83]. Hydrolysis is very similar to the hydrolysis of sodium and potassium borohydride and visible in equation 2.1. The boric acid formed during hydrolysis immediately ionises in water into $B(OH)_4^-$. Thermolysis starts at temperatures of 373K [134]. All in all, the following substances can be created when using AB:

- NH_4^+, ammonium (Hydrolysis reaction, relatively stable reaction)
- $B(OH)_4^-$, tetrahydroxyboranuide (Hydrolysis reaction, see SB, relatively stable reaction)
- NH_2BH_2, aminoborane, extremely unstable, oligomerises easily (Thermolysis, 100C)
- HNBH, iminoborane, extremely unstable, oligomerises easily (Thermolysis, 150C)
- Borazine (Thermolysis, result of oligomerization)

Hydrolysis

The main products of hydrolysis are NH_4^+ and $B(OH)_4^-$, the latter of which has been discussed in section 6.2.4 already. For the hydrolysis it is known that AB is relatively stable and needs a catalyst undergo dehydrogenation when it comes into contact with water, thus this might be less likely to happen [134]. Ammonium (NH_4^+) is a nitrogenous ion that is the conjugate of ammonia [259]. Dependent on the pH level of the solution, the balance of the equation goes to ammonia (high pH) or ammonium (low pH) [260]. As the sea has a general ph of 8.08 to 8.33 [261], it can be assumed that both ammonium and ammonia are present after the hydrolysis reaction. Ammonia will be discussed in more detail in section 6.2.6, as it can also be used as an alternative fuel by itself. Ammonium will be discussed here. Ammonium is commonly used in households, as cleaning agent but also for personal body hygiene [259]. Ammonium is corrosive to the eyes and causes skin irritation [259]. It causes an overabundant growth of aquatic plants, as it is a nutrient for them [260]. However, it can also become toxic when it transforms into ammonia. Ammonium itself is thus not considered to be toxic to aquatic life [259], [260].

Thermolysis

During thermolysis, dangerous gasses, such as borazine, are released, which is why hydrolysis is the most opted version of hydrogen release from AB [83], [111], [134]. However, as spontaneous thermolysis starts at 373K to 423K, it is relevant for safety purposes [134]. AB is not necessarily a stable substance due to this low thermolysis temperature. Thermolysis produces several products. The definition and accompanying names of these products of [111] are used here, which may differ from those of [262], [263]. After the first step at 373K, aminoborane is formed, but there is very limited information on this substance. However, it is mentioned to be highly reactive [111]. At 423K, aminoborane decomposes into HNBH (iminoborane) and hydrogen [111]. Iminoborane (also known as Boraneimine), BNH_2, is formed during an endothermic reaction. Both are mentioned to be similar to ethylene acetylene [111]. The final result from the thermolysis reactions, iminoborane, is thermodynamically unstable [264]. It oligomerizes easily into borazine ($H_3B_3N_3H_3$) [111], [264], [265]. Borazine is in its own a very dangerous substance, being flammable and corrosive to skin [266]. It reacts very violently with water and may ignite upon contact [266]. Thus, if the thermolysis steps were to happen, producing borazine, which in its turn can then ignite upon contact with water, triggering new thermolysis reactions and creating a positive feedback loop.

6.2.6 HAZARD IDENTIFICATION OF AMMONIA AND METHANOL

Ammonia and methanol are both widely produced and shipped all over the world [19]. Depending on the energy release mechanism, releasing energy from ammonia either produces NO_x or pure nitrogen. Ammonia is a flammable gas, although it requires preheating before ignition can occur [78]. The storage is difficult because it is gaseous at ambient conditions, corrosive to metals and skin, acutely toxic if inhaled and very toxic to aquatic life [20], [78], [126]. The first three issues are in the 'danger' category, the environmental hazard (toxicity to aquatic life) is considered to be a warning [78]. Even though ammonia is less reactive than conventional fuels, the toxicity is seen as a major issue for its use as a future fuel [126], [267]. Ammonia is usually stored under low temperature or slightly elevated pressure, so that it becomes a liquid. This way of storing it can cause dangerous, toxic clouds, which spread over a large area [126]. Another issue is that this toxic cloud can come into contact with water, resulting in the formation of a layer of toxic NH_4OH [184]. Thus the toxicity of ammonia is a major issue.

Methanol is a volatile substance and liquid under ambient conditions [184]. It is extremely flammable and can combust under ambient conditions [268]. Additionally, it can drop down to the source of its ignition and ignite again [184], [268], because it is heavier than air. Furthermore, methanol burns invisible, making it hard to detect in bright daylight [268]. Furthermore, methanol is acutely toxic and a health hazard [268]. It should not be touched as it is toxic in contact with the skin. If swallowed or inhaled, it also causes damage to organs and low exposure over the long term is dangerous [268]. For marine life, on the other hand, methanol is not classified by GHS as toxic [268].

6.2.7 OVERVIEW OF HAZARDS OF THE HYDROGEN CARRIERS AND REFERENCE FUELS BASED ON THE GHS SYSTEM

Table 6.1 gives an overview of the known GHS symbols of the hydrogen carriers. Hydrogenated and dehydrogenated versions of the carriers are taken into account.

Table 6.1: GHS categories for hydrogen carriers, ammonia, methanol and MDO. "D" stands for "Danger" which implies a more severe form of that said hazard than a "W". L is the lowest category, implying only a label has to be used, with no additional warning or danger marking [233]. It should be noted that only one of them can appear, always the most dangerous one is chosen. * is a hazard that occurs when in contact with water, ∧ when the substance has been thermolysed.

Hazard Class	**DBT**	**NEC**	**SB**	**KB**	**AB**	NH_3	**MeOH**	**MDO**
Flammable			D*	D*	D		D	
Acute Toxic			D	D	D*	D	D	D
Health Hazard	D		D	D*	D*		D	D
Corrosive to skin			D	D	W*/D^	D		
Irritant		W	W	W*	W			W
Environmental Hazard	W				W*	W		L

It should be noted here that even though MDO is categorised as flammable in the fourth category, this is not classified as a hazard in the GHS system [269]. Table 6.1 gives the danger and warning levels as advised by [233]. It can be seen from the table that the LOHCs have the least hazards and the borohydrides (and AB) have the most hazards.

The results of Table 6.1 can also be shown graphically. This way it becomes immediately clear which substances have similar properties. Figure 6.1 shows these. In this figure, all dangers and warnings are taken into account, including those that only occur when the substance is in contact with water or heated. This means that Figure 6.1 shows the worst-case scenario of all substances. It should be noted here again that this is a qualitative figure, as this chapter only looks at potential consequences. Figure 6.1 shows that MDO has a large amount of safety hazards. It can also be seen that methanol follows the same pattern as MDO for acute toxicity and health hazards. AB touches all possible limits in the chart, as environmental hazard and irritant only have the warning level, making it clearly the most dangerous substance. The borohydrides follow the exact same pattern, because the reactions with water

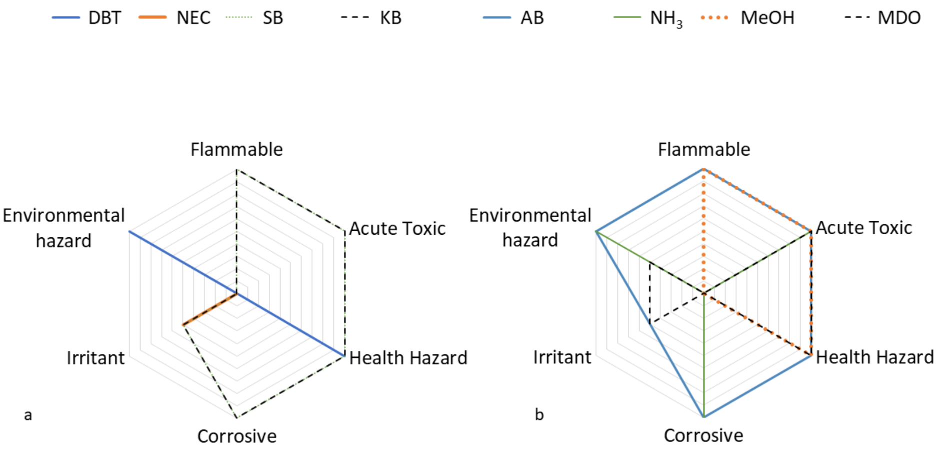

Figure 6.1: (a) spiderweb of safety hazards of LOHCs (DBT and NEC) and borohydrides (SB and KB); (b) spiderweb of safety hazards of AB (NH_3BH_3), ammonia, methanol and MDO

are also taken into account. Comparing this to Figure 6.1a, it can be seen that there only the borohydrides are corrosive to skin.

6.2.8 GENERAL HYDROGEN CARRIER HAZARDS

Besides the specific hazards discussed above, several general hazards exist due to the presence of hydrogen, of which two will be covered. First, as all considered fuels are able to release hydrogen (including methanol and ammonia through cracking), hydrogen fires present a substantial danger. Second, substances that are released in the air, for example in the case of a hydrogen fire, can extend the affected area far beyond the boundaries of a ship.

Hazard of hydrogen fire and explosion

When hydrogen is released, it can easily ignite, because of its broad flammability range of 4 to 75% [270]. Historically, the main cause of incidents involving hydrogen are mechanical failures, which can result in several reactions: jet fires, flash fires, explosions and atmospheric dispersion [271]. Ignition usually results in a jet flame, which is a long flame from the point of ignition that can even occur after an initial explosion [272], [273]. A flash fire is a fire without an explosion, which is started by an external ignition source [272], [274]. Such fires are likely to happen when liquid hydrogen is spilled [231] and its main property is a flame that travels back to the leak [274].

A considerable hazard of hydrogen is its explosive properties. These have been studied well, especially under practical circumstances, using liquid or pressurised hydrogen [231], [270], [271], [272], [274]. [231] found a realistic and conservative relation between the size of the fireball and the mass of hydrogen involved:

$$D_{hmsc,c} = 19.5 \times m_{H2}^{1/3}, \tag{6.1}$$

with $D_{hmsc,c}$ the diameter of a hydrogen fireball in meters and m_{H2} the mass of the hydrogen involved in kilograms. This equation shows that already small amounts of hydrogen can cause very big fireballs. Due to the very low density of hydrogen, these fireballs are almost never completely circular and the hydrogen can travel rather far before ignition (up to 30 meters from the source)[231], [275].

The detonation limit of hydrogen is 18.3-59% and explosions mostly occur due to over-pressure in concealed spaces. Possible reason for over-pressures are the expansion of cryogenic hydrogen after vaporizing (850 times increase) and poorly handled compressed hydrogen [276]. Venting is often used as a solution, but according to [277], the explosion peak over-pressure only decreases with larger vent sizes. Regarding the size of explosion, a study by [278] on the fukushima accident investigated the increase in damage 30 meters from the reactor core for larger amounts of hydrogen. They showed the pressure wave from 10kg of hydrogen results in minor structural damage, 80kg results in major structural damage and 200kg could result in partial demolition. An example of damage closer to the detonation is given by [270], who studied a hydrogen explosion in an ammonia plant. In this case, 10-20kg of hydrogen was discharged and only about 3.5-7kg of exploded. Nevertheless, this still resulted in concrete blocks weighing 1.2 metric tons being moved up to 16 meters [270].

Despite the power of the explosion, the heat flux is limited. For example, [231] shows that for a tank rupture test (35.7MPa, 1.64kg of hydrogen), the first-degree burn exposure (with the marker ‘pain’), is only 5 meters, with an exposure time of 2.8s. Despite the fact that hydrogen has an adiabatic flame temperature of 2403 K, this exposure is not enough to cause second (or even third) degree burns [231]. Consequently, even though hydrogen explosions have high power, their thermal doses are low, meaning the explosions are the most dangerous on the ship.

Aerosol hazard identification

For a substance to become dangerous outside the vessel boundaries, it would have to be either propelled away by an explosion, or be in the form of aerosols or other small particles. These are able to become "airborne", or spreading through the air by following air flows [279]. The exact size, density and humidity of the droplet are important parameters defining the spread [279]. For example, [279] showed that droplets with diameters smaller than 10 micrometers could be more dangerous than larger ones, as these stay in the air for longer periods of time, while droplets with diameters of 10 and 20 micrometers fell down after about 350 seconds. Besides this, small droplets can also spread rapidly, covering several meters in a matter of seconds. This principle is visualized in Figure 6.2, where different sized particles where released from the same location and simulated over 35 seconds. This confirms that substances which form particles smaller than approximately 10 micrometers, have a danger of becoming airborne, which could result in travel over large distances. This airborne hazard is relevant for cryogenic fuels, which create vapour clouds after spillage, and ammonia, which creates toxic ammonia clouds when a substantial amount comes into contact with water [19]. Consequently, it is evident that not only local effects, within the boundary of the ship, should be taken into account for these fuels.

6.3 CURRENT SAFETY APPROACH IN THE MARITIME INDUSTRY

This chapter investigates the current maritime regulations and guidelines to understand the influence of the chemical properties on the design of and the application on ships. The main philosophies and regulating structures are discussed to provide a better understanding on the origin and approach of safety regulations. The IMO is the main international organisation with regards to the regulation of international shipping and navigation for safety,

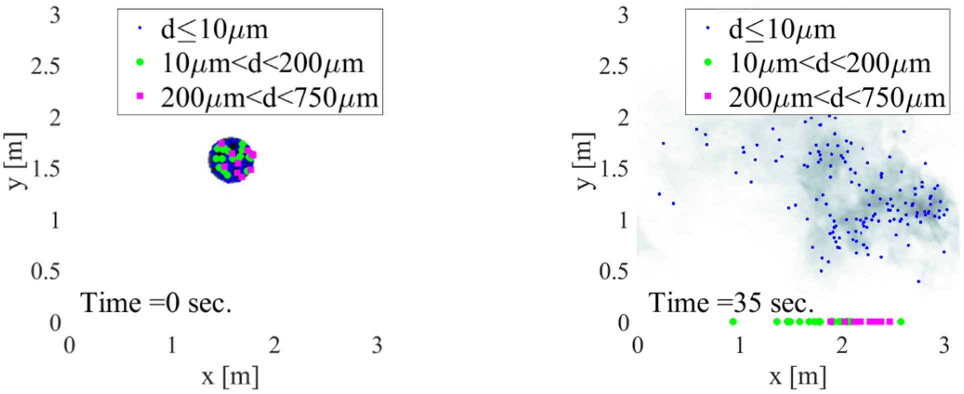

Figure 6.2: Flow of droplets over time, fluctuation level 0.05m/s RMS for three different droplet sizes, own work with use of DNSLab [280]

for vessel-source pollution, and for maritime security purposes. In this chapter, the IMO conventions and guidelines are used to determine how safety is currently defined onboard ships. Safety has been categorised in the following three safety aspects: First of all, the safety of life on board, such as safety of the crew and passengers. Secondly, there is the safety of the ship itself, the structural integrity of the ship. The third and final point is the safety of the ecosystem surrounding the ship. The surroundings of the ship are here defined as the area which a fuel (spill) can influence. Section 6.3.1 discusses the regulations regarding these safety aspects. Another categorisation can be made based on the regulation philosophy: prescriptive standards versus goal-based standards, the latter described in section 6.3.2.

6.3.1 IMO SAFETY REGULATIONS

The three before-mentioned safety aspects, of life on board, of the ship itself and of the ecosystem surrounding the ship, are covered in a range of conventions and regulations. Historically, these rules are based on incidents and written from a prescriptive perspective. For example, the international convention for the safety of life at sea (SOLAS) was adopted in 1914, motivated by the Titanic disaster in 1912 [281]. The first aspect, safety of life of crew members and passengers, is an inherent goal of convention SOLAS, which covers minimum prescriptive standards for construction, equipment and operations of ships [282]. In SOLAS, safety is defined as “protection from danger, risk or injury, in the context of non-intentional events, such as accidents or events cause by human error"[283]. Furthermore, the maritime labour convention (MLC) determines “the minimum working and living standards for all seafarers on those ships” [284]. The MLC, the authority on occupational safety, has defined a hazard as the inherent potential to cause injury, harm or damage to a seafarer’s health. This includes many sources, for example intrinsic (chemical) properties, situations, potential energy, the environment or human influence. Passenger safety, on the other hand, is mainly focused on communicating the relevant SOLAS requirements effectively to passengers [285]. For example, on passenger ships (ships designed to carry over 12 passengers), the regulatory safety aspects most relevant to crew are the general fire fighting system and the possible escape routes in case of a casualty [286]. Therefore, passenger safety does not seem to be directly influenced by chemical properties of potential fuels within a regulatory perspective.

The second safety aspect, ship safety and structural integrity, is part of the international code of safety for ships using gases or other low-flashpoint fuel (the IGF Code). The goal of this code is “to provide criteria for the arrangement and installation of machinery for propulsion and auxiliary purposes, using natural gas as fuel, which will have an equivalent level of integrity in terms of safety, reliability and dependability as that which can be achieved with a new and comparable conventional oil fuelled main and auxiliary machinery” [287]. The current IGF code is primarily prescriptive, even though a goal-based approach is followed. It has been amended using interim guidelines for alcohol fuels [288], while ammonia and hydrogen are still in the progress of being added [289]. Therefore, it is not yet applicable to all alternative fuels. Most importantly, it is only applicable to more prevalent alternative fuels, but not to the hydrogen carriers.

The main convention on environmental safety is the international convention for the prevention of pollution from ships (MARPOL) [290]. It applies to two different situations: during daily operation and in case of pollution by incidental causes. The Annexes of MARPOL mainly focus on water pollution, such as pollution by oil, noxious liquid substances, harmful substances carried by sea, sewage and garbage. Annex VI, however, aims to prevent air pollution, limiting GHG, SO_x, NO_x and particulate matter emissions.

As mentioned in section 6.2.8, aerosols with a small diameter can spread over significant areas depending on the wind speeds. This is only a risk for fuels that are gaseous at ambient conditions and have lower or similar densities compared to air [184]. Therefore, ammonia is the only fuel discussed in this study for which this risk applies. IMO considers the toxicity one of the key safety aspects in using ammonia, posing dangers for both life on board and nearby personnel [291].

6.3.2 GOAL-BASED STANDARDS (GBS)

MSC introduced a goal-based philosophy into the SOLAS Convention in 2002 [292]. The goal-based design approach aims to provide greater freedom in developing technical solutions and accommodating different standards. Goal-based regulation does not specify the means of achieving compliance but sets goals that allow alternative ways of achieving compliance in contrary to conventional 'prescriptive' standards [293]. A five-tier system was introduced to develop the GBS of which the first three (goals, functional requirements and verification of compliance criteria) are performed by IMO. Classification societies and industry are responsible for the fourth and fifth tier, respectively. This creates a responsibility distribution amongst all parties involved in safe and future-proof shipping.

The main goal of tier I is applicable to all new ships and as follows: "ships are to be designed and constructed for a specified design life to be safe and environmentally friendly..." [294]. Within Tier 1 of the GBS, the following objective relate directly to safety [294]:

1. Safe and environmentally friendly means that the ship shall have adequate strength, integrity and stability to minimize the risk of loss of the ship or pollution to the marine environment due to structural failure, including collapse, resulting in flooding or loss of watertight integrity.
2. Environmentally friendly also includes the ship being constructed of materials for environmentally acceptable dismantling and recycling.
3. Safety also includes the ship's structure being arranged to provide for safe access, escape, inspection and proper maintenance.

6.3.3 IMPLICATIONS OF IMO SAFETY REGULATIONS ON HYDROGEN CARRIERS

The IMO has recognised two main codes that deal with the safety of gas and low flash-point substances as cargo (IGC) and fuels (IGF). However, as shown for LNG by [295], codes like these often take many years to be adopted, while safety rules lack clear technical justification or limit application. Furthermore, as these codes focus on the application to specific substances, some hydrogen carriers are not covered. Therefore, the MSC, the IMO committee that creates legislation in the field of maritime safety and security [296], has approved 'Interim Guidelines for the safety of ships using fuel cell power installations'. This guideline states that safety, reliability and dependability of alternative fuels should be in line with general conventions [297].

Classification societies play a crucial role in the maritime industry by converting codes such as the IGC and the IGF into prescriptive rules, as well as overseeing compliance. Notably, some classification societies have recently published rules designed to provide guidance for alternative fuels like LNG, ammonia, and methanol [298], [299]. However, it should be emphasized that these regulations are not yet universally applicable to all hydrogen carriers.

Upon a thorough analysis of the current IMO regulations and conventions, it is evident that numerous safety aspects have been addressed based on lessons learned by past incidents. Serious steps have been made towards GBS, slowly moving away from prescriptive standards. However, the definition of safety for life on board, structural integrity and ecology remains somewhat elusive. The regulations are either not applicable on hydrogen carriers (prescriptive) or very broad (GBS). As such, the context in which alternative fuels such as hydrogen carriers are to be integrated into remains not strictly defined.

6.4 INFLUENCE OF HAZARDS ON THE APPROACH TO SAFETY ON SHIPS

In this section the connection between hazards and on board applications will be made, categorised in line with the previously introduced IMO safety aspects (ecological, public health, crew and ship). Potential mitigation strategies are not taken into account, as these can be major design choices. Public health is not included in this section, as its only applicable to one fuel, ammonia.

In this section the identified safety aspects as described in section 6.2 are categorised in the context of application onboard ships. Section 6.4.1 goes over the application of safety hazards that specifically influence the life onboard ships. Section 6.4.2 looks at the influence of safety hazards on the structural integrity of ships and section 6.4.3 regards the influence of the substances on the (aquatic) environment.

6.4.1 POSSIBLE INFLUENCE OF ALTERNATIVE FUELS ON LIFE ON BOARD

As mentioned in section 6.3.1, there are differences between the safety aspects of life of crew and passengers. For passengers, there are additional requirements regarding communication. The safety of all life on board is related to hazards, as these can cause injury or damage to health. Current fuels like MDO are already dangerous substances. Figure 6.3 shows a comparison of the hazards when compared to MDO.

All substances that are labeled corrosive are corrosive to the human skin, as can be seen in section 6.2. As visualized in Figure 6.3, some fuels have similar hazards, such as DBT, SB, KB and the products of hydrolysis of AB: boric acid and borax. The latter is also a rest product of hydrolysis of SB and KB. These substances are all capable of possible damage to the fertility or the unborn child. However, it is not clearly defined what this GHS statement means. This is problematic, as impact on reproductivity and pregnancies can be impacted even after exposure and the impact of chemicals on women is less known [300]. For example, the international labor organization (ILO) protects women that are pregnant or nursing by requiring measurements to ensure the workplace is safe [300]. This would most likely mean additional measurements for DBT, SB, KB and AB.

It can be seen that there are three substances on a similar safety level to the health of the crew compared to MDO. These are DBT, NEC and Methanol, which will be discussed here first. Ammonia follows and after that the borohydrides will be discussed as they have similar properties. Lastly AB is discussed.

Methanol and LOHCs DBT and NEC

Methanol has a similar acute toxicity and level of general health hazard compared to MDO. Even the exact health hazards are very similar, namely both

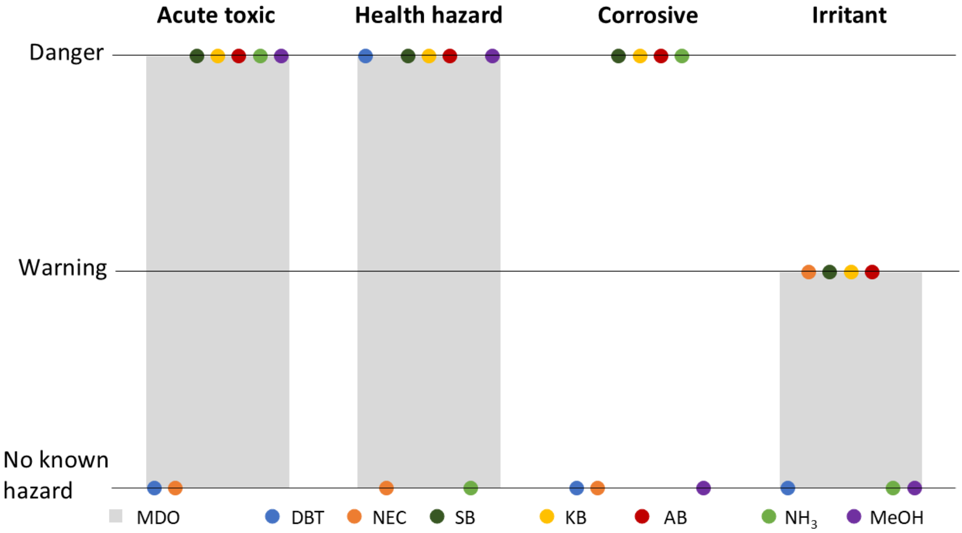

Figure 6.3: Danger and warning levels of alternative fuels relevant for the health of crew and passengers, compared to those of MDO

should not be swallowed or inhaled and cause skin irritation. Additionally, both cause damage to the organs. The main difference here is that MDO is also suspected of causing cancer, so methanol is less hazardous to life.

DBT and NEC are both less hazardous to life than MDO, since NEC only is a strong irritant. The main difference between the irritant properties of NEC and MDO is that NEC also causes eye irritation. NEC causes skin irritation and may cause respiratory irritation, but does not seem to be harmful if swallowed [240], [242]. As these irritation levels are only on warning level, NEC can be categorized as more safe to the crew of the ship than MDO. DBT is slightly more hazardous to the crew than NEC, as it poses a health hazard on danger level. This is because DBT may be fatal if swallowed, which is the same warning as MDO (H304). Additionally, as DBT can endanger the unborn child [235], while MDO does not have this warning. However, DBT is not considered acutely toxic or an irritant, making it in general more safe to the crew, especially if they are all male. This would mean that the above-mentioned three fuels are very likely to comply with the regulations of the MLC, as the hazards are less than those of MDO.

Borohydrides

A substance that scores a "danger" hazard on all levels is SB [133]. This is because it is extremely corrosive to the skin but also acutely toxic when swallowed. Additionally, it may damage fertility or the unborn child, which thus causes a health hazard. This substance should thus not come into contact with the crew of the ship at all. Unlike the other substances mentioned previously, SB is a powder and thus less likely to move around through the air on the ground. This, combined with the fact that it is only dangerous when touched or swallowed, results in that in the event of a spill, SB is less likely to pose a danger to the crew than ammonia (which can spread freely, being a gas at ambient conditions). Thus, a SB spill will be dangerous for the crew locally, but most likely less dangerous for passengers on board. KB has the same properties for acute toxicity and corrosiveness to skin, but it only becomes a health hazard and an irritant when it comes into contact with water. This is due to the formation of potassium metaborate and borax, which are a health hazard to the unborn child [249], [251]. Additionally, potassium metaborate is an irritant, but only on the warning level, as it causes eye irritation [249]. Thus, KB is in the end less hazardous than SB.

AB

AB only has a warning for being an irritant, so it should not be swallowed, touched or inhaled [258]. In itself, AB can thus be considered as less hazardous than MDO, as MDO is classified as warning in the hazard class irritant and also being dangerous in acute toxic and health hazard class. However, AB does become extremely dangerous when in contact with water, as it produces ammonia [111]. However, this reaction is considered to be relatively stable and requires catalysts [134]. But when this happens, AB forms ammonia as well as borax, which have been mentioned previously. Another danger is that AB can decompose under elevated temperatures (up to 423K). This results in the compound borazine. Borazine is corrosive to skin on a danger level [266]. To sum this up, AB itself is less hazardous than MDO. However, when heated, it becomes corrosive to skin (which MDO is not) and when in contact with water it becomes an irritant, health hazard and acutely toxic due to the formation of ammonia and borax.

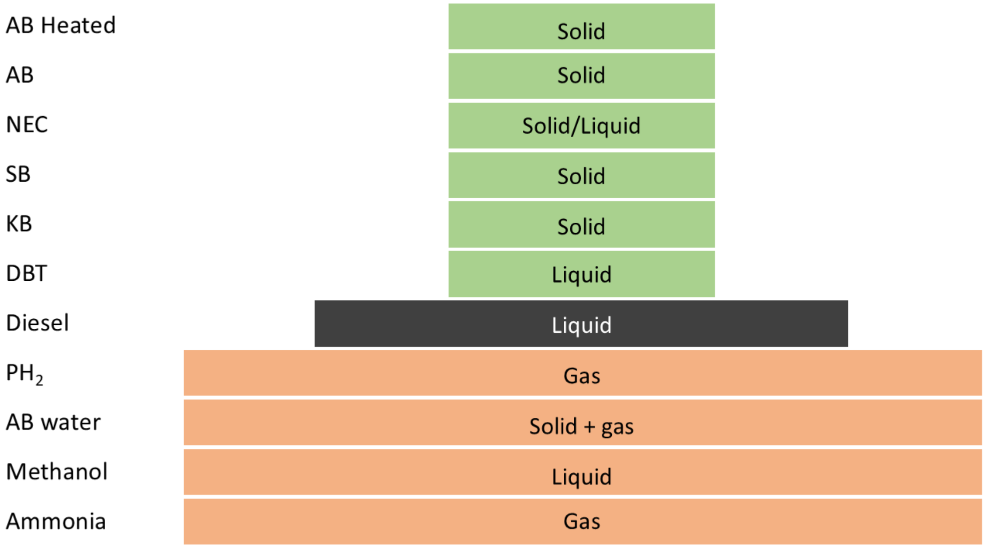

Figure 6.4: Qualitative comparison of hazards accompanied by future fuels and MDO relevant for the safety of crew and passengers. Here, only hazards are taken into account, no probabilities or resulting risks. Because of the different behaviour of substances due to their state, the state is taken into account

Ammonia

Ammonia is widely known that to be acutely toxic at inhalation [78], [126], [267]. Besides this, it is only classified as corrosive to the human skin [78]. Because of the few, but dangerous hazards, ammonia is hard to compare to MDO. Both have different hazards influencing human health and both may lead to death if entering the airways [78], [269]. MDO has additional hazards, such as health hazards, which ammonia does not have. This does not, however, make ammonia more safe than MDO. The hazards are expressed differently, as the risks are different. Additionally, ammonia is usually stored under slightly lower temperature than ambient conditions (240K), or 10 bar atmospheric [20], [184]. Because of this low temperature, ammonia can cause frostbite [301]. All of this combined it is expected that the MLC will require certain measures to mitigate the risk that ammonia poses to the crew on board, as having ammonia on board is dangerous for the crew and passengers.

The above-mentioned hazards related to life on board are summarized in Figure 6.4. Because of the large differences between AB and its reaction products, this is split up in three types. It should again be noted that this is a qualitative assessment and the numbers are arbitrary, it should only give a comparison compared to each other and to MDO.

6.4.2 POSSIBLE INFLUENCE OF ALTERNATIVE FUELS ON SHIP STRUCTURAL INTEGRITY

The functional safety and safety aspects regarding structural integrity of the ship are influenced by two GHS aspects of the hydrogen carriers studied: flammability and hydrogen explosions. Within GHS [232], flammability is (almost) always considered a hazard of danger level instead of a warning level. Two fuels are flammable without additional requirements: AB and methanol. Methanol burns with an invisible flame, resulting in additional the requirement of additional detection equipment. Therefore, only AB forms a direct threat to ship integrity based on it's flammability properties. Since conventional fuels share the same flammability properties, fire on board is a threat well-considered and included in IMO Conventions. Additionally, SB and KB also have flammable properties when in contact with water due to the release of hydrogen. The quantity of hydrogen released without a catalyst is limited, but still to be considered onboard ships. Finally, influence of hydrogen carriers in general on materials still have to be researched.

It is trivial that hydrogen is present at one stage in the process since it must be extracted from hydrogen carriers. Therefore, hazards related to hydrogen are applicable to all hydrogen carriers considered. One of these hazards has been mentioned in detail in section 6.2.8. Other hazards, such as permeation and the influence of hydrogen on other materials, are recommended for further research.

6.4.3 POSSIBLE INFLUENCE OF ALTERNATIVE FUELS ON THE ENVIRONMENT

Environmental hazards are always considered as a warning level threat instead of a danger level threat. It is also possible for environmental hazards to only have a pictogram, without a signal word [232]. The four fuels that, according to literature, pose a threat to the environment are DBT, AB, ammonia and MDO, with AB only after contact with water. DBT forms a hazard in the long term only, as it is extremely toxic to aquatic life in the long term. It is not persistent, with a high biodegradability. NEC on the other hand, is not biodegradable, but is also thought to be not acutely toxic. The exact consequence of this persistence is still to be studied, but there is a common understanding that it causes an environmental hazard. Especially when compared to MDO, this poses different hazards, as MDO is biodegradable [239]. AB is only toxic to aquatic life if it hydrolyzes, as then ammonia is released. Hydrolysis cannot be excluded here as it is likely to happen over time, despite AB being relatively stable in water. Ammonia is not only toxic to humans, but also to aquatic life. Moreover, contrary to conventional fuels, it cannot be flared to remove it from a marine environment. Similarly, AB cannot be flared because it is highly soluble in water and thus will not ignite despite its high flammability. Thus, it is hard to compare the effect on the aquatic environment due to the different types of effects of the alternative fuels. MARPOL [290] has appendices on oil spillage, which forms the main threat for environment by MDO. The spillage of ammonia, DBT and NEC is not mentioned in MARPOL as a risk to environment [302]. This shows that MARPOL has the potential to improve in the area concerning alternative fuels.

6.5 CONCLUSION

The discussed hydrogen carriers cannot be called safe by definition based on their GHS classifications as defined in chapter 6.2. Moreover, the safety of hydrogen carriers is not fully integrated in the IMO safety framework. The integration of the hydrogen carrier chemical safety with the maritime safety approach is limited due to the following characteristics. First, the maritime safety definition often lacks technical justification and the chemical safety categorisation is non-explicit. Therefore, matching these definitions induces an even greater level of uncertainty causing a fully subjective ranking of hydrogen carriers on their maritime safety level. The GHS classifications are quantitative, with only three classes: nothing, warning or danger. Even though these classifications are based on underlying criteria, these criteria are still divided in four hazard levels. The IMO classification of safety is found to be even more ambiguous, with either qualitative and abstract goal-based standards or prescriptive standards solely based on common practice with fossil fuels. This combination makes it challenging to assess hydrogen carriers

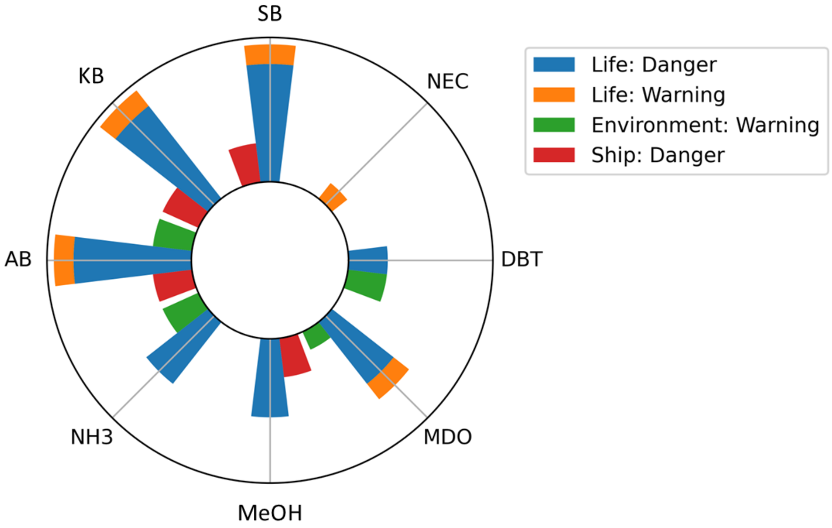

Figure 6.5: An overview of the alternative fuels and their hazards based on the three major focal points: life of on board (life), structural integrity of the ship (ship) and the aquatic environmental impact (environment), including the dangers and warnings stacked together. The bar height is based on the number of hazards per category, with D having more weight than W

on their safety level within a maritime context. It is noteworthy that MDO is also categorised as danger for multiple GHS labels. An attempt to connect the GHS labels to the three previously mentioned maritime safety aspects is shown in Figure 6.5. The three aspects are respectively safety of life on board, safety of ship structural integrity and safety of ecology. The "Warning" and "Danger" values are in line with Table 6.1.

Overall, it cannot be said that there is one hydrogen carrier that is the safest. The only real conclusion that can be made is whether substances have or have no influence on the certain safety aspects, but even this conclusion can change with design and mitigation.

6.5.1 DISCUSSION AND FURTHER RESEARCH

In order to draw strong conclusions on which hydrogen carriers are safer than others, future research should focus on ways of comparing qualitative safety values as well on mitigative or preventative measures. There are several frameworks of comparing qualitative and quantitative values to guide designers in making decisions when values may conflict or are hard to measure, as shown by [303]. Chapter 9 builds on this by examining safety-based values and their trade-offs. Comparing these strategies can lead to a clearer prioritisation of values within a maritime context.

Safety & Sustainability

7

MARITIME SAFETY HAZARDS

AN EXPERIMENTAL AND THEORETICAL PERSPECTIVE

> *"Fisken kom først. Mennesket er bare en*
> *seiglivet gjest ved havet"**
> — Roy Jacobsen, *Hvitt Hav*

CHAPTER SUMMARY

This chapter provides an experimental and theoretical perspective on safety hazards specific to the maritime world. The influence of impacts on ships (possibly causing spills or a fire) are evaluated. All four hydrogen carriers are evaluated on their spill behaviour, starting from a theoretical point of view (spill into the ocean, a fire and the results of a fire spilled into the ocean).

It is discovered that spent fuel of boron-based carriers can possibly act as a fire retardant, while the fuel itself will strongly increase the heat of a fire. Next, the spill behaviour of the hydrogen carriers is experimentally assessed. SB releases hydrogen faster in seawater than in fresh water; AB does not release hydrogen at all. The persistence of LOHCs in combination with them being extremely hard to detect, may be problematic in case of a spill.

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*The fish came first. Humans are just a tenacious guest by the sea.

7.1 INTRODUCTION

The previous chapter examined the specific safety hazards of each hydrogen carrier. Given that many hydrogen carriers are relatively under-researched substances, complete hazard identification cannot be achieved. Additionally, the level of safety testing and characterisation varies significantly across different carriers; some have been thoroughly investigated, while others have substantial data gaps. This uneven research coverage results in an incomplete hazard database. This lack of hazard data is problematic; it might be the reason a substance is chosen, even though it is not a large improvement over the current status, whilst substances may not be chosen despite having a large improvement over the current status. A lack of hazard data is therefore one of the five causes of so-called regrettable substitutions: substitutions of chemicals that do not come with a large improvement [304]. Time limitations and insufficient laboratory equipment are a major reason for this lack of data [304].

The previous chapter mentions many of the hazards that are mapped in great detail; these are the hazards that the GHS is based on. However, not all of these hazards have been examined within a maritime context. Maritime operations face inherent risks from both accidental fuel release and physical impact events. Recent years have seen increased collision risks from various sources, including deliberate attacks, vessel-to-vessel collisions, and encounters with natural obstacles like icebergs. These events can result in hull breaches, fires, and significant fuel spillage, making it essential to understand how alternative fuels behave under such conditions. This chapter examines the specific hazards applicable to hydrogen carrier use aboard ships, focusing on two critical scenarios: fuel spills and physical impact events. The objective

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The content of this chapter is based on the following articles:
E. S. van Rheenen, A. A. Kana, J. T. Padding, and K. Visser, “Solid hydrogen carriers as an Alternative Fuel and Impact Damper,” in Proceedings of the International Naval Engineering Conference (INEC), IMarEST, 2024.
E. S. van Rheenen, K. Visser, A. A. Kana, and J. T. Padding, “Spill Behaviour of Hydrogen Carriers as Alternative Fuels for Ships,” in Proc. 10th World Congress on Civil, Structural, and Environmental Engineering, CSEE 2025, H. El Naggar, J. Barros, and P. Cachim, Eds. Avestia Publishing, 2025.
and on the work of the ’BEP group’ of E.C. Vassis, M.K. Meerveld, M.J. Jonker, R.R.J. Doekers and T.A. Sluimer, "HET GEDRAG VAN LOHC’S IN ZEEWATER", 2025

is to analyse the consequences of both large-scale spills and impact incidents, recognising that impact events may subsequently lead to significant spillage.

7.1.1 FUEL SPILLS

Currently, post-Panamax ships can use up to 20,000 m^3 of fuel, and Panamax container ships and large cruise ships can use up to 7500 m^3 [305]. Even an inland tank barge (90 m long) can carry up to 4500 m^3 [305]. When using hydrogen carriers, these tanks can be up to 4 times larger to accommodate the same amount of energy [137]. The potential for fuel spills is thus significant, and the use of chemicals as fuels shifts the risk from relatively small-scale contamination to the potential for large-scale, unpredictable spills, which can cause catastrophic damage [306]. For instance, the Prestige oil spill resulted in 66% less species richness in specific locations, and these types of effects can persist up to 40 years after the incident [306], [307]. Moreover, such spills can have significant socio-economic effects. Unlike oil spills, the behaviour and impact of chemical spills are poorly understood and little documented. Additionally, maritime spills especially have the issue of social amplification, resulting in a skewed public view of marine pollution issues [306].

Critical parameters such as the predicted no-effect concentration (PNEC) and the GESAMP (Group of Experts on the Scientific Aspects of Marine Environmental Protection) hazard rating and persistence, bioaccumulation, and acute toxicity (PBT) are essential for evaluating spill hazards. However, these ratings do not predict how a substance behaves during a spill. Despite the OPRC-HNS (Protocol on Preparedness, Response and Co-operation to pollution Incidents by Hazardous and Noxious Substances) protocol of the IMO (in force) [308] and the HNS (Hazardous and Noxious Substances) convention (not in force) [309], the field of chemical spill treatment at sea remains underdeveloped, as highlighted in a white paper that discusses the dangers of HNS spills and compares them to oil spills [310].

Understanding the behaviour of the spilt chemical in the sea is of utmost importance, yet it remains to be discovered for all four above-mentioned hydrogen carriers. Existing classifications are usually based on laboratory data, in which factors in the maritime environment, such as wind and sun, as well as the salinity of seawater, are not considered [311]. Notably, in situ results incorporating environmental influences can differ significantly from laboratory outcomes [311]. This chapter addresses this gap through seawater-based laboratory testing, offering improved insights into hydrogen carrier behaviour under conditions that more closely represent maritime environments.

7.1.2 IMPACT

While solid hydrogen carriers themselves cannot prevent ships from sinking, their properties may offer potential safety advantages in the event of collisions. When stored within a ship's hull, these carriers may dampen the impact of a collision. The powdery nature of the hydrogen carrier could potentially solidify and even plug any resulting holes, reducing the release of the fuel through the hole. Additionally, some of these chemicals may have flame-retardant properties, potentially reducing large-scale fires. Finally, solid hydrogen carriers could minimize fuel loss compared to liquid alternatives. These characteristics suggest that solid hydrogen carriers may offer improved safety compared to conventional fuels like diesel or other liquid alternatives like methanol.

7.2 METHOD

Understanding hydrogen carrier behaviour in maritime scenarios requires a systematic approach, beginning with fundamental safety assessments. An initial literature review is essential to establish baseline safety parameters before progressing to experimental investigation. This chapter focuses on achievable experimental work within available constraints; spill behaviour testing was conducted using accessible substances and facilities, whilst impact analysis relied primarily on theoretical examination due to both the unavailability of a sufficiently large quantity of material and the complex experimental requirements for impact testing.

This method section is divided into three parts. Section 7.2.1 outlines the theoretical approach for assessing boron-based solid hydrogen carriers as impact-damping systems. Simple spill behaviour was tested in a lab setting. The method with which used to evaluate simple spill behaviour is discussed in section 7.2.2. As certain hydrogen carriers produce hydrogen during spills, extended tests were not possible in the labs available for this research. However, for those hydrogen carriers not producing hydrogen during spills, together with a group of Bachelor students, I was able to build a test setting mimicking waves. This is all discussed in section 7.2.3.

7.2.1 THEORETICAL RESEARCH - SOLID HYDROGEN CARRIERS

An approach based on chemical reactions is proposed to investigate the possible usage of solid hydrogen carriers as impact dampeners. The influence of heat, water and a combination of heat and water on the hydrogen carriers is investigated. The likelihood of reaching relevant temperatures depends on possible environmental conditions and is not taken into account in this chapter. However, the likely consequences of these impacts on hydrogen carriers are investigated. The mentioned hydrogen carriers are all circular in nature. Their empty fuel, called spent fuel, has to be stored on board and discharged and regenerated at a shore facility to enable renewable use. Thus, the ship will additionally carry the spent fuel of each of the carriers. The composition of the spent fuel depends on the reaction required to release the hydrogen. Both hydrogen carriers will release hydrogen through hydrolysis. For AB, the reaction is as follows:

$$\mathrm{NH_3BH_3} + 3\mathrm{H_2O} \rightarrow 3\mathrm{H_2} + \mathrm{B(OH)_3} + \mathrm{NH_3} \tag{7.1}$$

The spent fuel will thus be $B(OH)_3$, which can possibly be stored in the same tanks as the original fuels. Thus, the spent fuel must also be investigated. For SB, a similar reaction is regarded:

$$\mathrm{NaBH_4} + (2+x)\mathrm{H_2O} \rightarrow 4\mathrm{H_2} + \mathrm{NaBO_2}.x\mathrm{H_2O} \tag{7.2}$$

In this case, the spent fuel consists of $NaBO_2.xH_2O$. The x here depends on the exact temperature at which the spent fuel is removed from the solution through crystallisation and possibly additional dehydration steps [159]. To reduce weight, the x should be as small as possible. The resulting calculated weights of the spent fuel are given in table 7.1.

Thus, both the original fuel and the spent fuel will be investigated as to their chemical reaction to heat, water and a combination of heat and water. The final scenario considers a flash heat source, followed by water contact with the products. What would happen without heat and water, with just a lack of confinement from the fuel tank, is not part of this study. Figure 7.1 shows the pathway of the chemical reaction paths that will be investigated in this study.

Table 7.1: Relation of x in equation 7.2 and weight of spent fuel

x	Weight of spent fuel [kg] per kg SB
0	1.73
2	2.69
4	3.64

This research will focus on the chemical reactions and the results of these reactions. Many of these chemical processes are step-wise processes. Some of these steps are exothermic and thus self-sustaining. This can potentially cause unwanted runaway reactions. Endothermic reactions, on the other hand, absorb energy and will stop once the initial energy source disappears. When considering products derived from these reactions, it's important to factor in their corrosive properties and typical applications. These substances may have undesired properties, such as high toxicity or flammability. Gases present greater challenges than solids because of their tendency to disperse readily, potentially reaching undesired areas.

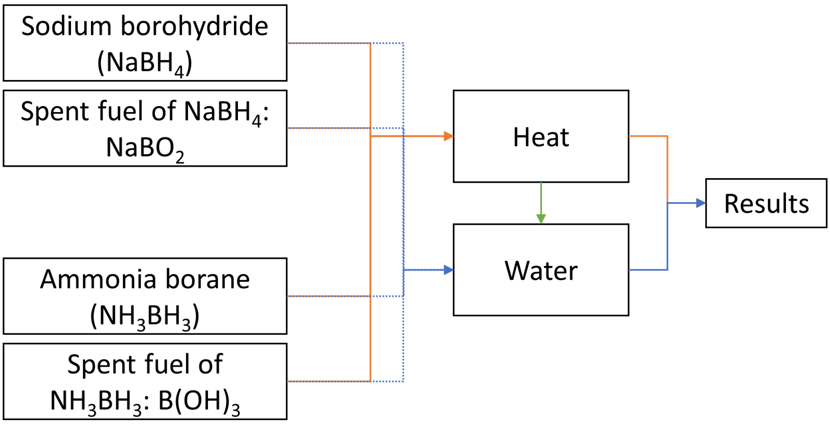


Figure 7.1: Overview of pathway to gain resulting chemical products for analysis in results

The substances formed will be evaluated based on their subsequent influence on the ship itself and the impact on the passengers and the environment. It is hard to quantify dangers exactly, especially as consequences depend

Substance	Grade	Supplier
N-ethylcarbazole	99%	Fisher Scientific
Perhydro n-ethylcarbazole	>95%	Voyex (SH2IPDRIVE partner)
Dibenzyltoluene	99%	Biosynth
Perhydro dibenzyltoluene	-	Not available
Sodium borohydride	98%	CPH Chemicals
Ammonia borane	>85%	TCI Chemicals
Instant Ocean Seawater	-	Aquarium Systems

Table 7.2: Used substances, suppliers and grades

greatly on the amount of substances produced and their location. However, a first overview of these dangers can be used to determine whether there are large issues or if these can be overcome. Estimating these dangers is possible this way [312]. The results can be used to determine the storage location of these hydrogen carriers based on whether they can or cannot be used as impact dampeners.

7.2.2 EXPERIMENTAL SETUP - LAB SCALE - ALL FOUR HYDROGEN CARRIERS

This research involved several experiments presented in separate sections due to the different approaches required for the boron-based carriers (AB and SB) compared to the LOHCs. As literature findings sometimes diverge from experimental results, as noted by Le Floch et al. [311], this study will also mention possible discrepancies. The experiments focussed on the solubility and behaviour of the mentioned hydrogen carriers (both hydrogenated and dehydrogenated) in seawater. Seawater is synthesised using the Instant Ocean brand Seawater from Aquarium Systems, an ion mixture. The mixture contains sodium-, chloride-, sulfate-, magnesium-, calcium-, and carbonate-ions, among others. Table 7.2 gives an overview of the substances used, the suppliers, and the purity grades.

Boron-based carriers

The boron-based carriers (AB and SB) were tested for their reaction with seawater (see eqs. (7.1) and (7.2)) . A pneumatic through is used to measure the hydrogen production from both AB and SB when reacting with seawater. Figure 7.2 gives an an overview of the test setup used in this research. The resulting substance from the SB reaction (visible in equation 7.2) will dissociate in water, resulting in Na+ and $B(OH)4^{-}$-ions. These strongly alkaline ions can result in a strongly alkaline solution [313]. To avoid the formation of such a very strongly alkaline solution, to mimic the conditions of open seawater, and because of limitations due to safety in the test set-up, a total of 0.15g of SB was added to a large surplus of 600mL of water. In the case of complete conversion of all SB, this is predicted to result in a pH of 10.52, regardless of whether salt is added. AB reacts similarly, raising the pH level of the solution to 9.1 when added to water [314], and thus the same amount of water was used. Experiments involved placing 0.15g of SB or AB in an airtight Erlenmeyer flask filled with seawater. This flask is connected via a tube to a pneumatic trough, allowing us to measure the volume of hydrogen gas the reaction generates. Temperature conditions were adjusted using a heating plate when necessary.

LOHCs

The behaviour of both LOHCs was tested. Since hydrogenated LOHCs are not commercially available, NEC was synthesised by SH2IPDRIVE partners [315], with only small amounts available for testing. Perhydro dibenzyltoluene could not be synthesised in time due to the failure of the machinery required to hydrogenate DBT. A small beaker containing Instant Ocean artificial seawater at a temperature of 22 °C was used for behaviour tests. The LOHC was added to the beaker, with LOHC always in a significantly lower quantity than seawater. The main aim is to categorise these substances using the Standard European Behaviour Classification (SEBC) [311]. The SEBC classifies substances into categories such as floaters, sinkers, and evaporators. These main groups have subgroups, e.g. substances that dissolve or evaporate. Combined, the SEBC has 12 behaviour groups [311].

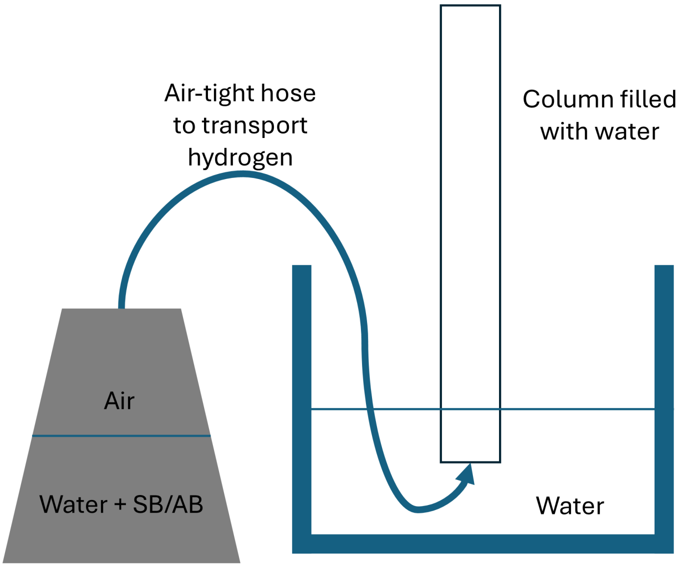


Figure 7.2: Schematic overview of test set-up to test self-hydrolysis of AB and SB in (sea)water.

7.2.3 EXPERIMENTAL SETUP - TANK - LOHCS

When a fuel is spilt at sea, the sea is likely not flat. Waves, currents and UV-light influence the dispersion and decomposition of the fuel. To simulate this, Bachelor students carried out an experiment in a tank with seawater and wavemakers. The tank had a size of 70 by 20 by 50 cm, and was filled with 15 L of water and 525 g of sea salt. No heating or cooling was involved, so everything was at room temperature. The has four different settings. The setting that generates the most consistent waves is used. Figure 7.3 shows the set-up, including the wavemaker and circulation pump.

7.3 THEORETICAL RESULTS - SOLID HYDROGEN CARRIERS

This section discusses the reaction equations, the temperature at which they occur, whether they are endothermic or exothermic and the resulting products.

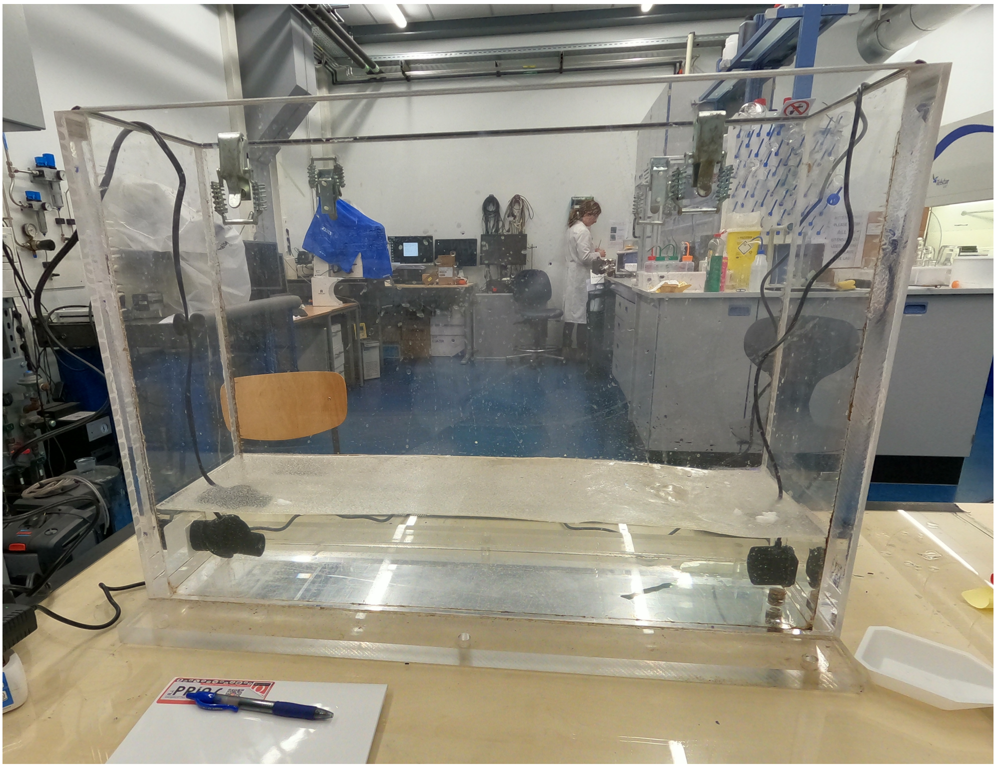


Figure 7.3: Set up of tank, including wavemaker (left) and circulation pump (right)

Pure hydrogen is often a byproduct of the reactions and is discussed separately.

7.3.1 AB

AB reacts strongly with water and heat, releasing hydrogen and other substances during these processes.

Reaction with heat

Figure 7.4 shows the resulting reactions when AB is heated. This figure is a simplified version, as the actual reactions are more complicated, see for example [83], [316]. The figure omits many intermediate steps with the same outcome, involving different but short-lived products. These in-between

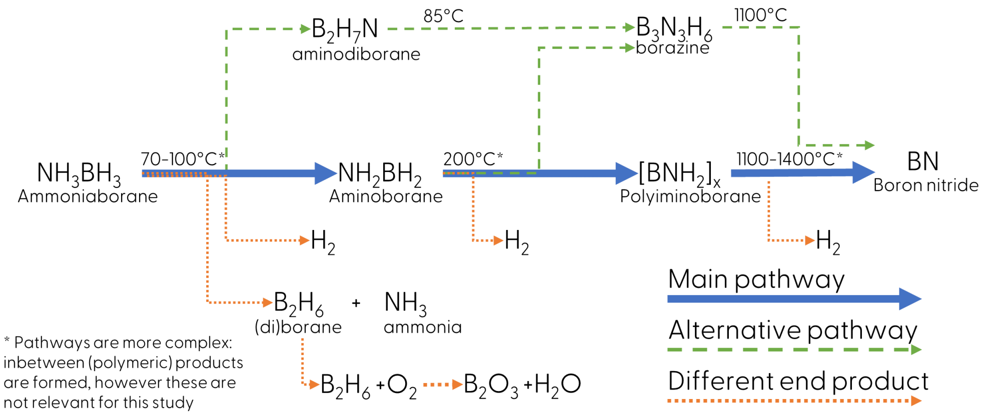


Figure 7.4: Reactions of AB in heat

products, often polymeric, usually decompose to the products as visible in figure 7.4. The only exception is polyiminoborane, which is thermodynamically stable and only releases hydrogen upon heating at higher (over 1000 °C) temperatures. Figure 7.4 shows multiple end products and several in-between products that are stable within rather large temperature windows.

Figure 7.4 shows a three-step process for the main pathway. The first step in this three-step process is an endothermic process, with a reaction energy of approximately 115 to 145 kJ/mol, producing aminoborane [317]. When aminoborane is heated to about 200 °C, it decomposes into hydrogen and polyiminoborane. This second step is an exothermic reaction, releasing approximately 21 kJ/mol [83]. It is thus self-sustaining, making aminoborane as an intermediate product less likely. The exact enthalpy of reaction, however, depends on the heating rate, as there are two, overlapping exothermic effects [318], especially as aminoborane is only stable until about 115 °C, after which it slowly decomposes [318]. The result, iminoborane (BNH_2), is illusive and highly reactive [319]. It quickly oligomerizes or polymerizes. Polyiminoborane is rather stable [320]. However, it slowly releases hydrogen upon heating [320]. When iminoborane oligomerizes, it is transformed into borazine.

Only at much higher temperatures, of around 1100 to 1400 °C, boron nitride is formed [321]. When borazine is heated, it also forms boron nitride. Boron nitride is a highly stable nitride, subliming at 2500 °C [83], [322].

During each of the steps, additional byproducts occur. Higher heating rates result in more volatile, unwanted byproducts like diborane and borazine [319], [323]. During the first step, diborane and aminodiborane are produced. Diborane (B_2H_4) is produced at a ratio of 0.02 to 0.04 mol per mol of AB [319]. Diborane, also known as borane, will readily oxidize (at temperatures lower than 54 °C) to B_2O_3 (boron trioxide) [324]. Boron trioxide is a stable solid substance, vaporizing at 1500 °C [322]. Boron trioxide is an ingredient in flame retardant [325], and is non-combustible. Next to diborane, ammonia is produced. Ammonia is a toxic gas and is lighter than air. Ammonia has a flash point of 132 °C.

Next to diborane, aminodiborane can be produced simultaneously during the first step [316], [326]. Aminodiborane transforms later into borazine; this reaction happens at temperatures as low as 75 °C [316]. However, it takes time to produce amino diborane; the reaction is relatively slow [316]. Aminodiborane is generally hard to produce, resulting in very limited information available [327]. It is reported as highly sensitive to air and moisture as it decomposes [328]. However, it is likely to react with an in-between product of the main pathway, diammoniate of diborane, resulting in an alternative but slower path to produce borazine [316].

Borazine is created during the second step as well. Approximately 0.03 to 0.06 moles of borazine per mol of AB are created during this process [319]. Borazine is a dangerous liquid, which is highly flammable and causes severe damage to the eyes and skin [266]. In water, it hydrolysis to ammonia, boric acid and hydrogen.

Reaction with water

AB reacts with water in a process called hydrolysis. Equation 7.1 gives an overview of what happens during this process [83]. There are no known side reactions or alternative pathways [83]. However, the reaction rate is considered to be slow, in the absence of catalysts or acids [83], [329]. Acids act as catalysts during hydrolysis; lower pH will result in faster reactions [329]. For higher pH, of about 10, no reaction was observed for 8 minutes, after which the experiment was stopped [329]. Additionally, the substance will self-stabilise if nothing is done about the pH value of the solution. Regardless of the concentration, the pH will become 8.7 to 9.1, close to seawater's pH (7.5 to 8.5) [261], [314], [330]. At these pH values, the solution is reported to be stable for 80 days in an inert atmosphere [314]. Another experiment showed that a maximum of 10% of the overall hydrogen available in AB was released over the course of several (at most 75) days [330]. Unfortunately, data on reactions in normal atmospheric conditions could not be found. Thus, AB is estimated to react extremely slowly in seawater. Regarding the produced products, $B(OH)_3$, the original spent fuel, will be discussed in section 7.3.3 and hydrogen in section 7.3.2. Ammonia is the main product specific to the hydrolysis of AB in water. Ammonia is highly soluble in water and will react with water and form a solution according to the following equation [83]:

$$NH_3 + H_2O \rightleftarrows NH_4^+ + OH^- \tag{7.3}$$

In this equation, ammonium (NH_4^+) and hydroxide (OH^-) combined are called ammonium hydroxide [184]. The amount of ammonia dissolved in water depends on the amount of water and whether some of the ammonia can be lost in the gas phase [83]. It is unclear whether all the ammonia will be dissolved in seawater. Some sources expect that some ammonia will still be in the gas phase [83], while others state that all ammonia that contacts water will be dissolved [184]. Thus, the assumption has to be made that pure ammonia as a gas will be released, as well as ammonium hydroxide. Ammonium hydroxide is alkaline and corrosive. It will inhibit the reaction of AB with water and corrode materials nearby. It is also harmful to sealife [184].

Combined heat and water

Figure 7.4 shows several products resulting from heating AB. Ammonia itself was discussed in section 7.3.1. Borane/diborane has likely already changed into B_2O_3 [324], as visible in figure 7.4; however, if this does not happen, borane will react with water as follows:

$$B_2H_6 + H_2O \rightarrow 2B(OH)_3 + 6H_2 \tag{7.4}$$

In this equation, hydrogen and boric acid are produced. The reaction is strongly exothermic [331]. Section 7.3.3 presents the reaction of boric acid with water.

This leaves aminodiborane and borazine. As mentioned in section 7.3.1, aminodiborane decomposes in water [328]. The exact decomposition reaction is not available in the literature. The reaction likely proceeds similarly to borazine, forming hydrogen, ammonia and $B(OH)_3$ upon hydrolysis [266],

[328], [332]. Generally, boron-nitrogen bonds are not stable in the presence of water [332].

7.3.2 SB

SB is a salt and looks like a white powder. It can be thermolyzed and hydrolyzed to release hydrogen and will thus react with heat and water [115], [333].

Reaction with heat

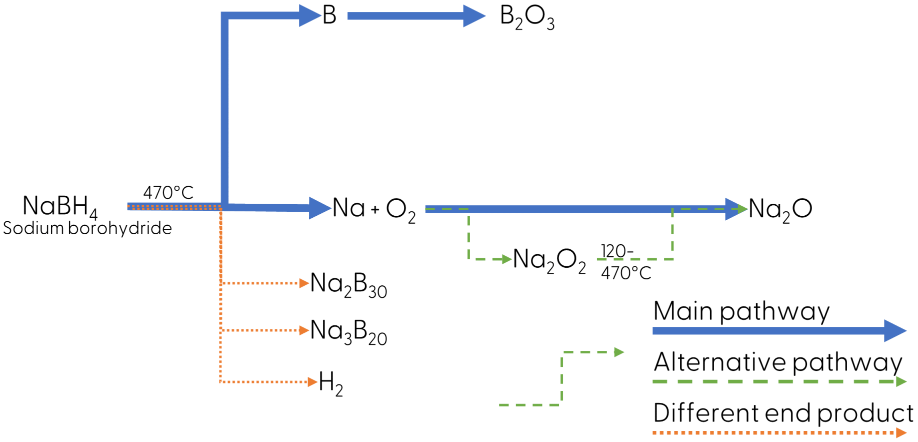


Figure 7.5: Reactions of SB in heat

Figure 7.5 gives an overview of the main and alternative pathways of thermal decomposition of SB. Thermal decomposition starts at 470 °C and is in general as follows [87], [333], [334]:

$$NaBH_4 \rightarrow B + Na + 2H_2 \tag{7.5}$$

All hydrogen is released at once when heated above 600 °C, although other sources estimate this to be 534 °C [87], [333]. The process is exothermic and thus self-sustaining, releasing about 108 kJ/mol [87], [333], [334]. The products formed are two solids (sodium and boron) as well as hydrogen.

Sodium is a well-known substance and is very volatile [335], [336]. Figure 7.5 shows the two main reaction pathways of sodium with oxygen, producing sodium oxide (Na_2O and sodium peroxide (Na_2O_2) [335]. This reaction occurs at temperatures at or below 105 °C and requires only 5% volumetric oxygen in the air [335], [337]. The burning of sodium can reach temperatures of up to 3600 °C under ideal circumstances [335].

Boron is a versatile material, and though it is generally categorized as interesting, there is still a lot unknown about this material [338]. Boron generally does not react easily at room temperature and is not very volatile [338]. It is known, however, to burn readily and produce B_2O_3 (boron trioxide), which has been discussed previously in section 7.3.1 [324].

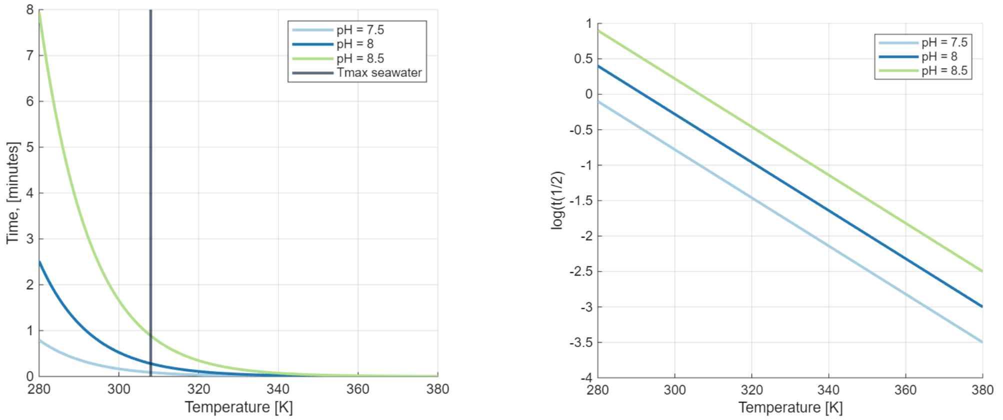
Next to these main products, also two combinations of boron and sodium are formed: Na_2B_{30} and Na_3B_{20}. Almost no data about Na_2B_{30} [339] is available and will thus not be discussed here. Na_3B_{20} is better studied. It is a pyrophoric substance if the particles are small, at larger particle size it is more stable [340], [341]. It is also possible that Na_3B_{20} only occurs at high temperatures (1050 °C) as it usually is synthesized at such high temperatures [341]. It is thermodynamically stable, and likely only very small quantities are produced.

Reaction with water

The reaction of SB with water is given in equation 7.2. No other pathways have been reported in the literature. The reaction rate is strongly dependent on temperature and pH value. A higher pH value, indicating a more alkaline solution, will inhibit the reaction, while higher temperatures will result in a higher reaction rate [342]. A higher concentration will result in a faster reaction rate, too [342]. A temperature of 25 °C and pH of 7.4, lower than that of seawater, will result in approximately 67% of all hydrogen generated within 5 minutes and reaction rates of 2.05 $\times 10^{-3}$ s^{-1} have been reported for pH values of around 8.5 [261], [342]. Another source cites a half-life of $NaBH_4$ of about 36.8 seconds when dissolved in a solution with a pH of 8. The half-life has been captured empirically as follows [343], [344]:

$$log(t_{1/2}) = pH - (0.034T - 1.92) \tag{7.6}$$

with $t_{1/2}$ in minutes and T, the temperature, in Kelvins. Figure 7.6 visualises the different half-life times, with figure 7.6b showing the logartihmic behaviour. Considering typical seawater temperatures of up to 35 °C (or 308K) [345], the shortest half-lifes lie under a minute (see figure 7.6a). These reactions can be considered fast.



(a) Release of half of the hydrogen from $NaBH_4$ during self-hydrolysis, temperature vs time

(b) Release of half of the hydrogen from $NaBH_4$ during self-hydrolysis, logarithmic plot

Figure 7.6: Release of half of the hydrogen from $NaBH_4$ during self-hydrolysis. Including the maximum temperature for which this equation, equation 7.6 has been validated, based on [343].

Combined heat and water

Sodium, known to be highly reactive with water, is part of many of the products in figure 7.5 [337]. However, if there is no air, the reaction may be non-explosive [337]. Figure 7.7 gives an overview of the resulting reactions. The reactions are all exothermic. One of the alternative endproducts, H_2O_2, is known to cause thermal runaways, as it decomposes at low temperatures, lower than 100 °C [346]. NaOH, the main reaction product, will dissolve in water, releasing heat [347]. This reaction can possibly ignite other substances, such as hydrogen peroxide. It splits into Na^+ and OH^- and is a salt. When not strongly diluted, it is extremely corrosive [347].

Boron is unlikely to react, as it is relatively stable and also present in seawater, with concentrations ranging from 0.5 to 9.6 mg/L [348]. This is both natural as well as due to human causes.

7.3.3 SPENT FUEL

The spent fuel of SB ($NaBO_2$) and that of AB ($B(OH)_3$) are very similar and composed of similar elements. Thus, they are considered both in this

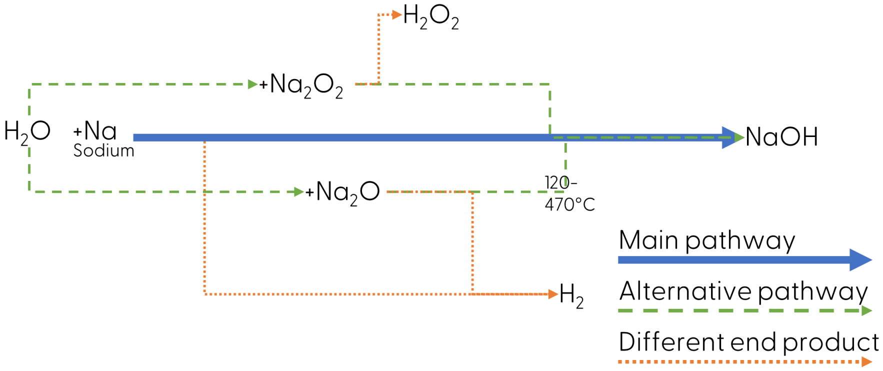


Figure 7.7: Reactions of products of SB in heat, with water

subsection. When dissolved in water, the spent fuel of SB splits up in Na^+ and $B(OH)_4^-$, the latter which is also the spent fuel of AB.

Equations 7.1 and 7.2 give a high-over reaction overview. The exact composition of the spent fuel depends on temperature, whether and how the water is extracted and the pressure [159], [349].

Heating of boric acid

Boric acid, $B(OH)_3$, is a very weak acid and has been used as flame retardant [324], [350]. Upon heating, boric acid releases its hydrogen and oxygen atoms in the form of water in a two-step reaction [350], [351], [352]:

$$B(OH)_3 \leftrightarrow HBO_2 + H_2O \tag{7.7}$$

occurring at temperatures below 130 °C. The next step occurs at higher temperatures of around 200 °C, with a maximum of about 450 °C [351], [352]. At temperatures higher than this, reactions will slow down. The second step is as follows:

$$2HBO_2 \rightarrow B_2O_3 + H_2O \tag{7.8}$$

It is possible that the second step already occurs before the first step is completed [352]. The end result, B_2O_3, is called boron oxide. The first reaction, equation 7.7, is a slow reaction, taking up to 3 days at low temperatures (up to 100 °C) and 45 minutes for temperatures above 300 °C [352]. The melting temperature of boron oxide depends on its structure. The exact structure of the end product of equation 7.8 is unclear, however the melting point will be around 450 to 500 °C [350]. Boron oxide is widely used, for example, in glass and ceramics, but it is also used as a fire retardant [350]. Boron oxide will evaporate at temperatures above 1025 °C [353].

Heating of Sodium metaborate

$NaBO_2$ is thermodynamically stable and does not react easily. It has a high melting and boiling point. The melting point lies at 966 °C and the boiling point at 1434 °C [247]. On the contrary, it has also been stated to evaporate at temperatures above 800 °C [353].

Reaction with water

The reactions of water with the spent fuels are straightforward. These reactions also happen during the original dehydrogenation process, as both fuels are dissolved in water during the hydrolysis process. Sodium metaborate splits into two ions, sodium and metaborate [354]:

$$NaBO_2 \xrightarrow{\text{Water}} Na^+ + B(OH)_4^- \tag{7.9}$$

As sodium ions are common in seawater, they are not of interest in this study. Thus, the authors will focus on the metaborate-ion, $B(OH_4^-)$. This ion is unstable in water [324], [348], [355]. It is the anion that is in balance with boric acid as follows:

$$B(OH)_3 + H_2O \leftrightarrow B(OH)_4^- + H^+ \tag{7.10}$$

The pH of the water strongly influences this balance. The balance lies at $B(OH)_3$ for low pH and switches to the right for pH levels higher than about 8.5; the exact pH value where the balance shifts depends strongly on the temperature [348], [355]. At seawater with a pH of 8.3, the balance in equation 7.10 shifts to the left, and most of the substance is in the form of boric acid [355].

In the case of having first a heating reaction and then a water reaction, boron oxide reacts with water exothermically to reform boric acid [356].

7

7.3.4 HYDROGEN

Risks of hydrogen in its pure form have been widely covered in the literature (for example, but not limited to [231], [270], [271], [272], [357]). The main issue with hydrogen explosions is not the heat source but the power resulting from the pressure of the explosion [231], [270]. Even relatively small hydrogen explosions, where about 3.5 to 7kg of hydrogen exploded, had destructive influences on nearby buildings [270]. As most explosions occur due to overpressure [357], however, it is hard to estimate whether a breach of a ship tank will result in hydrogen explosions.

7.4 EXPERIMENTAL RESULTS - LAB SCALE - ALL FOUR HYDROGEN CARRIERS

7.4.1 SB

Figure 7.8 presents an overview of the SB reaction results. The data indicate that seawater, compared to pure water, significantly enhances the hydrogen production rate. Regardless of the temperature, the seawater mixture consistently accelerates hydrogen generation compared to pure water. Due to the very low reaction rates at low temperatures, the tests could not be done at lower temperatures. However, estimates can be made for these lower temperatures based on the Arrhenius rate equation.

The results from Figure 7.8 indicate unexpected behaviour. The half-life time for self-hydrolysis of SB follows equation 7.6. This equation indicates a slower reaction rate for a higher pH value. As the starting pH value of seawater (8.2) is already above that of pure water (7.0), it can be expected from equation 7.6 that the SB hydrolysis reaction should be slower in seawater than in pure water. However, the results indicate the opposite: the reaction rate is faster in seawater than in pure water. In both seawater and pure water, the pH increased, as expected, but they increased to a very similar level of around 10.5. As both rose to this similar level, it can be safely assumed that the pH change does not explain the observed change in reaction rate. Something in the sea salt enhances the reaction rate, but further research is needed to determine the mechanism driving this increase.

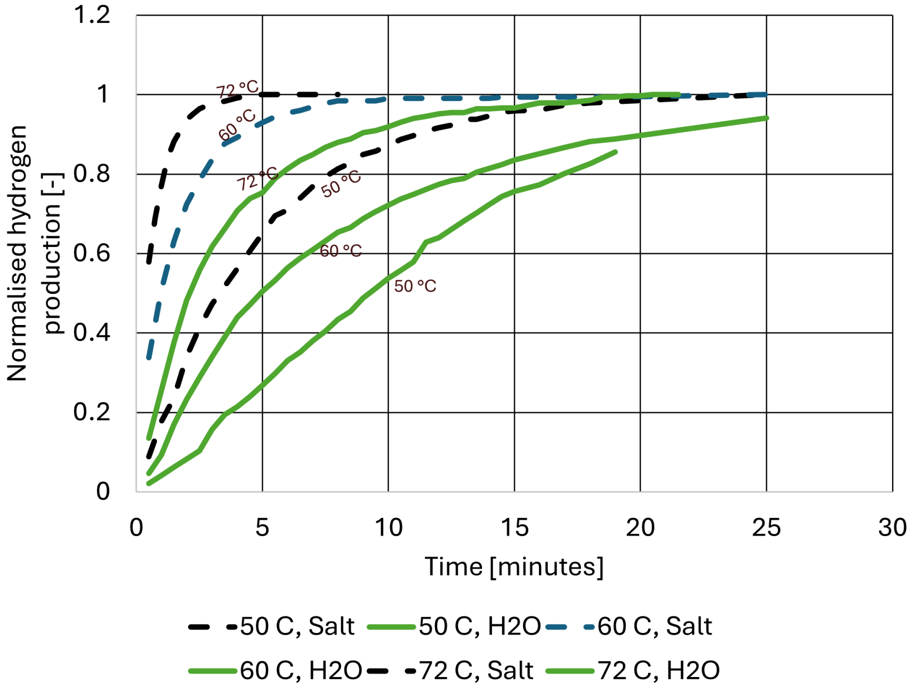


Figure 7.8: : Results of self-hydrolysis of SB in (sea)water. Hydrogen production as a function of temperature and water type, normalised for the highest hydrogen production in the experiment. Solid lines are in pure water, dashed lines in artificial sea water

7.4.2 AB

AB's self-hydrolysis in water is reportedly slow, showing no reaction after extended periods of up to 80 days [314]. Adding (solid) acids will lead to fast hydrogen release [314]. In seawater, with a pH of about 8.2, AB did not react within the time frame of an hour. As the reaction mechanism is likely similar to SB but with a much lower rate, the test was stopped as it was unlikely to react further on the time scale of hours. Because AB can be stable for up to 80 days [314], it is likely to disperse before it starts reacting, and it may not react at all. Since AB does not dissociate, it will not release ammonia or other harmful substances into the environment. However, dissolving AB in water may elevate the local pH to 9.1, depending on the concentration [314].

7.4.3 LOHCS

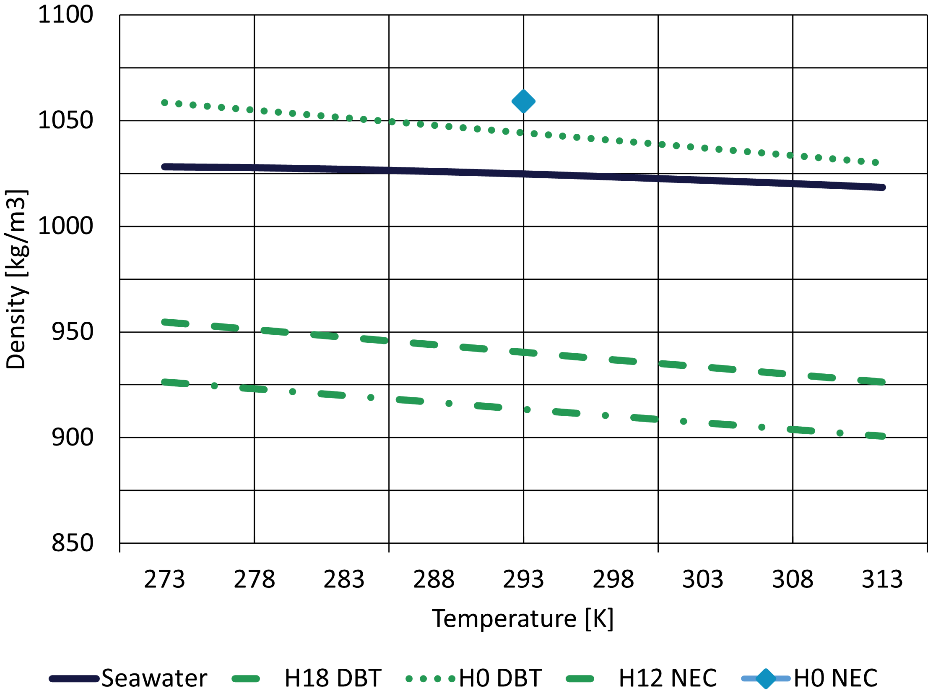


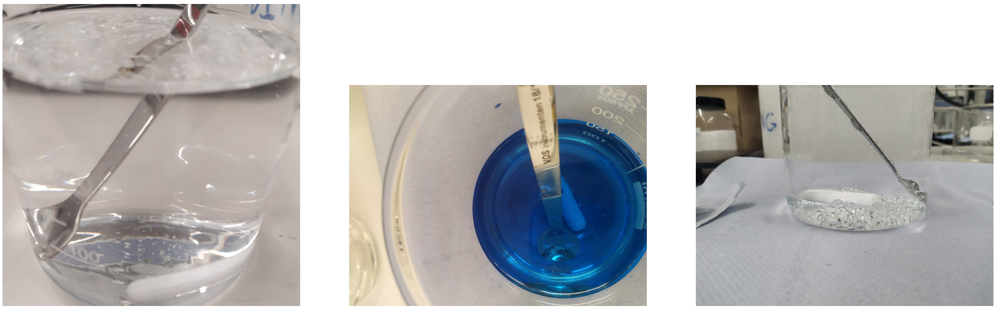
Figure 7.9: Theoretical densities of LOHCs and seawater for a reasonable range of seawater temperatures

Figure 7.9 shows the (theoretical) densities of LOHCs compared to seawater as a function of the temperature [151], [358], [359]. It indicates that at typical seawater temperatures (0 °C - 30 °C), both dehydrogenated versions (H0DBT and H0NEC) are denser than seawater, and both hydrogenated versions (H18DBT and H12NEC) are less dense than seawater. The dehydrogenated version of NEC is solid until approximately 68 to 70°C, and its exact density as a function of temperature in a solid state is unknown to these authors. Table 7.3 gives an overview of the behaviour of these substances in seawater, and Figure 7.10 shows pictures of the results.

NEC first aggregates on the surface of the water, but upon movement, it disintegrates into individual fragments. These fragments are visible in figure 7.10a. Some of these fragments settle to the bottom, while the majority remains

Table 7.3: Description of behaviour of LOHC substances in seawater

Substance	Description of behaviour	Classification
NEC	Predominantly floats. The structure is analogous to shards, where individual fragments do not remain cohesive. Some fragments either sink or circulate within the liquid. As the floating is due to surface tension, NEC is considered a sinker, but it can also behave as a floater in practical surroundings.	S (Sink), but depending on the particle size, it can also be F (Float)
Perhydro NEC	Floats, forms tiny droplets when disturbed. It appears to form a layer when undisturbed, but it is difficult to conclude due to the bad visibility of perhydro n-ethylcarbazole in water.	F (Float)
DBT	Predominantly sinks. Forms bubbles ranging in size from millimetres to approximately 2 centimetres. A single bubble remains buoyant. Upon disturbance, bubbles undergo fragmentation, reducing in size to only millimetres. However, over time, these small bubbles coalesce again into larger structures. Maximum bubble size appears to be about 2 centimetres.	S (Sink)



(a) NEC

(b) Perhydro NEC (with dye added for illustrative reasons)

(c) DBT

Figure 7.10: Behaviour of LOHCs in artificial seawater

buoyant. The structure consists of elongated particles resembling shards or splinters. Upon agitation, the fragments on the bottom are resuspended and dispersed, following the motion. The buoyancy of NEC is unexpected as, according to figure 7.9, the density of NEC is higher than that of seawater. The fragments remained buoyant even after vigorous agitation. However, the particles immediately drop to the bottom after adding dish soap to remove surface tension. Therefore, surface tension likely keeps NEC afloat, and NEC is a sinker. Testing in demineralised water revealed notable differences. In seawater, both large and small particles settled to the bottom, whereas in demineralised water, only smaller particles did. Additionally, NEC settled more quickly after movement.

Perhydro n-ethylcarbazole (H12-NEC) can be seen in Figure 7.10b. H12-NEC is barely visible in seawater, as it is transparent. Its visibility improved slightly after adding a dye (indigo carmine from Sigma Aldrich). However, it was sufficiently visible, even without dye, to allow some observations. Notably, H12-NEC remains afloat as expected. It forms extremely small droplets. Figure 7.10b illustrates some droplets floating in the seawater, away from the walls. H12-NEC disperses readily and appears to form a thin film on top of the water if undisturbed. Upon agitation, tiny droplets are formed. When adding dish soap, H12-NEC does not sink, but the film on the water's surface becomes more pronounced.

DBT forms large bubbles ranging from several millimetres to approximately a centimetre. As expected, most of these bubbles settle to the bottom, as visible in Figure 7.10c. Although the bubbles encounter each other, they do not coalesce. There appears to be a maximum bubble size of approximately 1 cm. A single large bubble, around 1 cm, remained at the surface, again possibly held there through surface tension. After agitation, the bubbles break apart and become significantly smaller. The surface bubble increases in size, reaching approximately 2 centimetres. An additional large bubble forms around the stirring magnet. With more vigorous agitation, the bubbles reduce further, with a maximum diameter of a few millimetres. However, when the system is at rest again, the bubbles grow larger due to coalescence. The surface bubble returns to its original size of about 1 cm. Notably, the bubble around the stirring magnet persists and cannot be displaced, even with substantial movement of the magnet. Due to the low solubility and low vapour pressure, DBT can be categorised as a 'sinker' in the SEBC classification. As perhydro dibenzyltoluene could not be synthesised in time, no results can be displayed in this chapter, and the behaviour of perhydro dibenzyltoluene is left for further research. However, it is still recommended that perhydro dibenzyltoluene be tested.

7.5 EXPERIMENTAL RESULTS - AQUARIUM SCALE – LOHCS

The wave generator and the circulation pump were operated for a sufficiently long duration to establish a stable wave motion and flow within the tank.

7.5.1 NEC

NEC, introduced in powder form, initially floated as a compact mass but gradually disintegrated into increasingly smaller particles.

To isolate the effect of the waves, the circulation pump was turned off. After a few minutes, the wave action forced part of the substance below the water surface, causing it to sink to the bottom, where it remained. Subsequently, the circulation pump was reactivated to observe the behaviour of the sunken particles. A portion of these particles was entrained by the pump-induced flow, remaining suspended in motion without settling again or rising to the surface, while another portion remained stationary on the tank floor. However, the majority of the substance continued to float.

Finally, the wave generator was deactivated. This change did not result in any noticeable alteration in the behaviour of the substance, as it had already been distributed throughout the tank by the previous wave activity. Thereafter, both the wave generator and the circulation pump were turned off. Consequently, the floating NEC remained at the surface, the sunken particles stayed on the bottom, and the suspended particles in the water retained their positions. Upon the addition of soap, the surface tension was reduced, which—as expected—caused all NEC particles to sink to the bottom.

7.5.2 PERHYDRO N-ETHYLCARBAZOLE

In this experiment, the hydrogenated NEC was pre-mixed with a hydrophobic dye. As a floating liquid, the substance was unaffected by the circulation pump's flow; only the wave motion had an influence. Upon introduction into the water, small, circular droplets were formed, which remained afloat in this configuration in the absence of wave activity. Once the wave generator was activated, the droplets rapidly disintegrated. Within a few minutes, the droplets had completely vanished, and the substance dispersed across the water surface as an oil-like film.

7.5.3 DBT

For this experiment, 20 mL of DBT was used, with both wave motion and circulation applied. The majority of the substance sank to the bottom, while a few droplets remained floating on the surface. Due to the influence of wave motion on the surface droplets and flow-induced forces on the submerged droplets, the substance gradually fragmented into progressively smaller particles.

First, the wave generator was deactivated. Once the wave motion ceased, several DBT droplets moved along with the flow. Larger droplets that had already settled on the bottom remained stationary, with their upper surfaces oscillating in response to the flow. Suspended DBT particles elongated and thinned in the vicinity of the circulation pump, where hydrodynamic forces were strongest, but regained their spherical shape further away from the pump. Subsequently, only the wave generator was reactivated, while the circulation pump remained off. The DBT droplets at the surface fragmented into smaller particles but did not sink. Finally, both devices were turned off. This resulted in all previously suspended particles settling to the bottom.

7.6 DISCUSSION

7.6.1 SOLID HYDROGEN CARRIERS

Table 7.4 gives an overview of all resulting products from each of the possible reactions. These products are not produced proportionally; some of the products only occur in very small quantities, making them less relevant. As the exact amounts of the products are unclear, they will all be taken into account in this analysis.

Heating of AB

AB reacts at lower temperatures, of up to 200 °C already. During these reactions, the toxic gasses ammonia and diborane and the flammable gas hydrogen are formed. Heating of AB thus forms a danger to both the ship and the people on board. As these substances are all gases, they are more dangerous but also safer. Their gas-like nature will result in a faster distribution and, thus, lower overall concentrations of each gas. This will make the gases safer, as lower concentrations are less likely to be dangerous.

Hydrogen has a lower flammability limit of 4% and is easily ignited. Thus, the release of hydrogen may cause an explosion and, thus, a secondary heat source. These types of reactions may become self-sustaining, resulting in more release of hydrogen and other dangerous gases. Diborane (B_2H_6) is also easily ignited, igniting in moist air at room temperature without external triggers [360]. The flammability and easy ignition of both hydrogen and diborane may influence the ship's integrity, as these substances are likely to ignite. Additionally, the spontaneous ignition of diborane, despite very low concentrations, may cause the ignition of hydrogen. Hydrogen is likely to be present in larger concentrations and can influence the integrity of the ship.

Ammonia is not easily ignited, but is extremely toxic, and concentrations as low as 2500 ppm are considered lethal [78]. Diborane is even more toxic. It has a strong smell and can be smelled at low concentrations, as low as 1.8 ppm [360]. It is extremely toxic and can be deadly at concentrations as low as 0.46 ppm if inhaled over longer amounts of time. At 7.3 ppm, it has immediate effects [360]. Another danger of diborane, as opposed to ammonia and hydrogen, is that it is heavier than air and thus will accumulate. Ammonia, on the other hand, is lighter than air and will disperse more easily. The toxicity

Table 7.4: Resulting products of reactions of NH3BH3, NaBH4 and the spent fuels with heat, water and a combination of heat and water

	Heat	Water	Heat and water
Ammonia borane	NH_3(g), H_2(g), B_2H_6 (g), B_2H_7N (l), $B_3N_3H_6$ (l) T<1000 °C: $[BNH_2]_x$ T>1000 °C: BN	NH_4^+ (aq) + OH^- (aq) H_2 $B(OH)_3$ (aq) $\leftrightarrow$ $B(OH)_4^-$ (aq) + H^+ (aq)	H_2, NH_3, $B(OH)_3$
Sodium borohydride	Na (s), B (s), H_2 (g), Na_2O (s), Na_2B_30 (s), Na_3B_20 (s), B_2O_3 (s)	$NaBO_2$ (aq), H_2 (g)	H_2O_2 (l), NaOH (s/aq), H_2 (g)
Spent fuel	B_2O_3 (s) (NH_3BH_3) $NaBO_2$ (s) ($NaBH_4$)	$B(OH)_3$ (aq) $\leftrightarrow$ $B(OH)_4^-$(aq) + H^+(aq)	B_2O_3 +H_2O $\rightarrow$ $B(OH)_3$(aq) Na^+ (aq), $B(OH)_4^-$ (aq)

of ammonia and diborane, especially the heavy weight and high toxicity of diborane, will strongly influence the safety of the people on board.

Finally, ammonia may influence sealife, but only if it touches water. If it comes into contact with water, it may have large consequences for local sea life [184]. As it is lighter than air, this is not necessarily likely. Diborane forms no environmental hazard according to the GHS standards, but as it is so toxic to people, it is likely to also influence sea life, and of these three gasses most likely to enter the ocean.

Two other substances that are formed are aminodiborane and borazine, both liquids. Borazine is a flammable and corrosive liquid with a clear smell and no colour [266]. The corrosiveness of borazine applies to the skin, as it causes skin burns and eye damage [266]. Aminodiborane is an unstable liquid, decomposing at room temperature, likely towards borazine [316], [361]. Release of these two liquids will likely result in contact with the environment. Aminodiborane will slowly hydrolyse, completing hydrolysis in 2 months at room temperature [361]. It is unknown if aminodiborane is toxic to the environment. However, it is not likely to influence the ship's integrity. Borazine will strongly influence the safety of the people on board, as it is a liquid that should not come into contact with people. It is flammable and reacts violently with water, which may influence the ship's integrity if this substance comes into contact with water [266].

Heating of SB

The resulting products of heating SB are dangerous. However, these products occur after heating at much higher temperatures (around 470 °C for SB, versus 200 °C for AB). In the case of SB, runaway reactions are more probable.

When heating SB, the structural integrity of the ship is likely influenced. A major product, sodium, is a dangerous solid due to its flammability and corrosivity. It burns violently and may also cause explosions. These explosions, in turn, can set off more explosions from hydrogen. The corrosivity of sodium may influence the metal the ship is made of. The other three substances (boron, sodium oxide (Na_2O) and boron oxide (B_2O_3)) are not likely to influence the ship itself.

Boron, sodium oxide (Na_2O) and boron oxide (B_2O_3) may all influence the safety of people on board. Boron is an irritant and should not be swallowed. Boron oxide is a typical boron-based product and only has a health hazard.

This health hazard is typical for boron-based compounds, such as boric acid and boron oxide: these may influence fertility or the unborn child [362]. It is thus unlikely to influence the people onboard strongly. Like sodium oxide, it does not harm the environment or the ship. Sodium oxide is also dangerous for the people onboard as it is corrosive to the skin and thus can cause eye damage. All of these substances should thus not be touched. As they are solids, they are not easily distributed, enhancing their safety.

Even though some reports suggest that boron compounds may cause long-lasting harmful effects on aquatic life, there is no consistency on this [253]. Whether any of the products resulting from heating SB will harm the environment is not known.

Reaction with water

Both substances will react with water. The most positive side is that no alternative substances are produced, only the substances that are known and well-studied. However, these substances are not necessarily safe.

Hydrolysis of AB will theoretically result in ammonia, hydrogen and boric acid. Still, AB appears to be relatively safe due to its apparent inertness. However, its impact is highly dependent on the amount released and the specific spill location, as it has the potential to raise the pH of the surrounding environment. In cases where a substantial amount is released, the pH of the surrounding seawater may increase locally, which could be detrimental to certain sensitive species. However, the immediate impact will likely be negligible if the spill occurs in the open ocean.

The spent fuel of AB, boric acid, may damage fertility or the unborn child, resulting in a health hazard [325]. However, no other dangers have been stated for this substance. When touching the water, it will sink and dissolve completely [325].

SB will only produce possibly explosive hydrogen. The enhanced hydrogen production rate of SB in seawater relative to pure water may cause potentially dangerous situations at sea. However, it must be realised that the increase in reaction rate is relatively mild, i.e. not by orders of magnitude. If the produced hydrogen gas is dispersed fast enough, it may not ignite. However, hydrogen explosions cannot be ruled out in the presence of an ignition source, such as a fire, and at relatively high sea surface temperatures.

The spent fuel, sodium metaborate, may be a danger to human reproduction and, thus, also likely to affect wildlife reproduction. However, the exact effects are unknown.

Combined heat and water

When heating AB, many different substances are produced. However, almost all of these substances react in a very similar way with water. The reactions are usually exothermic [328], [331], [332], and the resulting products are likely to be ammonia, hydrogen and boric acid. These products will likely influence all three pillars: the integrity of the ship, the safety of the people onboard and the environment and are extensively discussed in previous sections.

As the spent fuel of AB, boric acid, releases water upon heating, it changes into boron oxide. Boron oxide will absorb water exothermically. This reaction forms boric acid again. Thus, the reaction of boric acid upon first experiencing heat and then water is unlikely to result in different reactions as compared to experiencing water only.

The main products from SB, when heated, are sodium, boron and hydrogen, as well as sodium oxide and sodium peroxide. Some of these products are volatile. Sodium reacts strongly with water, forming sodium hydroxide (NaOH). This reaction is highly exothermic and may influence the integrity of the ship. NaOH is readily dissolved in water but is extremely corrosive and can thus influence the integrity of the ship. Similarly, sodium peroxide reacts with water, forming hydrogen peroxide. Hydrogen peroxide can cause thermal runaways [346]. Thus, heating SB, followed by adding water, may result in various explosions, resulting in additional heat sources and thus a chain reaction. This chain reaction will likely influence the integrity of the ship. Of these products, only hydrogen peroxide is dangerous to the people onboard and the environment. It can cause severe skin burns and eye damage and harm aquatic life [363].

As sodium metaborate is thermodynamically relatively stable, no other reactions are expected upon a combination of heating and water as compared to releasing sodium metaborate directly in water.

Overview

Table 7.5 gives an overview of all the hazards accompanied by heating, adding water or a combination of both. It is clear that both AB and SB release dangerous substances. Heating is the most dangerous for AB, as a chain reaction is likely. Heating of SB results in similarly dangerous products. However, as the products of SB are only released at much higher temperatures (over 500 °C), overall, SB is safer than AB upon heating. Both spent fuels are the safest. Boric acid is safer than sodium metaborate. Boric acid is a flame retardant and will release water, possibly extinguishing the fire, while sodium metaborate likely will not react. When adding water, AB produces the least safe products. However, as the reaction rate of AB with water is extremely slow, especially compared to SB, it is difficult to say which one is safer. Both have different hazards. Again, the spent fuels are safer than the original fuels.

Table 7.5: Resulting dangerous products of reactions of ammonia borane and sodium borohydride and their relative spent fuel with heat, water and a combination of heat and water

	Heat	Water	Heat and Water
Ammonia borane	Dangerous gasses and liquids, which will influence the ship's integrity, life onboard and environment	Dangerous gasses, which may influence the ship's integrity, life onboard and environment	Dangerous gasses and liquids, which may influence the ship's integrity, life onboard and environment
Spent fuel: Boric acid	Flame retardant, will release water	May influence reproducibility of local wildlife	May influence reproducibility of local wildlife
Sodium borohydride	Dangerous gasses and solids which will influence the ship's integrity, and possibly life onboard and environment	Dangerous gasses, which may influence the ship's integrity	Dangerous gasses and solids which will influence the ship's integrity, and possibly life onboard and environment
Spent fuel: Sodium metaborate	Unlikely to react	May influence reproducibility of local wildlife	May influence reproducibility of local wildlife

Finally, when first adding heat and then adding water, SB appears to be less safe. Heating SB produces, amongst others, sodium, which reacts violently with water. Heating AB produces mainly dangerous gasses, of which only one (diborane) is heavier than air. Diborane is also produced in less high quantities. The same applies to the liquids produced, which are mainly byproducts. Thus, AB is the safer fuel in this case. As before, both spent fuels are safer and are likely not to release dangerous substances.

7.6.2 LIQUID ORGANIC HYDROGEN CARRIERS

The results indicate that all three tested LOHCs are unlikely to be easily cleaned up due to their dispersion. The tendency to fragment during movement suggests that these substances would likely become even more dispersed in a real-world marine environment where wind and waves are present. Even though NEC is officially classified as a sinker, it is likely to stay afloat during an actual spill because it is very hydrophobic, and the surface tension is sufficient to keep small particles afloat. Whether it floats or sinks depends on the particle size, as larger objects have a larger volume-to-surface ratio and are, therefore, more likely to sink. The poor visibility of H12-NEC in seawater suggests that locating and cleaning it after a spill would be highly challenging. DBT tends to sink, so it poses a different cleanup challenge than floating substances. Moreover, its tendency to adhere to surfaces will complicate the cleanup process. Therefore, effective cleanup of all these substances in the event of a spill may prove highly challenging.

7.7 CONCLUSION AND RECOMMENDATION

While alternative fuels offer important zero-emission benefits, their implications for ship safety and the marine environment are both significant and multifaceted. Each fuel examined in this study introduces its own set of safety and environmental challenges in maritime applications.

Spills of solid hydrogen carriers in the ocean are unlikely to endanger the integrity of the ship or the safety of the crew. Hydrogen release during such spills is limited (SB) to negligible (AB), though these materials may affect the reproductive capacity of marine wildlife. Both carriers also present thermal reactivity concerns: AB decomposes at relatively low temperatures, whereas SB remains stable until much higher temperatures but releases volatile by-products when it does react. Safe storage strategies, therefore, need to be tailored to these differing behaviours. Notably, their spent fuels are comparatively stable and may offer safety advantages in the event of fire or impact.

Both LOHCs display complex and potentially hazardous behaviour in seawater. Their primary concerns relate to persistence in the marine environment and, in the case of DBT, toxicity. Clean-up efforts are complicated by limited visibility, small particle size, complex surface interactions, and the wide variation in density between fuel and spent fuel. These findings highlight the need for proactive safety measures, including optimal fuel placement, robust emergency-response planning, and clean-up strategies aligned with each fuel's specific properties.

The behaviour of the alternative fuels studied here contrasts with that of conventional marine fuels, for which the safety characteristics are generally better understood. Likewise, other alternative fuels such as ammonia, methanol, and pure hydrogen exhibit their own distinct risk profiles, though these fall outside the scope of the present assessment.

Each hydrogen carrier introduces unique challenges. Given the scale of maritime fuel systems, even small spills have the potential to cause significant environmental harm or compromise vessel integrity. Conversely, the spent fuels of solid hydrogen carriers may enhance onboard safety.

SAFETY & SUSTAINABILITY

8

IMPORTANCE OF SAFETY

> *"Show me a poorly uniformed troop and I'll show you a poorly uniformed leader"*
>
> — Robert Baden-Powell

CHAPTER SUMMARY

Emerging technologies, such as alternative fuels and advanced control systems, can reduce environmental impact but also introduce risks through added complexity and reduced transparency. Safety assessments often overlook the human factor, even though most accidents stem from design, organisational, or operational shortcomings rather than individual error. This chapter applies safety-science principles to evaluate maritime safety approaches and propose guidelines for safer vessel design. Safer ships require acknowledging human limitations early in the design process. Overreliance on automation is risky: it may ease workload but does not guarantee safety and can obscure system robustness. Simpler designs enhance safety but must be supported by strong operational practices. This demands resilient, human-centred systems and a non-victim-blaming safety culture. Expecting the unexpected, managing uncertainty, and fostering human–machine cooperation remain essential, though still underdeveloped, in the maritime sector.

8.1 INTRODUCTION

Since the sinking of the Titanic in 1912, maritime safety has increasingly become a central focal point within the industry. However, incidents and accidents with ships still occur regularly, with ships grounding or sinking resulting in deaths at least yearly. Research attributes the majority of accidents in the maritime sector to the human, even though the exact number accredited to this is debatable [364]. For example, one of the most recent large shipping accidents, the sinking of the HMNZS Manawanui, was attributed to human error [365]. Additionally, insurance companies such as Allianz share the view that 75% to even 96% of all accidents involve human error [366].

Next to enhancing safety, the maritime industry also wants to limit its GHG emissions: the IMO has set a goal for the industry to become net-zero GHG by 2050, as well as limits for NO_x emissions (as stipulated in Marpol Annex VI) [13], [367]. It is costly to reach these goals, and Allianz believes the investment in the crew will be reduced [366]. This reduction in investment will likely increase risks associated with human error.

One way to achieve the net-zero GHG goal is to use alternative fuels. However, this may have direct safety implications. While numerous alternative fuels are being explored, none can be considered inherently safe [312]. Nevertheless, it is important to note that conventional fuels such as MDO and HFO also carry safety risks [312].

Despite having a higher volumetric energy density than pure hydrogen, hydrogen carriers often have a lower energy density than conventionally used fuels such as marine diesel oil and heavy fuel oil. Thus, when aiming for a complete exchange of a vessel's operating fuel and energy system, efficiency increases become more and more relevant to maintain a similar autonomous travel distance, meaning the distance a vessel can travel without refuelling. While commonly used rule-based control systems perform reliably and well in their design conditions, they are limited in optimisation potential when diverging from those conditions [368]. Additionally, when NOx emissions are fully capped, fuel cells may be required, which in turn often require some sort of reactor (e.g. a reformer) to operate. In combination with the

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The content of this chapter is based on the following articles:
E. van Rheenen, C. Löffler, A. Kana, J. Padding, and K. Visser, "Integrating Safety Science into the design of future ships," Zenodo, presented at the Practical Design of Ships and other Floating Structures (PRADS), Ann Arbor, MI, USA, 19–23 Oct. 2025. doi:10.5281/zenodo.17305769

trend towards electric power trains [369], the overall complexity of the ship energy system will increase [368]. Operating those more complex energy systems is an additional challenge for rule-based control [370]. Hence, the trend is going more and more towards advanced control, automation and optimization for vessel operation. These developments lead to more complex, more interconnected systems which require well-designed advanced operation control. This also enhances the system's fallibility if not properly accounted for in the design process. As a result, the safety of the vessel may be decreased.

To counteract this, safety both from system set-up and operation management perspective needs to become more significant already in the early-stage design process of modern vessels. This future vessel design will be approached from an integral perspective, considering how an alternatively fuelled vessel can be designed with high safety for humans, systems and operations. First, a short introduction is provided on how the safety of systems and alternative fuels is currently assessed and why a rethinking of safety assessment might be needed (Section 8.2). Next, section 8.3 discusses the safe integration of alternative fuels. To showcase the integral perspective, the insights will be discussed in section 8.4, to provide guidelines for safe vessel design, incorporating major safety science findings. By combining the safety assessment of the vessel in a holistic analysis, the safety of a future vessel can be enhanced in the design process, allowing for the safe integration of alternative fuels in global shipping.

8.2 CURRENT SAFETY ASSESSMENT

As a United Nations body, the IMO sets standards for the construction and operation of international shipping. Originally, these conventions were rule-based, dictating exactly how a ship should be designed and built. Nowadays, the IMO is moving towards goal-based standards, which dictate that the ship has to be safe for the seafarers and the environment, whilst also being easily accessible for inspectors and maintenance crew. The movement towards goal-based standards is slow, changing one code at a time. The guidelines aim to ensure the ship's safety without limiting innovative design [292]. On the other hand, the standards are designed to be specific without leaving room for too much interpretation and are, consequently, developed for different codes, also outside of the ship construction domain [292].

There are several issues with the goal-based design approach, mainly because classifying things as safe is impossible. Many methods exist to estimate the safety of a system or process, but these all have major limitations. The following subsections briefly discuss the connection between the sustainability goals and the design process and safety of the vessel, the current methods used to assess safety and pinpoint the general, overarching issues associated with these methods.

8.2.1 HOW SUSTAINABILITY GOALS INFLUENCE THE VESSEL DESIGN PROCESS

Part of the UN sustainability goals' implementation results in the ambition of the IMO for the shipping industry to become net-zero emission by 2050. This ambition results in a drift towards many new, emission-reducing technologies such as electrification [369] to allow the integration of novel technologies, for example, batteries. However, to meet the defined emission-reduction goals, the most important change for the maritime sector is the introduction of alternative fuels into vessel power trains [371].

These introduce a variety of different fuel aggregation states (gas, liquid or solid), safety characteristics, new components and other aspects into the design of new vessels, which aim to follow along the rules of the IMO. While the amount of upcoming changes to maritime power trains are significant, some are more critical for the safety assessment than others. Previous research showed that the hazardous impact of alternative fuels can be quite severe [312]. As most future vessels will need to rely on alternative fuels in some form due to their required autonomous travel distance, getting insights into the safety of those novel and potentially hazardous substances is of high importance. Taking those findings into account already in the design process will be necessary to align the future of the maritime transport with the IMO sustainability goals. However, this sprawl of new technologies and fuels cannot be captured by the traditional rule-based standards and will potentially require a rethinking of the current safety assessment process.

Therefore, this chapter analyses the assessment of safety for the design process when integrating alternative fuels, with a focus on hydrogen carriers. Two aspects will be discussed in detail: designing for safety with an alternative fuel and safety from the point of view of the necessary control system.

8.2.2 GENERALLY USED METHODS TO ASSESS SAFETY

Standards and codes, such as those set up by the IMO, aim to ensure safety already in the vessel design stage. The goal is to safeguard the safety of ships, seafarers and the environment. Several techniques are currently in use to ensure this safety. The methods, also known as safety tools, discussed in the following are generally used to assess the safety of various processes and designs [372], [373], [374]. The first is fault tree analysis (FTA), with the objective to assess component failures and human errors leading to the occurrence of undesired events in the operation. Similarly, event tree analysis (ETA) can be used to quantify the possibility of consequences. With hazard and operability studies (HAZOP) the human and management factors, as well as programmable electric systems are analysed to draw conclusions for system improvements. Another safety tool, known as failure mode and effects analysis (FMEA), defines, identifies and eliminates known and potential failures, problems and errors in a system. One of the most encompassing, full-scale methods to assess risks is the quantitative risk assessment (QRA). The QRA is so well-known and widely used that the Dutch government published a book full of guidelines on how to do a QRA, the so-called purple book [375]. These types of risk assessments are also part of the Formal Safety Assessment (FSA) of the IMO, usually undertaken at step 2 of the FSA [376]. The formal safety assessment is a tool for policymakers to assess the rule making process of the IMO. Additionally, the QRA can be used to underpin compliance with the goal-based standards. Thus, a QRA often forms the basis of a large amount of safety management in general.

While there are many more [374], this selection is very commonly used in assessing safety for fuel-based transportation system or the fuels itself [377]. The aim of these tools is to detect disturbances in the process so that these can be analysed [372]. Applying those assessment methods should ultimately lead to enhanced safety and an improvement in operability. Each of these methodologies and techniques has its limitations and advantages. An overview of the main methods used to assess safety in previous literature [377], as well as a short description of these methods and their major limitations [374] can be found in table 8.1. From this overview, some general shortcomings that are relevant to all methods can be derived.

Table 8.1: Overview of methods used to assess safety of alternative fuels in literature and their major disadvantages [374], [377]

Method	**Short description**	**Limitations**
FTA (Failure Tree Analysis)	Determine component failures and human errors, which can result in the occurrence of an undesired event.	State-based; diverse or multiple top events are limited; no reliable results in complex relationship systems; failure probabilities treated as crisp numbers.
HAZOP (Hazard and Operability Studies)	Focuses on analysis of human factors, management factors, and programmable electric systems to improve the system.	Lack of experience in HAZOP; failure to communicate changes; shortage of technical information; complex relations difficult (focus on stand-alone events); focus on guide words only.
FMEA (Failure Modes and Effects Analysis)	Define, identify, eliminate known and potential failures, problems and errors; RPN = O × S × D.	No relative significance of O, S, or D; no scientific basis; no inter-dependencies or indirect relations; impact of single failure only.
ETA (Event Tree Analysis)	Quantifies the possibility of consequences.	Expert's (limited) knowledge; incomplete information; poor data quality; interpretation of failure mechanisms; assumption that likelihood of events is accurate.
QRA (Quantitative Risk Assessment)	Full-scale methodology used as a tool for comprehensive risk assessment in the chemical process industry.	Data quality issues; focus on failure of components; does not cover all phases of the plant cycle.

8.2.3 SHORTCOMINGS OF GENERAL METHODS WHEN INTEGRATING ALTERNATIVE FUELS

Most of the issues with the previous methods are technical issues, while others are more philosophical or ethical. First of all, the engineering approach of putting numbers on assessments and then comparing them, runs into (ethical) problems quickly. What is safe? How many people are allowed to die? Is the death of a sailor worse than the death of a bystander? How many injured people are worse than a dead person? How does damage to the environment relate to all these questions? This results in many ethical questions that need to be raised, and these ethical questions are very likely to be answered differently for each of the involved stakeholders.

Related to this is the desire to capture risk in a single number. The Dutch Health Council already warned in the 1990s that risk cannot be captured by a single number [372]. Quantifying risks in one number may result in disagreements between the calculated risks and those perceived by non-experts or citizens, which in turn may result in distrust of experts. Focusing too much on quantitative, number-based methods of assessing risk and, to an extent, safety should thus be avoided.

Next to these ethical questions, there are also more practical questions when trying to capture risk in numbers. Besides risk, often defined as probability times consequences [378], there are other parts that are often categorised as risk, but can also be considered as different principles [378], [379]. Other forms which are relevant for this research: scenario uncertainty, ignorance, indeterminacy and normative uncertainties [379]. Scenario uncertainty is defined as not knowing all failure mechanisms, which is required for all methods mentioned in table 8.1. The entire system has to be known in detail, and exact knowledge of what is happening (e.g. chemical processes) and where this is happening has to be available. All of these techniques are based on finding out where there may be failure mechanisms and what their result can be. However, when designing a future ship, much is unknown in the early design phase, whilst a sufficient amount of details is required to estimate the different failure modes.

In addition to scenario uncertainty, ignorance is also an issue. With ignorance, neither all failure mechanisms nor all undesirable consequences are known. This can also be seen from table 8.1, as practical data on failure is required to quantify risks. This data is often lacking, which results in an uncertainty margin on the desired numerical outcome. This margin is usually at least one order of magnitude, but can be up to five orders of magnitude [372], [373]. This issue has been known since 1982. Indeterminacy can also be seen as the human factor: the user operating the system in a way that was not foreseen [379]. This happens often, also in the maritime domain [380]. Automating processes may make it easier to quantify things (as quantifying human behaviour is extremely difficult [372]). However, this removes the main advantage of a human: the ability to think and improvise quickly. Humans have shown to be able to accomplish great things this way, as is shown by United Airlines Flight 232 [381]. After all hydraulics failed, the crew was still able to fly the plane by operating only its engines [381]. Even though such exceptional cases have not happened in the shipping industry, quick thinking did save the passengers of the MV Viking Sky, which ran into trouble after a loss of oil pressure in a rough sea [382]. Blindly removing the human factor, to automate and be able to quantify more easily, may thus not be the best course of action. As removing the human can lead to unforeseen issues, caution should be exercised when considering this.

The final category is normative uncertainties. Normative uncertainty is uncertainty about how to act in certain situations [379]. Because of the relative novelty of all alternative fuels, normative uncertainties are very likely to occur, as not all scenarios can be envisioned and trained for. These uncertainties cannot easily be anticipated, although it is of extreme importance to not only train the easy scenarios [383]. Even though this may sound obvious, training of only simplified scenarios is likely to have contributed to the sinking of the Ocean Ranger [383]. Summarised, all these techniques have shortcomings. This is captured very well by other authors such as Basheer et al.: "it is not possible to analyse all the aspects of a system using any single technique" [374]. Similarly, Taebi et al. mentioned that preventable accidents, such as the Fukushima Daichii incident, are a sobering warning against overconfidence in hazard prediction [379]. This is especially critical, as several methods assume perfect human performance, which is not realistic on ships [379], [380]. Most of these methods have the possibility of taking the human factor in account, even though in reality this is often omitted. For example, Skogdalen et al. [384] researched whether QRAs, in the oil and gas industry, took into account human and organizational factors, as most accidents have a social, administrative or managerial origin [372]. They found that none of the QRAs reached the level at which human and organizational factors are taken into account best. Most did not take the human and organisational factors into account (5 out of 15), or only explained it to a limited extent (8 out of 15) [384]. It is challenging to systematically include quantitative estimates on the impact of human factors and organisational impacts on failure in a QRA [384].

8.3 DESIGNING FOR SAFETY WHEN USING ALTERNATIVE FUELS

Mentioning what is wrong with previous methods is not difficult, nor is it innovative or particularly useful. Moving forward, towards how safety can be incorporated in the design phase of a ship fueled by an alternative fuel is much more relevant. The maritime industry can learn from other sectors, such as aviation and chemical industry and how they have incorporated safety in their respective designs. Yet, more importantly, the field of safety science offers many lessons on how designs affect safety.

The use of hydrogen carriers inevitably complicates the design. Figure 8.1 gives an overview of the alternative process, which now incorporates specialised fuel preparations and additional tanks to store the spent fuel, next to the energy converter (e.g. an internal combustion engine or fuel cell) to deliver the required power to the ship. Especially the tanks and the fuel preparation unit come with many unknowns, as these are likely new technology on this scale and in this environment.

This section will move from the shortcomings of the previously mentioned methods of assessing safety and risk, towards potential ways of incorporating safety science to deal with safety in a different way, with a focus on hydrogen carriers as alternative fuels onboard ships.

8.3.1 FROM QUANTIFYING RISKS TO AN INTEGRAL APPROACH

Currently, the results of a QRA or similar safety tool often form the basis of risk management [384]. A QRA should also be used to reveal the status of the so-called safety barriers: means that prevent, control or mitigate undesired events or accidents [372], [384]. These barriers can be physical, such as cofferdams, but this is not necessary. However, quantification methods, such as QRAs, face comparable challenges when applied during the design phase, especially when alternative fuels are incorporated. First of all, as mentioned

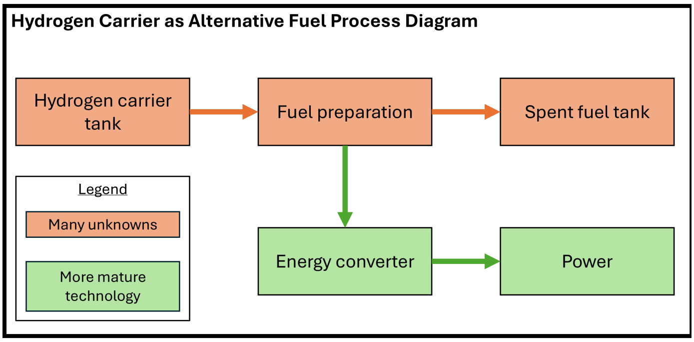

Figure 8.1: Hydrogen carrier process diagram, including indication which technologies are mature and less-mature

previously, they depend on data from previous accidents, which is unlikely to be available for new technology like hydrogen carriers. This can result in large uncertainties in a QRA. Secondly, QRAs also suffer from underreporting of non-lethal accidents. Accidents that are only minor, are often not reported as it is not deemed significant [372]. Another issue with the QRA is the illusion of equal comparison: when everything is expressed as numbers, it appears as though these can be compared. However, this often leads to confusion among non-experts and difficult ethical decisions. This becomes more apparent with fuels that already have a certain reputation with the public, such as ammonia. Even though orders for ships that can be powered by ammonia are plenty [385], [386], public opinion is very much against it [387]. At least the UK public prefers virtually any other fuel, including nuclear and heavy fuel oil, over the usage of ammonia [387].

Finally, the most important issue with the QRA for alternative fuels is the inclusion of human factors, which is not adequately considered. However, human performance and behaviour gain increased importance when handling new and potentially hazardous fuels. Another issue arises with a common solution for the problem of the human factor: automation. Often, engineers see automation as enhancing the safety of a process, as using automation is thought to lead to cause-and-effect relationships, which in turn can be quantified [372]. However, automation comes with multiple issues. Directly related to the QRA is the following: when significantly changing a process, which can occur when using e.g. robots, it does not necessarily result in less incidents, it might even result in a less well-founded QRA as the dominant accident scenarios might change [372]. As using alternative fuels already significantly alters the system, with many lesser-known process steps (as visible in figure 8.1), the dominant accident scenarios will likely already change compared to the conventional process. This will also increase the chance of completely overlooking accident scenarios, which is not unheard of [379]. Adding automation to this, changing it even further, will likely result in different dominant accident scenarios. Additionally, people learn by trial and error, by making mistakes and taking risks. These learnings are needed to understand the entire process and adequately respond to accidents [372].

Consequently, it is not possible to assess the safety of a hydrogen carrier system to the highest detail in the design stage momentarily using the current methods, as several problems arise due to the uncertainties inherent to the process. Combined, this shows that estimating all risks in advance in detail may not be possible when using alternative fuels such as hydrogen carriers on ships, due to the many complications and unknowns they bring. The Collingridge dilemma is relevant here: the more we know, so the further we are in the design phase, the more we will know of the related risks, but our control over it all grows less [379]. Thus, we have to move on from this rational image of trying to find an integral approach towards a more contextual picture.

8.3.2 FROM A RATIONAL IMAGE TO A CONTEXTUAL PICTURE: INCORPORATING THE HUMAN FACTOR

Even though the engineering approach is to reduce the human influence and presence as much as possible, especially when using "dangerous" alternative fuels, such as ammonia, this may not directly be the perfect course [372]. The most important reasoning for this is that humans are good at quick problem-solving, not repetitive tasks. Additionally, as mentioned previously, humans learn by trial and error, and have several ways to learn. For example, humans should not learn from books how to react in emergency situations, but from experience and thus, practising these kind of situations [380]. If the human factor is completely removed from the system, the human's understanding of the system will be reduced. This is highly problematic in case humans are expected to solve the problem [380]. Yet, it is true that humans, or better worded the human and operational factor, is the cause of many accidents.

However, this does not necessarily mean that a process with many possibly dangerous factors is directly correlating to many accidents. An example as mentioned by [372] tells of an industrial location, where everything could hurt people, yet with an exceptionally high amount of days without accidents. So, it is possible for humans to operate in dangerous conditions without failure. Incorporating the human factor in the design of a ship, especially a ship with such complex and possibly dangerous additions as when using hydrogen carriers as alternative fuels, is thus of utmost importance.

When entering the human in design, it is important to take into account the human's good and bad qualities. Humans have physical and mental limitations. Physical limitations should be incorporated at all times, and are, for example, health hazards or (very) heavy lifting. Time-critical operations are better avoided as well. Human operation in rooms with high temperatures, high noise levels or strong vibrations, such as in an engine room, is also detrimental to human functioning. Other human limitations are mental. Humans do not do well with repetition, so that should be avoided. Besides, over- and understimulation of human senses should be prevented. Additionally, in the maritime domain, 71% of the errors involving humans are caused by a lack of situational awareness [380]. Situational awareness has gained a lot of attention in the aviation sector, from which the maritime industry could benefit [380]. Situational awareness should not be confused with the awareness of danger: even people with high motivation and the highest degree of safety awareness will have accidents [388]. Improving motivation and awareness is also a dead-end: much has been done on that level, and it is assumed not much more is possible [388]. The most effective way to improve safety is by changing the environment [388]. The focus should be on ensuring that all technology is designed from a human-centred perspective and aligned with maritime needs [380]. For example, when alarms are used, it should be instantly clear which alarm is going off, which is not always the case [380]. A proper work environment has to be created [388]. Other factors are more operational, such as avoiding victim blaming and catering the training and inspection to the specific ship, instead of having general employee training [372]. Figure 8.2 gives an overview of both the design and operational aspects of incorporating the human factor to enhance the safety of ships.

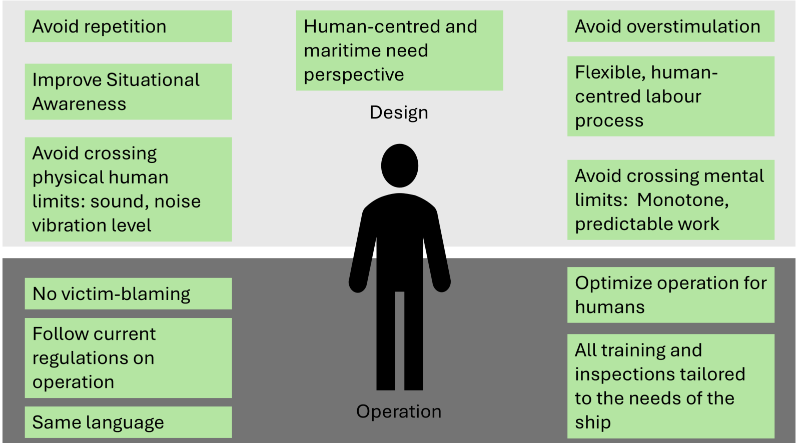

Figure 8.2: How to design with keeping humans in mind

8.3.3 HOW TO DEAL WITH UNCERTAINTIES

Finally, uncertainty will still exist even when incorporating the human factor during the design and operation. Hindsight cannot save us [383], we have to look ahead into the unknown. Engineers often try to make the system foolproof and in shipping especially changing the hardware is a traditional approach to solving a problem, even if that problem was the result of human error [388]. However, there are several issues with this approach.

First of all, behaviour of humans can be unexpected. Secondly, people will try to look for loopholes to make their life easier, yet undermining the foolproofness of the system [388]. Trying to make a system foolproof is thus expensive, but with low effect. Additionally, when adding complexity, foolproofing is even more difficult. It is clear that complex interactive processes and tight coupling of steps make accidents inevitable and, worse, unforeseen by designers nor understood by operators [372]. Most of the principles to operating high-reliability organisations lie on operational level. Examples are the detection of small failures anywhere or the differentiation of categories [381]. Basically all accidents have had some form of precursor incidents happening before the actual accident [383].

However, one of the principles is related to the design of the process, the principle of sensitivity to operations [381]. The aim of this principle is to set apart the work itself, seeing what we are doing instead of focussing on intentions or designs [381]. This can be attributed to the resilience of the system: a system that can continue to function as required, even after a serious incident has occurred [381]. The function as required does not mean the system is completely intact; the system just has to be able to continue the required operations, albeit in a degraded form [381].

In practical terms, in the design we should stimulate a system with graceful degradation and avoid a system performance with a single point of failure. Interestingly, the alternative fuel system configurations give these opportunities: high numbers of cells in batteries and stacks in fuel cells give graceful degradation options, where traditional internal combustion engines might fail with one driving gear failure. In real life, with all its uncertainties and unexpected events, coping with the unexpected and having an anticipatory mind-set is more important than anticipating occurrences [381]. Precise identification of issues is not always possible in an emergency situation, so a combination of keeping errors checked, improvising such that the system keeps functioning (even if only minimally) and absorbing change while persisting is required [381].

8.4 INSIGHTS FOR SAFE VESSEL DESIGN

Many steps can be taken to improve the safety of a vessel starting in the design process. This section outlines several methods for enhancing safety, as summarised in figure 8.3. On the left side of the figure are the measures that should always be taken. These standard measures are very relevant, and are the fist steps to control safety during design [380]. The first step is the removal of the problem. If an alternative fuel is such an extent unsafe in a certain context, it should not be used at all. Secondly, if a certain fuel is absolutely necessary, yet not entirely safe, a barrier should be put around it to avoid incidents outside its area of operation. These two steps have to be taken during the earlier design process, while the third step, implementation of warnings, can be taken later on.

However, only taking these steps is not sufficient. Robust design of components and all included control systems is required as well. Especially, the disturbance-free operation of critical infrastructure needs to be ensured and

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For the full reasoning, see the original paper. The section “Designing for Safe and More Complex Control Systems” was written by Charlotte Löffler.

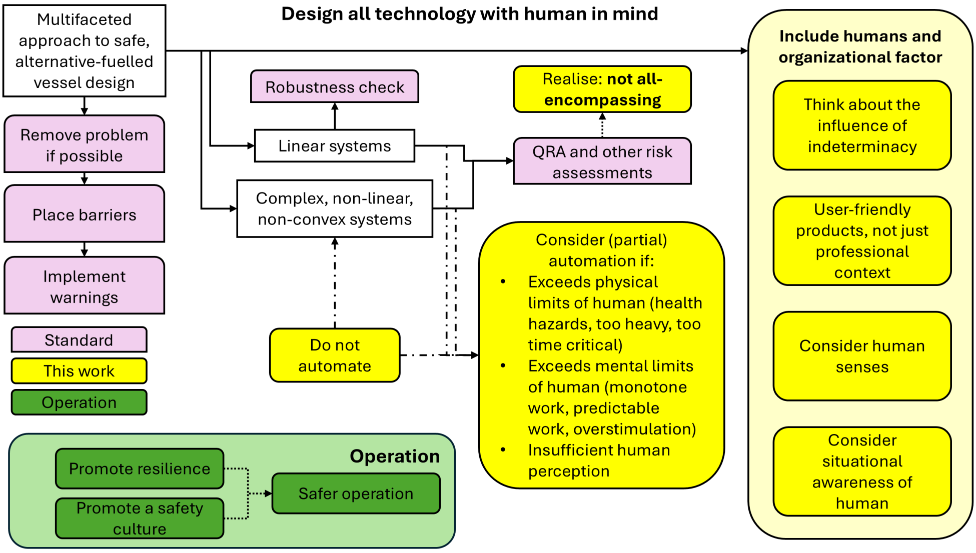

Figure 8.3: Insights in how to design a safe, alternative-fuelled vessel using a multifaceted approach

designed appropriately. While this is easier to ensure for simple component controls, it presents a challenge when moving towards autonomous or advanced control approaches. When implementing the latter, proving their robustness under operation gets more difficult. For optimization-based control approaches the difficulty lies in the mathematical complexity of the system. Therefore, directly proving that an advanced control of an operation is safe in the design process might not be possible, as is visible in figure 8.3: a clear distinction between linear systems and complex, non-linear and non-convex systems is made.

Another option to prove the fail-safety of advanced control of the vessel operation is the more time-consuming trial-and-error for the algorithm. This way, a statistical approach could be used to identify the spread of expected outputs for a set of inputs. However, using this approach allows for an understanding of the algorithms accuracy, but cannot completely neglect the possibility of the algorithm ending up in a not-desired solution. Still, it can be considered a first step towards the application of advanced control algorithms that can improve the safety of the human and operation. To enhance safety, the focus should lie on minimizing the necessary complexity of the system during the design process. Even though this might lead into a higher fuel usage, it helps create more reliable and failproof control systems. This all contributes to a vessel that is designed as safe as possible; however all these procedures will not result in a foolproof, 100% safe ship. In addition, besides the three main steps, the overall technical process should still be evaluated using current methods as mentioned in table 8.1. However, the precaution should exist that these are limited and additional investigation is required. Additionally, the human factor should be taken into account within these risk assessments.

Moreover, the procedures focus mainly on the safety of the ship, yet the human factor is extremely important, too. To make the ship more safe while incorporating humans, the human operator should be taken into account directly during the design phase. Processes should be designed such that humans do what they are good at: varied tasks, that are within the scope of the human capability, without crossing physical or mental limits of humans. Linear systems are often easier to automate than complex systems. Automating everything is not the solution, but automating certain tasks is part of the solution. Tasks that should be automated are for example tasks that are not compatible with the human physics, such as tasks that threaten human health, or human lives, tasks that exceed the physical limits (which may be legally limited) of humans, and tasks for which humans are too slow. Other tasks to automate are those that do not comply with the human mind. Examples are monotone or predictable work, as well as overstimulation of the human mind by data flooding. Finally, for some tasks the human perception is insufficient. A major sidenote to this, is that tasks or processes that are highly influential for the safety on board, should not be automated completely: humans are much better at responding and (creatively) fixing problems of processes that they know much about, than if they have to deal with less-familiar processes.

Besides, during design phase, human and operational factors should be considered. Indeterminacy (humans not using systems as envisioned) should be taken into account, for example by multiple simulations with the process and humans, especially in less-than-ideal situations, but also in common situations. Additionally, products should be designed user-friendly, something that was often not the case in the maritime industry [380]. Finally, the situational awareness of humans has to be taken into account within design.

During the design phase, the two most important things to acknowledge are the following. First of all, no design is inherently safe and the uncertain will always happen. Secondly, design is only part of the whole process, operation is at least equally, if not more, important for safety.

8.4.1 OPERATION

Figure 8.3 has an additional part, which has not been discussed until now: the operational factor. Even though the operation of the ship is not in the scope of this research, some of the key-insights of safety science on how and why extremely dangerous and complex workplaces can have very limited (to even no) accidents are discussed here.

Safe operation is one of the most important ways to enhance safety [372], [389]. The operational aspects and, as a result, whether a system is error-inducing, error-neutral or error-reducing, is often considered more relevant to safety than tightly coupled or highly complex systems [389]. A good, safe operation and a safety-focussed operation will result in a safer environment, yet unfortunately safety and efficiency are often regarded as opposing forces, especially in the shipping industry [389], [390]. Cost-efficient operation is part of organisational behaviour [372]. However, safety and (cost)-efficiency are not necessarily opposites, process intensification in chemical engineering and management, for example, does not have safety as prime target, yet results in safer processes regardless [372].

A large part of safe operation is the removal of victim blaming [372], which is often prominent in error-inducing systems [389]. Companies that are likely to dismiss, punish and blame people, are less likely to learn from incidents and accidents [372]. The international safety management code (ISM)-code from the IMO supports this [380], [391]. The ISM code specifically states that good safety management is commitment from the top [391]. Additionally, the ISM code requires companies to develop safety management systems and preparations for emergencies, as well as requiring companies to report incidents and accidents [391]. However, a drawback of this code is that whilst a shipping organisation may be compliant to the ISM code, it does not mean that the system is actually effective [380]. Not only is it hard for organisations and individuals to adhere to the code, the motivation to comply to the code also varies [380].

In general, the shipping sector has for long been regarded as an error-inducing system [389]. Despite this observation being older, made in 1986, it unfortunately remains relevant today. Error-prone systems are not easily changed, despite regulations like the ISM-code [380], [389], [391]. The social organisation, economic pressure, structure of the industry, influence of insurance companies and difficulties of national and international regulations (which are often both relevant), still operate in such a way to resist solutions to reduce errors [389]. An example of how all these come together in one accident is the sinking of El Faro in 2015. El Faro disappeared with all hands as it sailed through the Caribbean in 2015 [392]. The main actions identified were the decision (by the captain) to sail in close proximity to a hurricane and not complying to the ISM code, as not all the material was in good order and no necessary shoreside support was available [392]. This only underscores the difficulty of change, as the underlying, social organisational issues have been known for many years already [389].

Often mentioned as problematic are the different cultures of the crew on board ships [372], [389], [390]. However, this appears to be a relative weak argument, as the aviation sector has similarly diverse crews, yet does not see this as a problem [390]. In the aviation sector, the protocols are of such a standard that local culture is not deemed to be relevant [390]. This is one of many operational differences between the shipping and aviation industry, where the aviation industry can be regarded as much further ahead safety-wise [390]. This also highlights the difference between error-inducing and error-reducing systems: the aviation system is an error-reducing system and thus language is less of a problem [389]. However, lessons can still be learned from the aviation system: especially the training (including human factor training), safety reports, automation, situation awareness and implementation of a just culture and a safety culture are mentioned as very promising [390]. Perrow's examination of the more distant past—spanning the late 19th to early 20th century—reveals a rather discouraging continuity, as he notes little substantive progress during that period [389]. More than three decades later, a similar assessment may still hold: operational advancements remain limited, and implementing substantial change continues to pose significant challenges.

8.5 CONCLUSION

Safety is of high importance in the maritime sector. Many methods are used to assess the safety of ships. However, current methods often overlook the human factor, which in turn is regarded as the main cause of many maritime accidents. Safety science can be used to avoid this.

Safety science teaches us that human failure is often the result of design, organisational or operational problems, and not a cause on its own. Taking human failure into account is difficult, due to a lack of data, scenario uncertainty, indeterminacy and more. Due to the uncertainty characterised by future accidents and incidents, it is impossible to use a watertight approach to designing a safe vessel. Yet, good design can account for a vessel that is at least safer.

When looking from a safety science perspective, the following becomes clear. There are several standard steps, which should always be taken. These steps are: removing problems, placing barriers and implementation of warnings. Additionally, uncertainty needs to be embraced and complex interactive processes and tight coupling of steps should be avoided or simplified. The system's sensitivity to incidents should be reduced, part of which can be assessed by checking the robustness of the system.

However, all this only covers part of enhancing the safety. To optimally design a safe vessel, all systems, processes and technology have to be designed with the human in mind. Despite all these measures, design is only one part; the operation of the vessel is equally important in enhancing its safety. A safe working culture with a focus on safety and less on efficiency is required for safer ships. The shipping industry has much to learn here, particularly from the field of safety science, which emphasizes systemic thinking, resilience, and learning from near-misses as well as failures.

Finally, the notion that nothing can be inherently safe and that accidents can always happen is something that should always be in the back of everybody's mind: expect the unexpected. That, combined with optimal human and machine collaboration will result in safer vessels and thus, a safer shipping sector.

Safety & Sustainability

9

SAFETY OF ALTERNATIVE FUELS

> *"It is important to draw wisdom from*
> *many different places. If you take it from only*
> *one place, it becomes rigid and stale."*
> — Uncle Iroh, *Avatar: The Last Airbender*

CHAPTER SUMMARY

Alternative fuels will strongly influence many values, including the multifaceted values of safety and sustainability. This chapter presents a value-based framework for evaluating hydrogen carriers by examining their effects on subvalues such as environmental performance, crew and port safety, survivability, long-term viability, justice, public safety, and economic impact. Because the relevance of each subvalue differs across maritime environments, the framework provides context-specific assessments rather than universal rankings. Instead of reducing complex trade-offs, the framework enables qualitative comparisons within individual values. The framework is designed to be transparent and flexible, yet reflects normative choices. Application of the framework reveals substantial variation across carriers and criteria. Many carriers exhibit mixed or uncertain aspects, with no clear "best" option emerging. By making underlying assumptions explicit and highlighting context-dependent trade-offs, the framework helps bridge gaps between technical, regulatory, and societal perspectives in the maritime fuel transition.

9.1 INTRODUCTION

The use of alternative fuels for ships calls into question long-standing assumptions about maritime safety: what was once assumed to remain stable and universally applicable must now be reassessed in light of new fuel types and their varied risks. Additionally, new dimensions are brought to the forefront, including questions of sustainability, fuel availability and standardization, and implications for global market dynamics [41]. The results of this transition and its additional dimensions are visible in the regulatory sphere as well as in the scientific literature; the IMO, for example, is transitioning from prescriptive rules to goal-based standards (GBS), creating a more flexible regulatory environment to safely accommodate new fuel types [292]. This regulatory flexibility, however, raises questions about how different fuel options should be valued, evaluated and compared.

The maritime sector presents a unique combination of operational, regulatory, and value-based considerations that current frameworks struggle to address comprehensively. The GBS does demonstrate a broader openness to innovation. However, delegating more freedom to ship designers, while simultaneously increasing complexity reveals a deeper, underlying issue that is intrinsically linked to the multiple values that are significant when introducing new fuels. The multitude of values involved, including but not limited to safety, sustainability and economics, inevitably leads to value conflicts [393]. However, the issue is more fundamental; these values are rarely made explicit by regulators such as the IMO, which exacerbates these conflicts and prevents their proper resolution. On the other hand, these values are operationalised, ranked and weighted by scientific literature, often using stakeholders [33], [34], [35]. This lack of explicit value articulation by regulators complicates stakeholder dialogue, creates uncertainty in regulatory decision-making, and makes it more difficult to systematically address tensions between competing priorities such as safety, sustainability, and economic viability. Therefore, it is essential to identify and critically reflect upon these values to ensure a robust, technically sound energy transition in the maritime sector. This highlights the need to not only identify the relevant values impacted by such a transition, but

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This chapter is based on the following article:
E.S. van Rheenen, K. Visser, A.A. Kana, O.E. Popa, "A Value-Conflict Design Approach to Evaluating Hydrogen Carriers for Maritime Use: Safety and Sustainability in Focus, " under review at Maritime and Transport Research as of 2025

to develop methods that can meaningfully incorporate them into regulatory and design contexts.

Bridging this gap requires new qualitative, analytical approaches. Recognising the impobrtance of explicit value consideration and the resulting value conflicts is only the first step; translating this insight into practical decision-making demands appropriate analytical frameworks. To make well-informed choices about alternative fuels for maritime use, there is a need for a structured approach that enables broad and context-sensitive evaluation in the early design phase. Such early evaluations are particularly important in the context of maritime infrastructure - a domain particularly prone to long-term path dependency and technological lock-in [394]. Aside from this, arguments have recently been made in the field of responsible innovation and philosophy of technology that integrating value-conflicts in the design of new technologies is a moral imperative arising from the need to pay due heed to undervalued scenarios and stakeholder groups [395], [396], [397], [398]. While it is not always possible to satisfy all values simultaneously and equally, a broader analytical view can contribute to a better understanding of the intricate dynamics between values served and values disserved [399].

This chapter makes two contributions to better connect values and policy. First, it introduces a visual evaluation framework that links relevant value dimensions to the specific regulatory and operational environments in which ships function. Second, it demonstrates the utility of this framework by applying it to the case of hydrogen-based alternative fuels in maritime contexts. In this application, particular attention is given to hydrogen carriers such as SB and LOHCs due to their novelty, early-stage development, and potential. They present unique value trade-offs that are particularly suited to demonstrate the framework's ability to handle complex, multi-dimensional assessments, while not requiring large amounts of information, as these hydrogen carriers are emerging technologies and relatively little is known about them, as compared to more mature fuels as ammonia or methanol. This framework is essential because, without explicit evaluation across different fuel options, important values may be overlooked or underestimated. As each fuel likely impacts value dimensions differently, some may strongly affect certain values while leaving others untouched. To obtain a complete overview of these varied impacts and trade-offs, an integrated perspective that systematically examines all relevant fuels is necessary.

For practical purposes and to ensure the framework remains manageable and actionable, this study focuses specifically on safety and sustainability as the primary value dimensions. Safety and sustainability are considered among the most important criteria upon which hydrogen carriers are to be judged [400]. Both will be defined in detail later. This focused approach allows for a concrete demonstration of the framework's utility while maintaining analytical depth and practical applicability. The framework enables comparative assessment that reflects diverse interpretations of these key values across different maritime settings, thereby informing early-stage fuel selection in a way that aligns with both practical and normative considerations.

9.2 METHOD - FROM FRAMEWORK DEVELOPMENT TO ASSESSMENT

This section outlines the methodological steps taken to develop and apply an argumentative approach for evaluating hydrogen carriers in the maritime context. Figure 9.1 gives an overview of these steps. The goal is to create a structured, value-informed evaluation tool that can support early-stage decision-making, where trade-offs between key value-sets, such as safety,

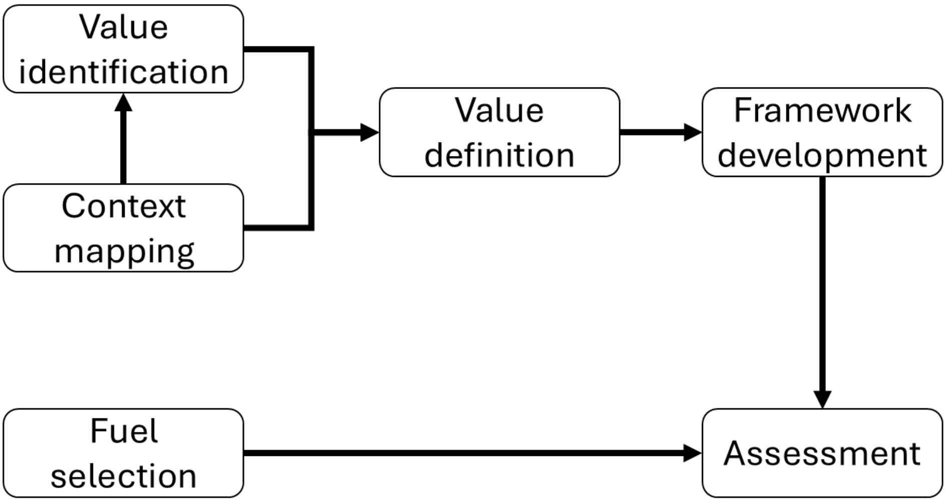

Figure 9.1: Overview of steps taken for framework development and assessment

sustainability and economic viability, are still flexible but impactful. These values are defined in the following section, prior to the development of the framework.

The evaluation framework is developed through a systematic process, beginning with the identification of values and subvalues relevant to the assessment of hydrogen carriers in maritime applications. These values can be geographically dependent, and emerge from a contextual analysis of the specific operational and regulatory environments in which fuels are deployed. A geographical lens not only helps identify these values but also shapes their definition. Once identified, the values are structured into a coherent argumentative framework. Potential value conflicts and trade-offs between competing objectives are discussed as part of this process.

Simultaneously, the hydrogen carriers selected for evaluation in this study are identified and examined. This includes establishing their technical characteristics and their properties relevant for safety, sustainability, and techno-economic analysis. Finally, the framework is applied to assess each hydrogen carrier, enabling a systematic comparison of their performance across the identified value dimensions. The results are presented in a structured, side-by-side format.

Expert interviews were conducted to validate the theoretical framework developed. Maritime sector professionals with expertise in alternative fuels were interviewed to assess the framework's comprehensiveness and relevance. The expert group included representatives from inland shipping, naval forces, industry, policymakers, and academia. These interviews informed the framework development but are not reported as separate findings.

9.3 FRAMEWORK FOR EVALUATING VALUE IMPACT

The shipping industry faces significant challenges when implementing alternative fuels. Industry experts evaluate these fuels using specific criteria, including energy density, production costs, and operational feasibility. However, beneath these technical discussions lie two fundamental value sets that often conflict: safety and sustainability.

This tension between safety and sustainability creates concrete dilemmas for decision-makers. Safety priorities may favour proven but less environmentally friendly options, while sustainability goals push toward newer, potentially riskier alternatives. Understanding this conflict is essential because it shapes how the industry approaches fuel selection and determines which alternatives gain adoption.

Both safety and sustainability are multi-faceted value sets with different aspects. Defining safety and sustainability can vary dramatically across different maritime spaces. Their interpretation varies depending on where and how impacts occur: on board, at sea, in port, or even beyond maritime boundaries [312], [401], [402]. To reflect this, values are considered in relation to distinct maritime environments, each with its own risks, responsibilities, and regulatory relevance. The spatial structure is illustrated in Figure 9.2. The figure places the ship at the centre of a layered spatial structure that includes the marine environment, port infrastructure, nearby urban areas, and broader global systems.

This section aims to develop and operationalise a framework for evaluating the multi-faceted nature of safety and sustainability in maritime alternative fuel adoption. By identifying values within each principal value set, the framework provides insight into how alternative fuels influence specific dimensions of safety and sustainability, enabling more nuanced evaluation of fuel options. The section is structured as follows: Subsection 9.3.1 identifies and defines these values within their maritime contexts. Subsection 9.3.2 presents an overview of the complete framework. Subsections 9.3.3 and 9.3.4 operationalise the framework by focusing on the most critical values, providing practical direction for evaluation and implementation.

9.3.1 DEFINING VALUES IN CONTEXT

This subsection identifies and defines safety and sustainability values within the abovementioned maritime contexts. Given that these values manifest differently across the spatial environments shown in Figure 9.2, the analysis takes a two-step approach: first, identifying the core values and their constituent values that emerge from maritime literature and industry practice, then examining how these operate within different spatial contexts.

Identifying values is not a straightforward task. To begin, it is important to consider the overarching values of safety, typically defined as the protection of human life [403], and sustainability, often defined as a method of using a resource without permanently damaging or depleting that resource [404]. With these general definitions in mind, the specific environments relevant to the maritime sector are considered. Examining the situations that may arise

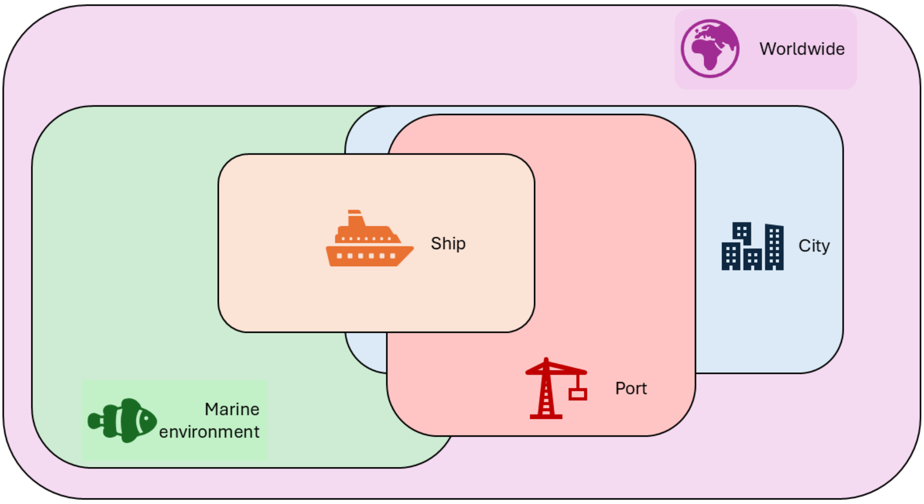

Figure 9.2: Relevant Environments for the Maritime Sector

within each of these environments, provides insight into how these situations influence or challenge the values of safety and sustainability. This approach is similar to how the IMO has historically developed its safety conventions: beginning with a concrete incident, such as the sinking of the Titanic. This sinking can be used to identify the core value at stake: human life. To prevent this from happening again, the Safety of Life at Sea convention (SOLAS) came into action [282]. While this analysis will not prescribe specific measures, it does follow a similar logic by using environment-specific scenarios to identify which values are at play.

For the value set of safety, the extensive body of IMO conventions and regulations is used as a basis. Unlike safety, which is tightly regulated by IMO conventions, sustainability involves a broader set of ethical, social, and technological considerations. For sustainability, this involves exploring how renewable resources intersect with technological developments, such as alternative fuels, and identifying the values affected in this context. The sustainability aspects are discussed in greater detail in Section 9.3.1.

Charting Key Safety Values

The IMO operationalises safety through specific standards and requirements in different conventions, such as SOLAS and MARPOL (Marine Pollution) and protocols like the HNS protocol (Hazardous and Noxious Substances) [401]. Even though this approach is functional, rather than definitional, it can still be used to define the concept of safety and find its specific values. From these conventions, it follows that the IMO mainly focuses on the safety of humans - either crew or passengers. Most conventions deal with the prevention of harm to humans, directly or indirectly. The exception is MARPOL and the other conventions relating to prevention of marine pollution. Polluted seas negatively influence the health of people living around them, as well as the health of people having to work on the seas. Thus, the safety of the marine environment can be added here as well. The environmental impact of a fuel can manifest at both local and global scales; fuels that dissipate quickly may only have local effects, while fuels that are extremely persistent in a maritime environment may have influence all over the world. Additionally, fires may alter fuel chemistry (e.g. through thermolysis or pyrolysis), producing more harmful by-products.

However, this is just one of the many values that will be impacted by the shift to alternative fuels. When introducing alternative fuels, the health of the crew (and passengers) may be affected in several ways. First, working conditions can change. While the workplace should not pose an immediate threat to crew members, poor working conditions can impact long-term safety. Closely related is the safety of the crew. Here, the focus shifts from the environment to the people themselves. The aim is to ensure that the introduction of alternative fuels does not create new hazards for those working with or around them. Importantly, what is harmful to the crew is not always harmful to the ship; however, what is harmful to the ship is likely influencing the health of the crew as well. The maritime industry refers to this as ship survivability: the vessel's ability to withstand severe onboard safety threats, such as a hull breach leading to water ingress, that directly influence the ship's integrity. Finally, the interaction between the ship and the port must be considered. Alternative fuels may require changes to port infrastructure, potentially altering the safety profile of fuel handling operations on shore.

Figure 9.3 gives an overview of the values that are part of safety; these values are directly influenced by the IMO and its regulations.

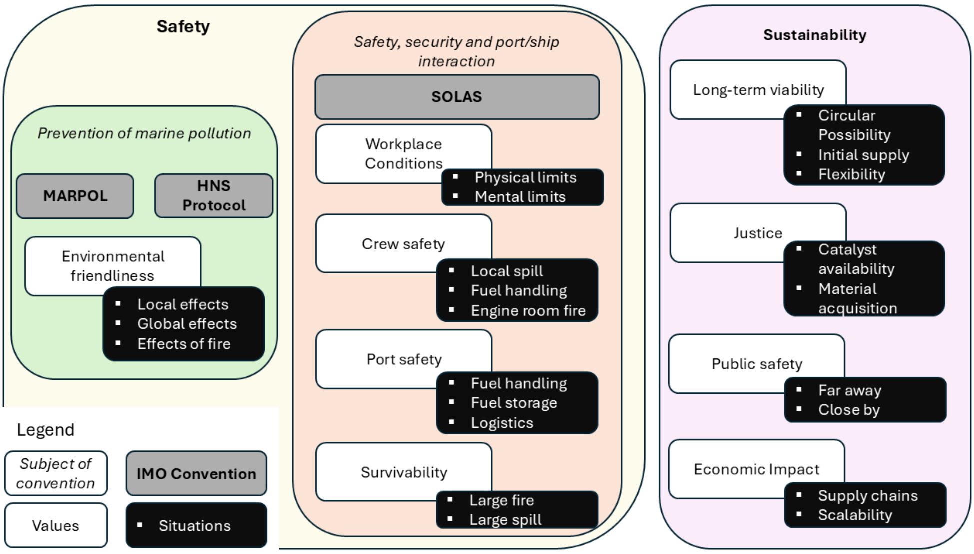

Figure 9.3: Values based on Safety and Sustainability, including relevant IMO conventions and examples used to derive these values

Charting Key Sustainability Values

Alternative fuel selection creates broader impacts beyond the IMO's direct regulatory control. The values affected are within the sphere of influence of the IMO and are mainly part of the sustainability value set. Different fuels will have different long-term, ethical effects and will be regarded differently by society. Although a complete, all-encompassing overview of values is impossible, the selected values adequately capture the notion of 'sustainability'. In this context, sustainability is defined as the requirement that a new fuel be viable for long-term use in an ethically responsible manner. These values support this definition:

Long-Term Viability Alternative fuels must remain viable over the entire operational lifetime of ships, which often exceeds 25 years. Because ships are produced in classes and retrofitting is costly and complex, fuels must be reliably available, supported by infrastructure, and accredited over decades. This also demands sustainable use of raw materials. Circular fuels should allow for efficient loading/unloading cycles, while non-circular fuels must rely on stable, low-impact production processes. Flexibility in recharging and low dependence on rare raw materials further increase long-term viability.

Finally, public perception plays a large role in long-term viability; even if a fuel appears to be perfect on paper, negative public acceptance can still hamper its applicability.

Justice The production of alternative fuels raises critical questions about global equity: Who controls production capacity? Where do raw materials come from? Who bears the environmental and social costs? The production, refinery and demand of raw materials are often disconnected [405]. The resulting complex supply chains are highly sensitive to geopolitical issues (such as the 2010 rare earth crisis) and have historically contributed to conflict [405], [406]. However, mining is not only shaped by geological and economic factors, but also by socio-political conditions, including labour rights and legal aspects [406]. Fair distribution of production capacity and ethical sourcing of materials are essential to avoid replicating existing geopolitical inequalities. Achieving justice in maritime transitions requires that the benefits and burdens of alternative fuel adoption be distributed equitably across all affected regions and communities.

Public health The IMO's conventions focus on safety aboard ships and protection of the marine environment, but do not regulate the health impacts of maritime operations on the general public or coastal communities. However, alternative fuel choices can significantly affect public health beyond the ship and port boundaries. For instance, ammonia's toxicity and hydrogen's explosiveness may endanger nearby communities in case of accidents or routine operations. Air quality impacts from different fuels can affect coastal populations, while fuel production processes may create health burdens in source regions. Even where technical risks are low, public perception of health risks can strongly influence community acceptance of new fuels. Fuels with minimal negative impact on public health are more likely to gain social acceptance and regulatory support from national and local authorities.

Economic Impact Alternative fuels can significantly disrupt existing maritime infrastructure and supply chains. Differences in physical state or handling requirements may require costly modifications to ships, ports, and procedures. These changes affect the economic feasibility and scalability of fuel adoption across the sector.

Definitions of values

Figure 9.3 gives an overview of the relevant IMO conventions, the values derived from those (which are connected to safety) and the values derived from sustainability, which are only influenced by the IMO. The figure also connects the values to their respective examples. In this section, these values will be explicitly and briefly defined in a maritime context.

Environmental Friendliness Environmental friendliness is the direct and long-term influence on the marine environment. While modern ships are highly reliable, fuel selection cannot assume perfect containment - even minor incidents may result in fuel spills with environmental consequences. Whether this is harmful depends on the fuel's aquatic ecotoxicity, the fuel's persistence, and the clean-up possibilities. The clean-up possibilities are based on the behaviour of the fuel in (sea)water.

Workplace Conditions The workplace conditions in ships depend on many things, some related to the exact fuel used. Workplace conditions can impact human safety in the long term; bad working conditions are detrimental in the end. The choice of fuel may affect the workplace condition as certain fuels require more delicate or complex equipment and operating systems, which may result in over-stimulation (or under-stimulation in case of large automation). Physically, alternative fuels such as powders may also impact the crew. Thus, in short, this value is defined as the influence of equipment used with alternative fuels as well as alternative fuels themselves on the workplace conditions of the crew.

Crew Safety Crew safety reflects the potential impact of a substance on human health during its use on board. This value is derived from established chemical safety classifications, such as the GHS, and regulatory testing frameworks like REACH. These sources provide standardised information on health hazards, forming the basis for understanding how a substance may affect crew members.

Port Safety The influence of alternative fuels on the health, safety and working conditions of people working in the port, as well as on the infrastructure of the port. This value is not necessarily ship-specific, even though the IMO governs it.

Survivability The survivability indicates the ability of the ship to stay afloat in an upright condition. Though, again, impacted by many processes on board, the choice of a fuel may influence this ability. This is mainly influenced by the alternative fuels' material properties, such as flammability and explosivity.

Long-term viability Sustainability is defined here as intergenerational justice; to keep the planet liveable with similar or higher standards of living for next generations. Again, to make this value more specific for alternative fuels in the maritime sector, a focus lies on the possibility of circularity, availability (and production process) of the initial supply and flexibility of recharging the alternative fuel. These properties are mainly influenced by production and recirculation processes, which define the life cycle of the alternative fuel.

Justice Justice addresses the equitable distribution of costs and benefits from alternative fuel adoption across different regions and populations. These new fuels can be seen as enabling a more balanced distribution of costs and benefit. The ideal future fuel should have a balanced distribution, with countries benefiting from the maritime industry also bearing the brunt of the price. Even if it is not possible to distribute this entirely evenly, the goal should be to get as close to a just distribution as possible. The production and recycling processes are very important in creating this new world.

Public Safety Public safety is defined as the influence of these alternative fuels on the health and safety of people not directly related to the shipping sector. Although many ships spend a considerable time far away from land, ships running on alternative fuels may affect public health and safety. Firstly, many ships are sailing inland or along the coasts; they are always near the human population. Additionally, even deep-sea ships have to load and unload at places. The effect of alternative fuels on public health and safety depends on the dispersivity of the fuel in air; will the fuel be able to travel (or have effects that travel) sufficient distance to affect the public?

Economic Impact Economic impact encompasses the financial consequences of alternative fuel adoption across ship, port, and supply chain levels. This includes direct costs such as ship modifications and fuel price differentials, infrastructure investments for fuel handling and storage, and broader supply chain scalability challenges. The economic viability of alternative fuels determines their adoption speed and market penetration across the maritime sector.

9.3.2 GENERAL FRAMEWORK FOR VALUE EVALUATION

Having derived values by examining the types of situations that may occur in different maritime environments, the next step is the development of a general framework. This framework formalises the connections between three key elements: **values**, **environments**, and **situations**. While values were initially identified through specific situations, their relevance often extends beyond their point of origin. The framework reflects this broader significance by mapping how values are connected not only to particular situations from which they were derived, but also to other environments and situations.

1. **Values** These are the values previously identified, grouped under either safety or sustainability.
2. **Environments** These refer to the context in which the maritime sector operates. The environments are defined in figure 9.2. In each environment, safety and sustainability may be affected
3. **Situations**: These are specific events or conditions that may occur within a given environment. For example, in the port environment, relevant situations may include fuel handling and storage. Some environments contain multiple sets of situations, which differ in terms of severity, frequency or impact.

Environments and situations are obviously closely connected. Even though certain situations are similar, or connected (such as large fires on board of ships and the influence of such a fire on the marine environment), this is not connected in the framework; separation is chosen as the influence on each of the environments is significantly different and the focus is placed more on the environments. The situations and values are also connected. These are always connected through environments, or sets of situations. A single situation is not connected to a value.

If multiple sets of situations occur at one environment, it may be that only one or two of these sets is connected to a value. For example, the physical and mental limits of humans on board is connected to the value of workplace conditions, as the other two sets of situations do not influence the workplace conditions. Similarly, only a large-scale spill or a large fire influence the survivability of the ship. Yet, all three sets of situations directly influence the safety of the crew.

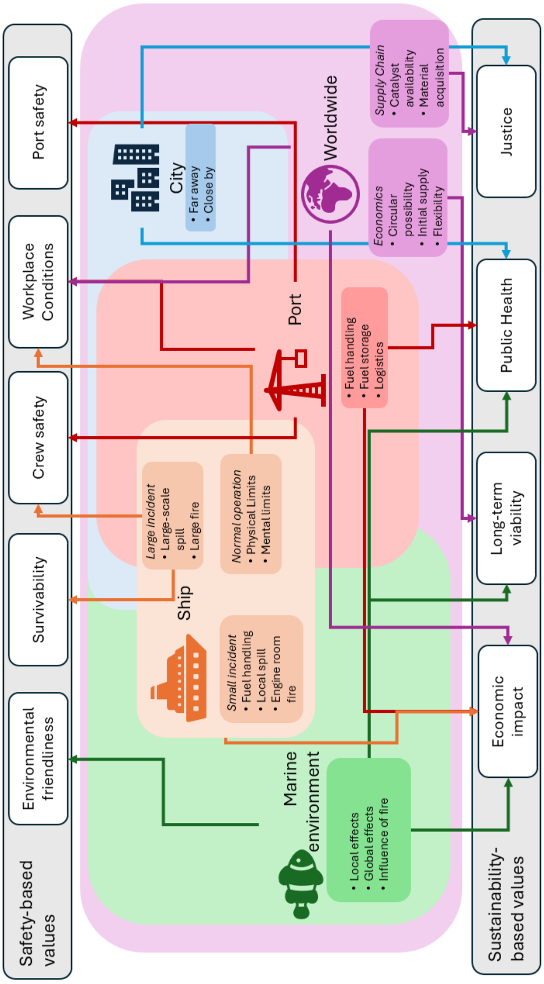

Figure 9.4: Framework to assess the safety and sustainability of hydrogen carriers as alternative fuels on ships. This framework makes use of a set of values, part of which derived directly from the International Maritime Organisation (IMO), part from other literature on safety and sustainability. These values are connected to specific maritime domains, called environments. These environments each have (sets of) examples of relevant situations that can occur in each of these environments. When a value is only connected to a subset of an environment, thus, to a situation in that environment, it is only relevant for this specific situation. When it is connected to the entire environment, it is relevant to all situations within that environment. For environments with only one type of situation, this is not applicable.

Using the connections in figure 9.4, the environments and situations connected to certain values can be identified. The figure highlights the complexity of evaluating safety and sustainability of alternative fuels; multiple values are at stake, and several, not always directly connected, relevant environments and situations will be influenced. Visualising these connections is a first step in assessing the safety and sustainability of an alternative fuel. Using a bottom-up approach, the analysis begins by examining each situation individually and considering what could happen when a specific fuel is involved. These situation-level evaluations can then be combined to understand the effects within an entire environment.

As the framework gives insight into which environment is connected to which value, the insight into what happens in an environment, enables determination on how outcomes in an environment impact the values, and how broader safety and sustainability goals are affected. Thus, alternative fuels can be assessed in a transparent, repeatable and value-sensitive way.

9.3.3 OPERATIONALISING VALUES IN THE CONTEXT OF MARITIME ALTERNATIVE FUELS

To evaluate each value, an assessment is made on how alternative fuels perform across a set of realistic maritime situations, using publicly available chemical databases (such as REACH and PubChem), supplemented with scientific literature where needed. The situations used in the assessment are those previously introduced and shown in figure 9.3. Figure 9.5 provides an overview of the key criteria needed to evaluate each value in its respective environment. The figure outlines the physical, chemical and operational factors that influence safety and sustainability outcomes in each environment.

For the **Marine Environment** local ecotoxicity, global persistence, and environmental effects of combustion are considered. Local effects are drawn from toxicity classifications; global effects are assessed using persistence data from the literature. For fire scenarios, decomposition products are identified and their environmental impact is assessed using the same sources.

Normal Operation The influence of alternative fuels on normal operation is hard to estimate. Real-world experience with many hydrogen carriers is extremely limited. So, the only way to judge normal operations is to use qualitative assessments based on likely fuel/energy system combinations and their expected effects on human workload and operational complexity.

Onboard the Ship: Small Incidents Safety risks are assessed for three main situations: normal handling, local spills, and engine room fires. Toxicity, physical state, flammability, and perceptibility are considered. Relevant data are taken from REACH, PubChem, and safety literature.

Onboard the Ship: Large Incidents How large fires and spills could compromise the ship's structural integrity is assessed here. Key parameters include explosivity, dispersivity, and combustion byproducts. Both the ignition risk and the severity of outcomes are considered.

Port Evaluation focuses on two aspects: changes to infrastructure (based on material handling requirements) and risks to port workers (similar to crew

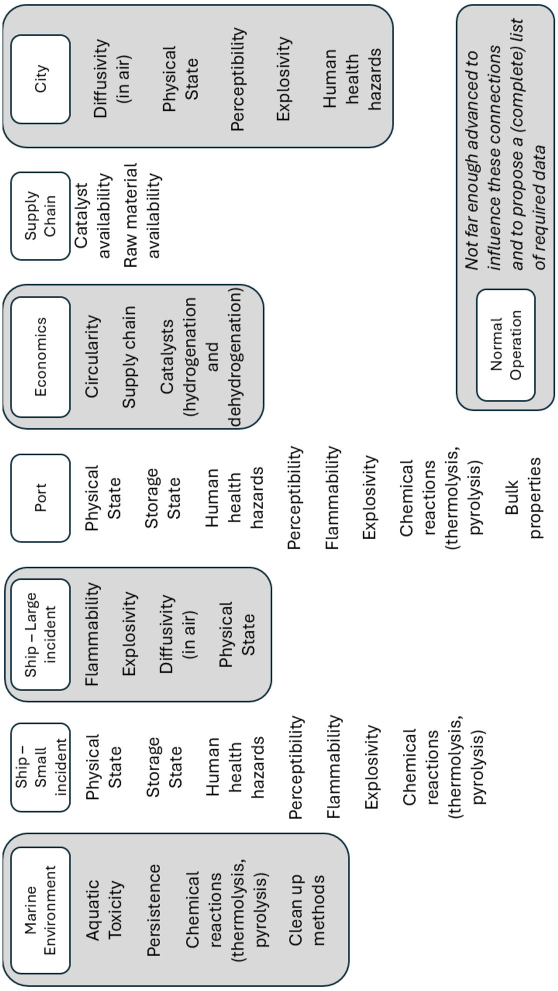

Figure 9.5: Overview of environment-specific factors that influence the evaluation of safety and sustainability values of alternative fuels. These include physical, chemical, and operational characteristics that may affect outcomes in each context.

safety, but considering different scales and spatial dynamics). Bulk material behaviour is considered where available.

Economics Circularity (including ease of recharging and degree of recyclability), the production impact of the initial fuel supply, and the flexibility in sourcing raw materials or hydrogen alternatives are assessed. More mature fuels generally offer more reliable data.

Supply Chain Potential justice concerns based on catalyst availability and material sourcing are evaluated. Literature on material origins, labour practices, and geopolitical implications informs this analysis.

City There is a distinction between near-field and far-field effects. The differences lies at approximately 100 m, with everything less being near-field. Toxicity and explosion risks are assessed using diffusivity, explosivity, and physical state. Heavier-than-air gases or highly explosive materials pose higher risks, especially in populated port areas.

9.3.4 FOCUS ON CERTAIN VALUES

The results of all fuels will mainly focus on survivability, crew safety, public health, long-term viability, environmental friendliness and port safety. Economic impact, workplace conditions, and justice are not taken into account. Here, the reasons for this are discussed.

Many alternative fuels have at most a medium technology readiness level. Only ammonia and methanol are currently being used as a fuel on a (limited) number of ships. These fuels are relatively old when compared with hydrogen carriers; the production processes for both are in a rather mature stage. Most alternative fuels are still in a rather immature state. There is a large difference between innovating alternative fuels and commercialising these alternative fuels [407]. Most hydrogen carriers are mainly under research at universities and research institutes; the practical implementations often lag behind. The supply chain and economic viability of new technologies are generally developed later [407], [408]. Not only does this pose the risk that supply chains may be unable to keep pace with future demand, but at earlier stages of development, supply chain data is often too limited—or entirely unavailable—to be of practical use. Most hydrogen carriers are still in the technical development phase. Current research primarily focuses on catalyst selection and the optimisation of hydrogenation and dehydrogenation processes, while practical applications receive comparatively less attention. Comprehensive assessments such as supply chain evaluations or life cycle assessments are rare, and in many cases entirely absent for the hydrogen carriers under investigation. As a result, certain components of this framework cannot yet be implemented in practice; data required to assess values such as economic impact and justice are extremely limited or non-existent at this stage. The technological development of these carriers is simply not mature enough for such considerations to be integrated into current research, let alone prioritised. Additionally, the current lack of data is accompanied by another, related issue. Even though supply chain and life cycle data may be available for certain fuels (such as ammonia and methanol), meaningful comparison remains difficult. Consequently, the implementation of this framework will need to focus on other value domains.

9.4 ILLUSTRATIVE CASE APPLICATIONS: EVALUATING HYDROGEN CARRIERS

To demonstrate the application of the evaluation tool, four hydrogen carriers were selected and compared to four reference fuels, all of which were introduced in Section 9.2. The hydrogen carriers were chosen for their diversity in terms of technological maturity (ranging from established to emerging), physical state (powder, liquid, gas), and associated safety characteristics. This selection demonstrates the broad applicability of the tool to a wide spectrum of alternative fuels. Moreover, the distinct characteristics of these carriers were expected to yield particularly insightful results. Ultimately, this exercise served as a proof of concept: it illustrated that, despite the inherent complexity, the tool can support a relative comparison of fuels—something that is otherwise extremely difficult to achieve. This comparison is carried out in the final subsection, where an initial attempt is made to assess and contrast the selected hydrogen carriers, without oversimplifying.

9.4.1 DBT

Figure 9.6 gives an overview of the tool as applied to DBT. The figure shows several outcomes. Within the figure, the relevant facts and data relative to this situation for DBT are discussed briefly. The first conclusion following from this figure is that DBT influences certain values in different ways; e.g. public health is influenced in a negative way and in a positive way. Additionally, it is also clear that within an environment, different situations can influence values in all three possibilities (positive, negative or neutral). The figure also clearly shows that DBT negatively influences a set of values, which are all related to the marine environment.

The influence of using DBT on the ship is positive for crew safety (1) and survivability (2); DBT is a relatively inert and safe substance, and even though it is invisible, it is only toxic if inhaled. Its high viscosity at room temperature also limits movement throughout the ship. The human-friendly characteristics

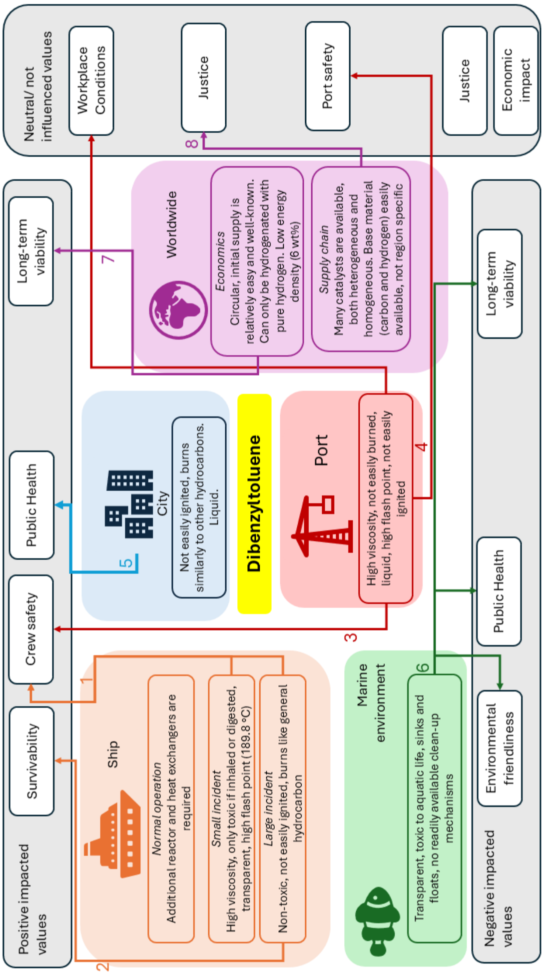

Figure 9.6: Tool applied to DBT. The values of justice and economic impact are not (always) connected, as there is not enough data available to connect certain environments and situations to these values in a meaningful way.

also affect the port crew's safety in a positive way (3), while their respective workplace conditions are unclear to be influenced. The general safety of the port is unlikely to be influenced; DBT is extremely similar to current fuels, so a switch would likely not make any difference (4). Additionally, DBT is unlikely to influence public health, which is positive (5).

The impact on the environment, as indicated by environmental friendliness, will likely be influenced negatively (6). DBT is transparent and toxic to aquatic life. Its spent fuel sinks, while the fuel itself will float. Clean-up is likely impossible, resulting in a negative impact on environmental friendliness. This also impacts public health in the long term - poisoning of sea life will result in poisoning of the entire (sea)food chain. Additionally, this impacts the long-term viability. Something that may be detrimental to the marine environment is not viable in the long term.

On a different, non-local scale, DBT has a positive influence on long-term viability (7). It is circular, and the initial supply process is well-known. A small downside is that it can only be hydrogenated with pure hydrogen; however, this should not be too much of an issue. Regarding the supply chain, there are many catalysts available, while the base materials are also easily available. Whether this will positively or negatively influence the value of justice is unknown; however, as the production processes and supply chain are not mature enough to be investigated to the required detail (8).

9.4.2 NEC

Figure 9.7 gives an overview of the framework applied to NEC. In general, NEC influences several values in a positive way, several in a negative way, and also many in a neutral way. Certain values are impacted in two different ways; both positive and negative, while for others, such as the economic impact, the effect cannot be predicted yet.

The influence of NEC on the ship itself is considered to be positive. Both the crew safety (1) and the survivability (2) are positively influenced, as NEC is non-toxic to humans, not easily ignited and has a high flashpoint.

This relates to additional safety for the crew in the port (3); they, too, are positively influenced by the relative inertness of NEC. Whether the safety of the port itself changes is hard to estimate, yet unlikely (4). NEC is relatively inert, but its spent fuel is solid at room temperatures. Thus, either it has to be heated to temperatures above 70°C, or a separate debunkering system has to be designed and applied. Because NEC is so inert, it is unlikely to negatively influence public health (5); thus, NEC is deemed to be more positively impacting this value than the reference case.

The influence of NEC within the marine environment, on the other hand, is rather negative. NEC is not visible in the ocean and thus hard to clean up. Its hydrogenated fuel will float, while its spent fuel may sink, depending on the surface tension. However, the major issue is its toxicity to aquatic life and its persistence: it may influence the marine environment negatively for a long time, resulting in a negative impact on the values environmental friendliness, public health and long-term viability (6).

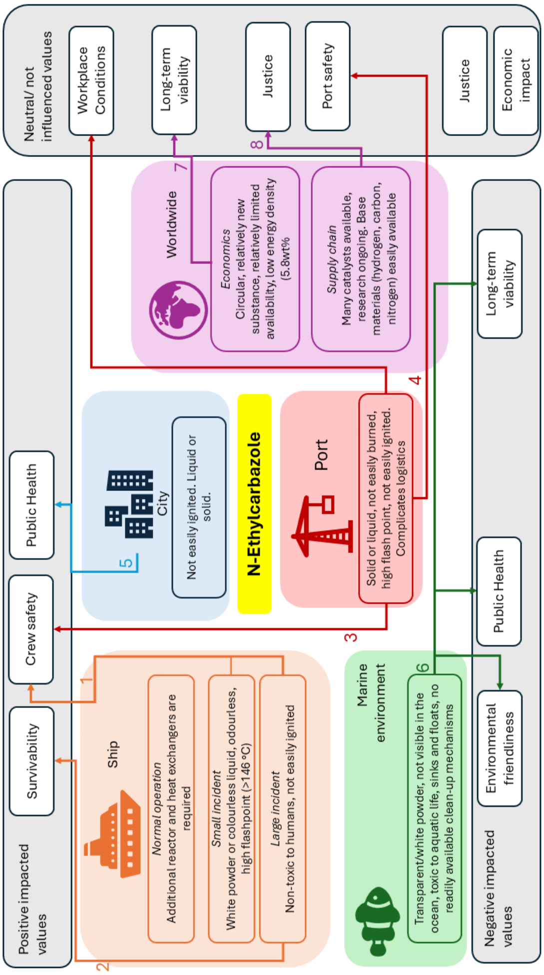

Figure 9.7: Framework applied to NEC

Finally, the worldwide influence of NEC is assumed to be rather neutral for the long-term viability and justice. At this moment, NEC is relatively new, has a low TRL and limited availability, limiting the economic long-term viability (7). Additionally, much research is going on within the supply chain. With many available catalysts and easily available base materials, it may be that justice (8) is positively influenced; however, a real assessment has to wait until more information is available.

9.4.3 SB

Figure 9.8 shows the framework applied to SB. This figure shows that, again, certain values are influenced dually; especially the crew safety and long-term viability. In normal operation and small incidents, SB will not influence the safety of the crew (1). It is an easily detectable, white powder. It is only toxic upon touch, but due to its nature, it can be easily avoided. Additionally, it is not easily ignited, and although it releases some hydrogen when in contact with water, the rate is very slow at room temperatures, and proper venting will make sure no hydrogen build-up occurs. However, at higher temperatures, the speed of this reaction goes up, and at very high temperatures, above 400°C, thermal runaway occurs, as amongst others, sodium is produced. This may influence the integrity of the ship - and thus the survivability and, this time negatively, the crew safety (2). Similarly, the relatively inert solid will likely enhance crew safety in the port (3), as it will only react at high temperatures. However, the general working conditions may be influenced negatively (4); it is a solid and should be kept away from water. The latter not only because of safety (slow production of hydrogen), but also because water makes the substance stickier. So, the overall process in the port will become much more complicated. SB is relatively inert, not easily ignited and only toxic upon touch. However, if ignited, it does produce toxic gases and hydrogen, which can create large explosions. As this takes quite some additional energy, more than for example required for MDO, the public health is neutrally influenced (5). The probability of ignition is smaller than with MDO, yet the impact will be higher; thus, no real conclusion can be drawn without a sufficient risk analysis.

When zooming out towards the marine environment, SB will unlikely have a (negative) influence. When coming into contact with water, it decomposes into Na^+ and $B(OH)_4^-$. The former is abundant in oceans, while the latter will not likely have a large impact, thus resulting in apositie connection to long-term viability and environmental friendliness (6). Finally, when looking at SBs influence worldwide, the supply chain may positively influence the value of justice (7). The base materials of SB are distributed (albeit not evenly), but most importantly, the regeneration is very modular. Regeneration requires magnesium (step 1), which in turn has to be regenerated as well (step 2, from magnesium oxide back to magnesium). This two-step process does not have to occur at the same location, enhancing flexibility and reducing dependence

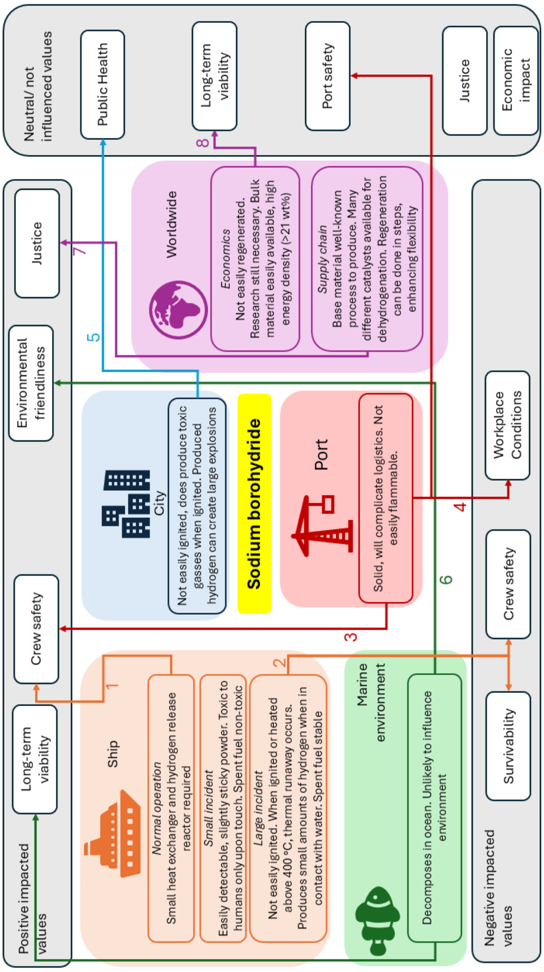

Figure 9.8: Framework applied to SB

on one location. Finally, economically speaking, the regeneration is still at a low technology readiness level [409], requiring more research, even though the bulk material is easily available and has a high energy density. However, as the regeneration is a key component of the economical frame, currently it is unclear how long-term viability economy-wise will be influenced (8).

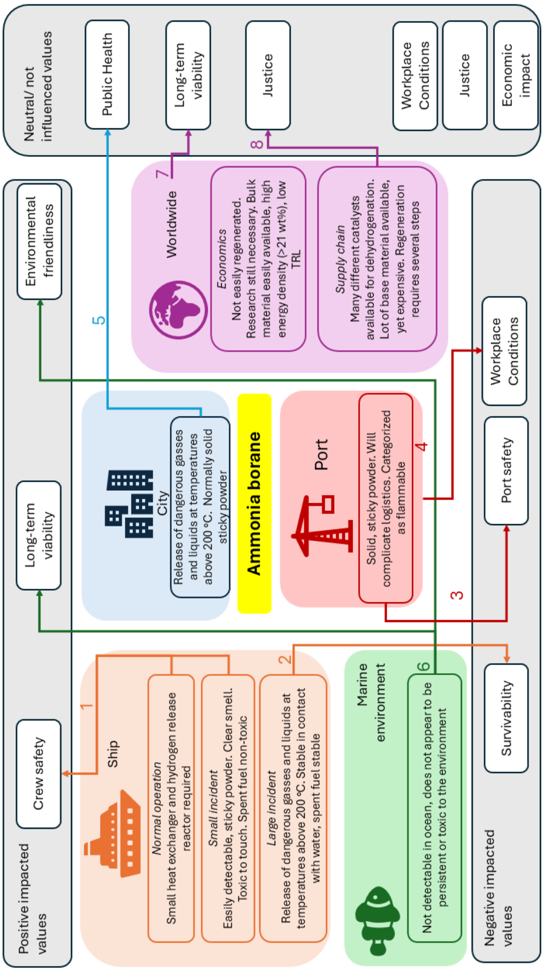

Figure 9.9: Framework applied to AB

9.4.4 AB

Figure 9.9 displays how the values may be influenced by AB. AB is significantly less researched as compared to the other hydrogen carriers, resulting in more uncertainty. However, figure 9.9 shows that the framework can still be applied. For example, AB is easily detectable; it has a distinct smell. Additionally, it is a white, sticky powder, which limits its movement in case of an accidental release. It is an irritant, resulting in skin and eye irritation if touched, and may cause respiratory irritation in case of inhalation. In case of a small spill, this will enhance the crew's safety (1), because of its relative non-toxicity and easy detectability. However, in the case of large incidents and especially when heated, dangerous gases and liquids will be released, already at temperatures above 200°C. Thermal runaway is likely in this case as well. This can negatively influence the survivability of the ship (2) and thus, also, the safety of the crew. As it is categorized as flammable, and it is a solid, sticky powder, both the safety of the port (3) and the workplace conditions inside the port (4) will be negatively influenced. Safety measures will need to be taken to avoid fires and thermal runaways. Furthermore, the entire logistical operation of bunkering and removing the spent fuel will be more complicated due to the nature of AB.

Regarding AB in the city or other built environment, the exact influence is again dependent on risk. AB is generally a solid, sticky powder, not posing any dangers to public health. However, when heated, the release of dangerous gases can negatively impact human health, as some of these gases are lighter than air (others are heavier and will not easily spread). So, the exact effect of having AB in the built environment on the public health compared to MDO is hard to estimate, which is why this will be categorized as neutral (5). The marine environment, on the other hand, and the environmental friendliness (6) may be positively influenced. Even though AB is unlikely to be detectable, it does not appear to be persistent or toxic to the environment, resulting in an overall positive effect on the environmental friendliness. Finally, the world-wide environment is where the uncertainties come into play. Regeneration of AB is done through regeneration of SB, meaning that research is still necessary. Similarly to SB, the bulk materials are easily available and the energy density is high, which will both have a positive effect on long-term viability. However, the overall effect on long-term viability (7) is hard to estimate due to the low TRL, resulting in a neutral value at the moment, subject to change. Similarly, the supply chain (8) is considered to not influence justice at the moment, due to the complexity of the process, and the current expenses.

9.4.5 AMMONIA

Figure 9.10 gives an overview of ammonia. Ammonia is very different from the previously mentioned hydrogen carriers, starting with the fact that it is a gas. This physical state has a large influence; gases are much more easily dispersed than fluids or solids. This is one of the reasons the influence of having ammonia on the ship in general (so, safety under normal operation,

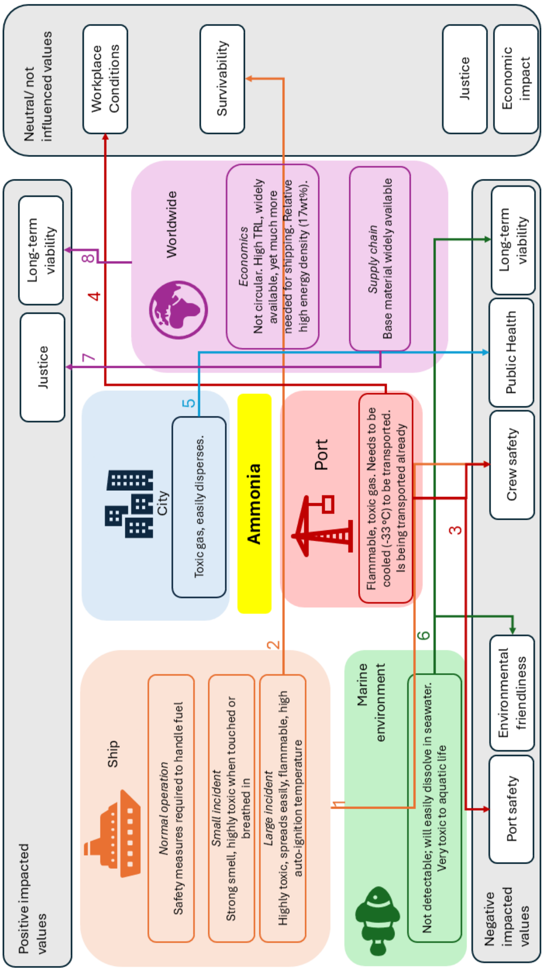

Figure 9.10: Framework applied to Ammonia

during small and large incidents) will possibly result in a negative impact on the safety of the crew - when comparing to MDO, ammonia is less safe to the crew. Ammonia requires specialised equipment and measures for handling during normal operation, due to its toxicity. This toxicity also influences the safety of the crew during a small incident and a large incident (1). Despite the strong odour of ammonia, the lethal threshold can still be reached before there was the chance to leave the room, and besides the lethal threshold, lower concentrations can still result in (permanent) health damage. Ammonia is considered to be flammable, but has a very high auto-ignition temperature, and its flammability range is limited between 15 and 28%, with others saying its hardly flammable. Because of this, the influence of ammonia on the survivability of the ship itself is regarded to be neutral; ammonia may not endanger the ship's integrity, but if the ship's crew is incapacitated, the ship's integrity may be influenced after all. This is the opposite of what usually happens (ship's integrity influencing the crew's safety), but a possibility with ammonia. This is the main reason ammonia is regarded to influence the survivability of the ship in a neutral way; it is hard to estimate exactly.

Similarly, because of the toxicity and the gas-phase, the safety of the port itself and that of the crew in the port are effected negatively. The cooling is necessary for transport and storage - liquid ammonia is the preferred way of storage for ships. However, despite the negative influence, it is being done already; ammonia is currently being stored and transported through several countries on a rather large scale, as it is the base material for other substances. So, there is definitely experience here, which is why the workplace conditions (4) are considered to be neutrally influenced; it is possible and is currently being done, in a rather safe and legal way).

However, the influence of an ammonia leak on the built environment and subsequently the public health should not be underestimated. As it is a toxic gas, it can easily disperse and have large influence on many people. So, the public health is in this regard negatively impacted (5). As for the marine environment, ammonia is not detectable and will easily dissolve in seawater. The major issue here, is the toxicity to aquatic life; ammonia is extremely toxic to aquatic life as well, resulting in a negative influence on both the environmental friendliness and the long-term viability (6).

The base materials of ammonia (nitrogen and hydrogen) are widely and easily available, resulting in possibly better distributed production and thus, a positive influence on the value of justice (7). The long-term viability worldwide, both on the economics side and the supply chain side is generally positively influenced (8). Despite ammonia not being circular, it does have a high TRL and is already widely available. The overall production would have to be scaled-up if used as alternative fuel. On the other hand, it does have a rather high energy density and is currently being considered as an alternative fuel already; on the long-term worldwide there are no major showstoppers.

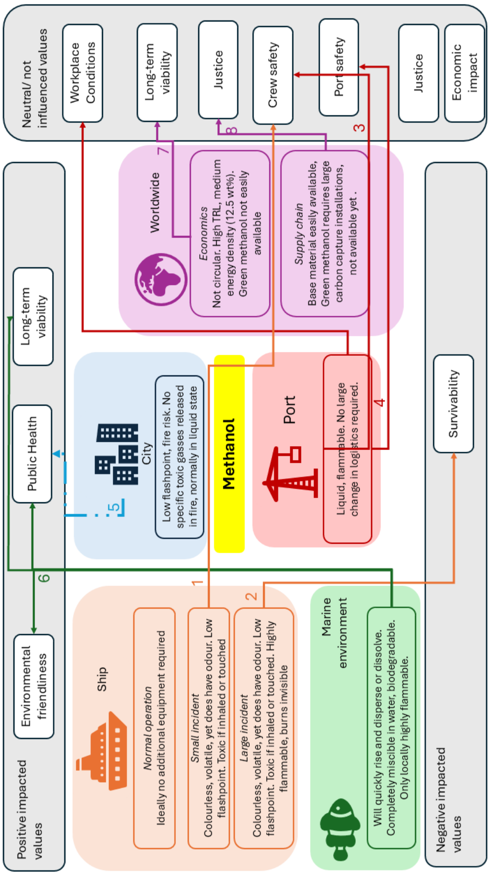

Figure 9.11: Framework applied to Methanol

9.4.6 METHANOL

Methanol is another widely considered alternative fuel for shipping, and is often compared to ammonia (and considered to be more safe). The results of the framework applied to methanol can be seen in figure 9.11. Methanol is a rather volatile liquid, with an invisible burn. However, it does have a pungent odour. It should not be inhaled or touched, but similarly MDO should not be inhaled or touched either. In the end, the safety of the crew is not influenced, during normal operation or small incidents, as both methanol and MDO are rather similar (1). The survivability of the ship, is negatively influenced:

methanol has an extremely low flashpoint and is thus much more easily ignited than MDO. Firefighting is complicated due to the invisibility of the flame. So, the risk of fires and related issues is higher and the possibility of countering them is less, resulting in a negatively impacted survivability (2).

Regarding the port, methanol is a flammable liquid. Even though it is more flammable than MDO, no large change in logistics is assumed to be required, resulting in a very limited impact on the safety of the crew within the port (3) and the port in general (4). Despite the low flashpoint and high fire risk, no specific toxic gases are released when methanol is ignited. Additionally, methanol itself is in a liquid state, limiting its dispersivity. So, overall, the influence of a methanol release on the public health is very limited, only affecting the public when burning. This combined results in a positive influence on the public health (5). When looking at the marine environment, methanol is a volatile substance and will respond fast when spilled. It will either quickly rise and disperse, or dissolve in seawater. It is completely miscible in water and biodegradable with a short half-life time of only a few days. Locally, it can be highly flammable, but due to its rapid dispersion this risk is limited. All in all, it will have a positive influence on the environmental friendliness, public health and consequently on the long-term viability (6).

Finally, methanol presents a significant challenge, as it is not circular and sustainably sourced feedstocks (also for biomethanol) are difficult to obtain. Consequently, green methanol (produced from hydrogen and carbon) is still scarce and costly. Methanol, in general, has a high TRL and medium energy density, yet for it to be completely circular and, thus, carbon-neutral, more research and more investments are required. Additionally, capturing CO_2 at a large scale is extremely difficult, so the long-term viability is at the moment neutral/not influenced (7), as it is very similar making green methanol as making green MDO. The supply chain is similarly affected (8), with the influence on justice extremely difficult to predict; it can be both positively and negatively influenced depending on choice of catalyst and location of carbon capture installations.

9.4.7 LIQUID HYDROGEN

Hydrogen does not need to be stored in hydrogen carriers, it can also be liquefied. Liquefied hydrogen has very specialized concerns, split in two: the temperature at which hydrogen becomes liquid is extremely low (-252°C),

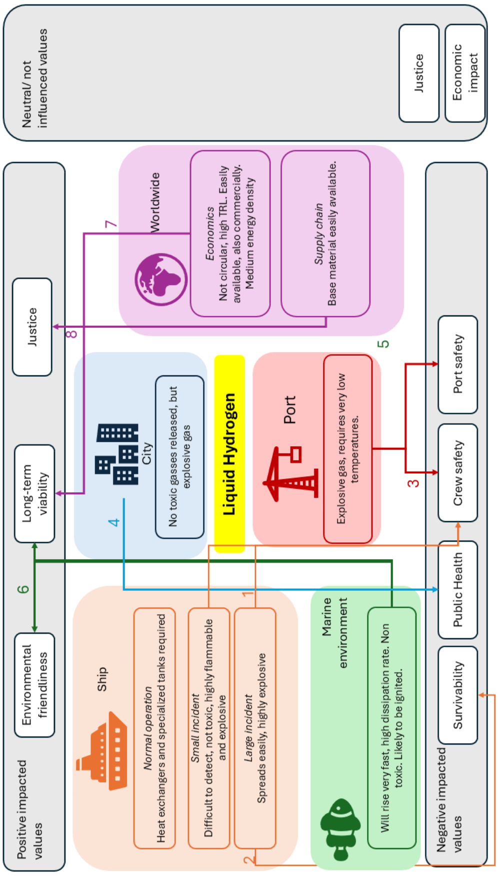

Figure 9.12: Framework applied to liquid hydrogen

which results in safety concerns. Additionally, hydrogen in general has its own safety concerns as well. Combined with a high TRL, the results (shown in figure 9.12), show many positive or negative influenced values, and almost no neutral/not-influenced values.

Because of the low temperature, specialized equipment is required to store hydrogen, and heat exchangers are used to heat it when it is needed. This complicates the process. If hydrogen is spilled, it endangered the crew. Nearby crew is endangered because of the extreme cold (1), even though hydrogen is not flammable. The difficulty of detection hydrogen combined with the explosivity results in negative impact on the crew safety during small and large incidents (1). Additionally, this negatively influences the survivability of the ship, as hydrogen build up can create powerful explosions and may cause embrittlement in surrounding materials (2). Proper venting can significantly reduce this risk, but it is not unavoidable, and more dangerous than MDO. These results also reflect within the port; the explosivity and low temperatures required will negatively influence the safety of the crew in the port (3). Only the explosivity will influence the safety of the port in general, yet also in a negative way. Similarly, the public health in the built environment is impacted in a negative way (4); hydrogens explosivity can have significant consequences, as hydrogen can cause large and strong explosions.

When looking at the marine environment, hydrogen is rather benign. Hydrogen will rise fast and has a high dissipation rate. Even though it is unlikely to reach the marine environment, it is also non-toxic, resulting in likely no effect on the marine environment at all. This means that both the environmental friendliness and long-term viability of hydrogen as a fuel for the marine environment are positively influenced (6). Hydrogen would be able to affect local marine wildlife, due to the cold of the spill, or, if ignited, the fire or explosion risks.

Finally, hydrogen worldwide has positive effects as well. Hydrogen is not circular, yet has a high TRL. Both the economic case and the supply chain case are favourable for hydrogen; when comparing to almost all of the other hydrogen carriers, they also need other base materials or catalysts, besides hydrogen. Hydrogen is the base material for almost all hydrogen carriers. Thus, hydrogen will positively influence the long-term viability, as prices need to be lower (7) for any alternative to become valid. Additionally, regarding the supply chain, the base material (H_2O) is readily available, and a supply chain for hydrogen is already coming into existence in many places. Producing hydrogen is not really location dependent, resulting in a positive influence on the value of justice (8).

9.4.8 MARINE DIESEL OIL

While MDO is the current reference fuel in maritime operations, it is not assumed to be neutral or to have no influence on the values. Nevertheless, in practice, many of these values are assessed as unaffected, as visible in figure 9.13. For example, normal vessel operation does not alter workplace conditions (1), as handling and storage procedures for MDO are long established and

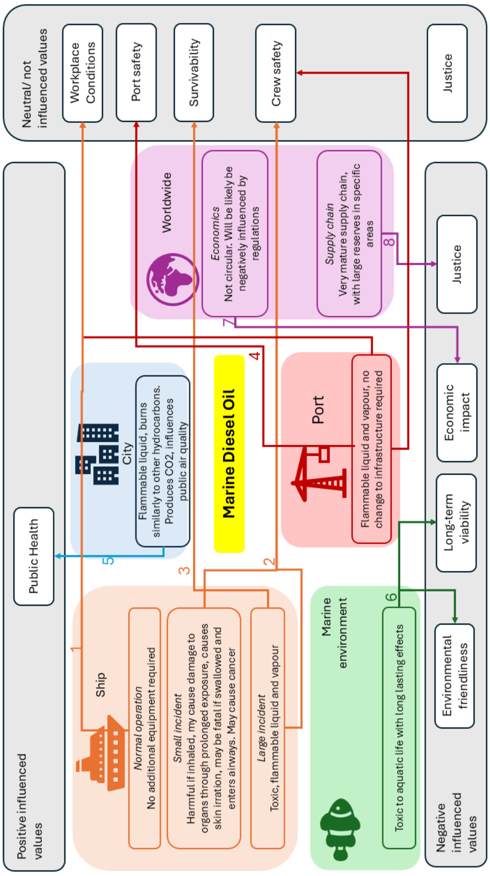

Figure 9.13: Framework applied to MDO

fully integrated into routine operations. Similarly, crew safety is not evaluated as being positively or negatively influenced in incident scenarios (2). This is not because MDO is harmless; it contains compounds that are hazardous when inhaled. However, such risks are familiar, well-documented, and embedded in standard safety practices. Over time, these risks have become normalised, leading crews to perceive them as part of the ordinary working environment rather than as exceptional dangers. Consequently, the perception of "no additional risk" outweighs the objective fact that exposure can still be harmful.

A similar reasoning applies to ship survivability (3): while MDO is flammable, existing fire-prevention and suppression systems are designed with such fuels in mind, so its hazards are regarded as baseline conditions rather than added vulnerabilities. Similarly, port safety (4) is seen as unaffected, as MDO requires no changes to infrastructure, reinforcing the perception that it presents no incremental challenges beyond the established status quo.

As MDO burns similarly to other hydrocarbons, producing CO_2 and NO_x, it poses no major direct danger to the general public. While a large-scale fire could temporarily affect air quality, the likelihood of large explosions is low. As a result, public health is generally considered to be positively affected (5), since the risks are limited and well managed compared to other fuels. This assessment is further supported by the fact that members of the public are permitted to bunker MDO themselves, without the need for additional safety requirements, which reinforces the perception of MDO as a comparatively safe fuel in this regard.

In contrast, accidental releases of MDO into the marine environment negatively affect both environmental friendliness and long-term viability (6), as MDO is toxic to aquatic life and can cause long-lasting ecological damage. On a global scale, MDO also carries broader implications. Economically, it is regarded as disadvantageous: it is not circular, and future regulatory changes are likely to impose stricter limitations on its use. In addition, the uneven geographical distribution of oil reserves has historically created disparities, meaning that continued reliance on MDO undermines the value of justice (8).

9.4.9 COMPARISON

This analysis originally aimed is to enable a comparison of hydrogen carriers in terms of safety and sustainability. As the preceding subsections have shown, however, evaluating these technologies and determining whether their impacts on key values are positive or negative is highly complex. Even when the system is simplified, as has been done in the previous subsections, the trade-offs and uncertainties remain significant, and a straightforward ranking is not possible.

Nonetheless, comparison, particularly against a benchmark such as diesel, is both valuable and necessary as it provides a reference point to assess whether alternatives represent an improvement. It is important to note, however, that any such comparison must be interpreted with care. First, the assessments should not be treated as a simple scoring system where positive and negative impacts can be tallied to determine an overall "winner" or "loser" among carriers. Second, meaningful comparisons can only be made within individual values (across different carriers), not across different values (within a single carrier), as each value represents distinct criteria that cannot be directly compared or weighted against one another. Therefore, a qualitative overview is provided indicating whether the impact on each value is assessed as positive, negative, or mixed. In cases where a technology is expected to have both positive and negative effects on a given value, this is indicated explicitly (e.g., "positive/negative") rather than classifying it as neutral.

This summary is intended to offer a high-level impression of how the various carriers perform across key criteria. For a more accurate and nuanced understanding, readers are referred to the detailed visual representations and descriptions provided earlier. Despite the limitations inherent in such a simplification, this overview can still serve as a useful point of entry for further discussion and analysis. The results of this analysis can be found in table 9.1.

When examining the assessment criteria individually, the complexity of these trade-offs becomes even more apparent. **Environmental friendliness** presents a particularly nuanced picture, where carriers may simultaneously exhibit both positive and negative influences. The exact nature of these influences varies considerably and depends heavily on factors such as persistence and toxicity levels. Crucially, most substances that negatively impact the environment are impossible to remediate once released, a characteristic shared by nearly all alternative fuels under consideration [184].

Crew safety assessments prove similarly challenging to quantify precisely, as the actual risk level is strongly dependent on the design of additional safety materials and systems. Nevertheless, clear distinctions can be drawn regarding the relative toxicity of different substances when compared to diesel. Port safety is generally assessed as neutral for most carriers, with negative ratings reserved only for substances that are exceptionally flammable or toxic. Even though differences in port safety can be substantial, many of these substances are already transported through ports in considerable quantities as cargo rather than fuel, providing existing frameworks for safe handling.

Survivability assessments reveal significant variation among carriers, though these outcomes are again heavily influenced by system design considerations. While proper engineering can mitigate many potential problems, this analysis deliberately excludes design-specific modifications to maintain comparability

	Environmental Friendliness	Crew Safety	Port Safety	Survivability	Long-term Viability	Justice	Public Health
MDO	Negative	Neutral	Neutral	Neutral	Negative	Negative	Positive
DBT	Negative	Positive	Neutral	Positive	Positive/ Negative	Neutral	Positive/ Negative
NEC	Negative	Positive	Neutral	Positive	Positive/ Neutral	Neutral	Positive/ Negative
SB	Positive	Positive/ Negative	Neutral	Negative	Positive/ Neutral	Positive	Neutral
AB	Positive	Positive	Negative	Negative	Positive/ Neutral	Neutral	Neutral
NH3	Negative	Negative	Negative	Neutral	Positive/ Negative	Positive	Negative
MeOH	Positive	Neutral	Neutral	Negative	Positive/ Neutral	Neutral	Positive
LH2	Positive	Negative	Negative	Negative	Positive	Positive	Negative

Table 9.1: Comparison based on individual cases

with marine diesel oil as a reference point. This approach should not be interpreted as representing final or optimal safety outcomes.

Long-term viability presents perhaps the most complex assessment challenge. Many carriers demonstrate positive influences due to their recyclability or beneficial environmental effects, including in spill scenarios, while simultaneously exhibiting negative or neutral impacts in other dimensions. The multitude of variables subject to change over time makes predicting overall long-term viability outcomes extremely difficult. However, it is notable that all alternative carriers are expected to contribute at least some positive influence to long-term viability compared to conventional fuels.

Justice considerations prove equally difficult to quantify, with only a limited number of carriers demonstrating clearly positive effects. These tend to be technologies that have been employed for extended periods and offer multiple production and regeneration pathways, as flexibility in supply chains generally correlates with more equitable outcomes. For newer technologies, the flexibility of future supply chains remains highly uncertain, resulting in neutral assessments.

Public health impacts vary considerably across carrier types. LOHCs present a paradoxical profile, positively affecting public health through their chemical inertness while potentially creating negative impacts through environmental damage pathways. Most other carriers receive neutral assessments, with notable exceptions being ammonia (negative due to toxicity) and LH2 (negative due to explosion risks).

This analysis reveals that each value dimension is affected quite differently by the various carriers, and that simple positive, negative, or neutral classifications inadequately capture the nuanced reality of these impacts. Even within identical classifications, the magnitude and nature of effects vary substantially. Therefore, this framework should not be used for direct comparison or ranking, but rather as a tool for identifying carriers that may be particularly suitable when specific values are prioritized. Such prioritization decisions are inherently context-dependent and value-laden, extending beyond the scope of this technical analysis.

9.5 DISCUSSION

The discussion is structured into four parts to reflect the multi-layered nature of the evaluation framework. It begins with assessing the regulatory complexity, followed by technical design considerations, human factors, and ends with a ethical reflection. This structure allows for both practical and conceptual insights into the tool's development and application.

9.5.1 REFLECTING ON REGULATORY COMPLEXITY

The maritime industry operates under a complex web of regulatory authorities, with the IMO serving as the primary global governing body. However, the regulatory landscape extends far beyond the IMO, creating a fragmented system of oversight. Regional authorities each bring their own jurisdictional focus and priorities: the Central Commission for Navigation on the Rhine (CCNR) governs the European inland waterways of the Rhine, while the U.S. Coast Guard regulates American waters. These regional differences mean that regulatory emphasis varies significantly depending on location and local values. Adding another layer of complexity are classification societies, non-governmental organisations like Lloyd's Register (LR), DNV, and RINA. These CS verify whether a ship complies with safety and technical standards. While these societies perform crucial verification functions, each operates under its own set of standards and criteria, further fragmenting the regulatory environment. This multi-layered, fragmented system creates significant challenges for the maritime industry. Shipping companies must navigate overlapping jurisdictions, varying standards, and different regulatory priorities, making compliance both difficult and costly. The lack of harmonisation across authorities and classification societies complicates legal compliance and creates uncertainty for operators seeking to meet all applicable requirements.

9.5.2 TECHNOLOGICAL DESIGN CONSIDERATIONS

Risk analysis is an integral part of safety. Risk is often denoted by the frequency of occurrence times the severity of consequences, so probability times impact. However, both probability and impact are influenced by the ship itself. Firstly, the sheer size of the ship and its task will define the amount of fuel it requires. The amount of fuel directly influences the severity of consequences in case of an incident; a small ship carrying little fuel will result in fewer consequences in case of a total spill, for example, than a large ship with several tonnes of fuel.

The design of a ship further influences the risk, as design can decrease risk and enhance safety. Often denoted by safe-by-design, practical applications in ship design are the size and location of the fuel tank, but this becomes particularly critical for alternative fuels. For instance, hydrogen storage requires specialised containment systems and ventilation, while ammonia storage demands different safety protocols and emergency response systems compared to conventional fuels. Consequently, design choices can significantly influence the probability of incidents occurring.

Ship design offers additional opportunities to reduce risk through fuel consumption reduction. Beyond switching to alternative fuels, greenhouse gas emissions can be reduced by minimising overall fuel requirements. This approach encompasses various strategies: hydrodynamic improvements such as hydrofoils to reduce drag, hybrid propulsion systems combining conventional fuels with batteries for optimal engine efficiency, and advanced energy management systems. By reducing total fuel consumption, these design innovations inherently decrease the quantity of fuel stored onboard, thereby reducing both the probability and potential severity of fuel-related incidents.

9.5.3 SOCIAL FACTORS

Besides the previous, more technical, factors, there are also the social factors. society does not always immediately trust science due to lack of societal awareness from a scientific perspective or simplifications used within academic research. Hydrogen, for example, is known for its explosivity, and crew have already attested that they refuse to work on a hydrogen-fuelled ship. They perceive the danger to be too much to safely work and sleep on a vessel, despite risk analyses proving otherwise. Obviously, these types of perception are more often occurring with more well-known alternative fuels; lesser-known alternative fuels are less influenced by public opinion, but can also suffer from these unknowns. This perception is not limited to the crew; the general public perception matters as well, especially for substances that can become airborne and influence the general public, such as ammonia. These social factors will likely play an important role in the adoption of alternative fuels and may influence decision-making at a higher level. Fuels which are not perceived as safe, despite science perhaps telling otherwise, may be at a disadvantage, especially when crew often still compares alternative fuels to MDO, which is generally perceived as safe. This creates a significant hurdle for alternative fuel adoption, as new technologies must not only prove their safety scientifically but also overcome deeply ingrained perceptions of conventional fuel safety.

9.5.4 ETHICS AND APPLICATION

Decision-making tools for alternative fuel selection are inherently situated, reflecting the priorities and context of their creators rather than providing neutral, objective guidance. Even though this tool aims to be as objective as possible, by avoiding a direct overall comparison, it is not neutral either, reflecting values that are deemed to be important enough to encompass. This tool, like any other, embodies normative choices about what values and outcomes considered most important for reflecting the current situation, with a focus on safety and environmental impact rather than economic efficiency or social acceptance.

The primacy value of this tool lies not in providing definitive answers, or reducing complex trade-offs to simple metrics - an approach that is intentionally avoided. The main aim is to facilitate value-informed reasoning among stakeholders. By making underlying assumptions explicit and structuring the analysis of trade-offs, uncertainties, and potential impacts, this approach helps navigate the multifaceted challenges identified in the previous sections, with a focus on safety and sustainability.

Most importantly, this tool is specifically designed to generate meaningful dialogue. This goal was to create a framework that brings engineers, policymakers, ship operators, and broader society together around structured discussions. Rather than delivering answers, the aim is for people to discuss, debate, and deliberate using this framework as a foundation. This tool serves as a catalyst for bridging the gaps between technical feasibility, regulatory requirements, and social acceptance that currently fragment decision-making in alternative fuel adoption. The real value emerges when stakeholders engage with the tool together, using it to articulate their perspectives, challenge assumptions, and work toward more informed collective decisions.

9.6 CONCLUSION

Alternative fuels like hydrogen carriers will have a significant influence on safety and sustainability in the maritime sector. Safety and sustainability are multi-faceted values, consisting of subvalues as environmental friendliness, crew and port safety and survivability (safety) and long-term viability, justice, public safety and economic impact (sustainability). These values are connected to several maritime environments, as each subvalue may have different (or no) influence within a different environment. This paper has developed a framework to assess the safety and sustainability of alternative fuels on ships by looking at these connections. While this framework aims for transparency and systematic analysis, it reflects normative choices, particularly in emphasizing safety and sustainability over economic viability or social acceptance. Rather than aiming for a simplistic ranking, the framework acknowledges the complexity, uncertainty and context-dependence involved in evaluating alternative fuels. By avoiding prescriptive metrics that may become outdated, the framework's flexible structure can accommodate emerging technologies, evolving risk profiles, and changing regulatory environments.

Comparisons are possible, but complex and are consequently made qualitatively and within individual values instead of across values, so as to respect the incommensurable nature of these values. The primary purpose of this framework is not to provide definitive answers, but to support value-informed reasoning. Additionally, the results of this framework provide a structured approach with a balanced consideration, allowing stakeholders to identify trade-offs and prioritize actions based on context-specific needs.

The application of this framework to various hydrogen carriers reveals substantial variation across individual criteria. No carrier emerges as universally preferable; instead, each exhibits a mix of positive, negative, or uncertain impacts depending on the value considered. For instance, environmental friendliness often involves trade-offs related to toxicity and persistence; while persistence may be detrimental in environmental contexts it is often considered beneficial for long-term viability. Meanwhile, long-term viability and justice are influenced by future uncertainties, such as technological maturity and the flexibility of supply chains. Crew safety, by contrast, is particularly sensitive to system design and operational conditions. These results highlight the complexity of value-based assessments and underscore the importance of qualitative, context-specific evaluation over simplified or aggregated comparisons.

Most importantly, the framework is intended to serve as a catalyst for dialogue, to encourage collaboration and shared understanding among engineers, policymakers, ship operators and the public. By making values explicit, the framework can help bridge the gaps between technical, regulatory, and societal perspectives in the maritime fuel transition.

PART 4: SYNTHESIS AND OUTLOOK

> *"And so, does the destination matter? Or is it the path we take? I declare that no accomplishment has substance nearly as great as the road used to achieve it. We are not creatures of destinations. It is the journey that shapes us. Our callused feet, our backs strong from carrying the weight of our travels, our eyes open with the fresh delight of experiences lived."*
>
> — Brandon Sanderson, *The Way of Kings*

PART SUMMARY

This part consists of the synthesis and outlook - the best hydrogen carrier will be discussed here. However, as best fully depends on what is valued most, the best hydrogen carrier per definition does not exist - it all depends on the values chosen to assess the hydrogen carriers on.

10

THE BEST HYDROGEN CARRIER

> *"What is it we value? Innovation. Originality.*
> *Novelty. But most importantly...timeliness. I*
> *fear you may be too late, my confused,*
> *unfortunate, friend."*
>
> — Brandon Sanderson, *The Way of Kings*

CHAPTER SUMMARY

This chapter discusses the concept of 'the best hydrogen carrier' through a value-based approach. While the thesis aimed to identify optimal hydrogen carrier and energy converter combinations, the findings show that no single solution excels across all criteria. What is considered "best" depends on how values are defined and prioritized, as well as the specific context of application. Additionally, suitability depends highly on context; values such as safety and technical feasibility yield different results when assessed in a different context. The chapter distinguishes between value-sets that are discussed in this thesis (such as technical feasibility, safety, and sustainability) and others, which are acknowledged yet beyond scope (such as economic, societal, and life-cycle aspects). Assessment is further hindered by limited and difficult-to-interpret data, as well as the influence of operational conditions on safety. Ultimately, the success of hydrogen carriers may depend less on performance than on timing: if adoption comes too late, other alternative fuels may become locked in, turning late into never.

10.1 INTRODUCTION

The purpose of this thesis is to identify suitable combinations of hydrogen carriers and energy converters. The motivation behind this work stems from the industry's preference for simplicity and standardization: ideally, a single, universally applicable solution — a "silver bullet" — would satisfy all operational and environmental requirements. However, the results revealed that such a singular option is unlikely to exist. Four relevant dimensions were investigated: power density, energy density, safety and sustainability. None of the investigated hydrogen carriers or converter systems excels across all relevant dimensions. Moreover, even within individual dimensions, there is often no single carrier that can be considered the best. None of the solutions is the best in every single case - it all depends on the application. These findings contribute to the growing body of research on hydrogen carriers by emphasizing the importance of context-dependent evaluation rather than universal ranking. They also highlight the potential benefits of maintaining diversity in the energy system rather than striving for homogeneity.

This chapter will discuss the findings through the lens of value-based assessment. It will explore how different criteria influence the perceived suitability of hydrogen carriers.

10.2 DEFINING AND ASSESSING BEST HYDROGEN CARRIER

How to define the best hydrogen carrier is value-dependent. The central question, therefore, is:

Best in what regard?

And in what regard is defined as by what is valued more; that is, on what is valued most by decision-makers or within a given context. This section will highlight the values that were taken into account in this thesis, some of which are assessed in detail, while others are only touched upon. Additionally, there are values that were not discussed at all; this section highlights several of the most relevant ones, although it does not aim to be exhaustive.

10.2.1 VALUE SETS DISCUSSED AND DISREGARDED

Not all values relevant to hydrogen carrier assessment are addressed equally in this thesis. Some are discussed in greater depth because they form the foundation of whether to regard or disregard a hydrogen carrier - the main advantages of hydrogen carriers over pure hydrogen is their (supposedly) higher energy density and increased safety (removal of explosivity). Thus, technical feasibility and safety are the value-sets regarded in detail. Sustainability is here regarded partly as long-term safety; a safe substance should also be sustainable. Technical feasibility focusses on power and energy density, but this value-set comprises of more. Together, they capture both the technical performance and the long-term viability of hydrogen carriers in maritime and other energy systems. The value sets and what they may be lacking will be discussed in the following subsections.

However, more value-sets than just technical feasibility and safety exist. When discussing the use of alternative energy sources, seven value-sets are often used, although not always within the same research. These seven criteria are technical (feasibility), economical, environmental, ecological footprint, social, security of supply and life cycle sustainability [410], [411]. These each have their own values, societal for example consists of values such as employment, social acceptance, social development, health impact (taken into account in safety & sustainability), governance, visual impact, knowledge and awareness, cultural value and social justice (partially taken into account in safety & sustainability) [412].

Some of these seven criteria are (partially) covered here; societal is only covered for a small part. Technical feasibility is covered for a large part, and will be discussed in the subsection regarding power & energy density. Economical impact is only covered slightly, in chapter 9, yet is not covered in detail due to the novelty of hydrogen carriers - assessing the economic impact of these carriers is not deemed realistically possible. The environment is covered, but only the marine aspect of it, and is regarded to be part of safety. The possible environmental impact of the entire chain is not covered, again, due to the novelty of the technology. The ecological footprint is not discussed in detail, but is implicitly taken into account. By assuming a high percentage of regeneration (over 99%) and the zero-emission property of hydrogen carriers as fuels, the ecological footprint should be relatively small and, most importantly, not differ between the hydrogen carriers. All of these carriers should have a similarly, negligibly small ecological footprint.

The security of supply is similarly not regarded; in the end, this research had a major focus on tank-to-wake operations, rather than the well-to-tank aspects. Additionally, all of these carriers require hydrogen, resulting in a uniform assessment regarding supply. The manufacturing of the hydrogen carriers themselves is different, and is shortly discussed in chapter 9 as well, yet is too out of scope to be regarded into detail.

Finally, a life cycle sustainability assessment would strongly enhance the case of hydrogen carriers. Not regarding well-to-tank is a deliberate choice, but does result in this research not reaching the completeness that it would benefit from. Unfortunately, a life cycle (sustainability) assessment requires ample data - data that is often not available. Assumptions have great influence, and the amount of uncertainty inevitably needed to complete a life cycle (sustainability) assessment will not result in reliable results. However, this could possibly change within a relatively short timespan of a few years, and a life cycle (sustainability) assessment would be the first piece of future research that should be undertaken to strongly enhance the credibility and usability of this work.

10.2.2 POWER AND ENERGY DENSITY VALUE SET

The power and energy density value set has a name that perhaps does not fully encompass its scope; the name was chosen as it reflects the main focus of the part of the thesis. However, most of the values usually seen under technical feasibility are incorporated in this value-set and within the research. Aspects of this value set are volumetric and gravimetric capacity, bunkering and storage and efficiency of the system [48]. The volumetric and gravimetric capacities are closely tied to the system's efficiency; a higher efficiency requires less fuel, thus resulting in a higher volumetric and gravimetric capacity. Here, the system's efficiency refers to the tank-to-wake efficiency; the well-to-wake efficiency does not impact the technical feasibility onboard the ship, but it does influence the overall technical feasibility of the solution. Here, it is essential to consider that a solution may be technically feasible on the ship, but not as a whole; the opposite is also possible. Bunkering and storage are only referred to shortly in chapter 2, and the only limitation placed on hydrogen carriers regarding these values is that bunkering and storage should be possible and not require extreme conditions such as extremely low temperatures or high pressures.

However, besides these values, which are regarded in the thesis, there are several values influencing the technical feasibility, which are not regarded at all or, similarly to bunkering and storage, only slightly. Values not (extensively) evaluated include, for example, the reliability of the technology onboard the ship, technology readiness, the operability of the ship with this equipment, scalability, and logistics for storage and transport. The reliability of technology onboard the ship is of great importance, as the safety and structural integrity of the ship depend on the availability of power. A ship without power can quickly find itself in dangerous situations, especially near coastlines. However, the reliability of the technology depends on the technology readiness, a value that has been touched upon, but not in much detail. Most of the hydrogen carriers discussed here have a similar, low to medium, technology readiness level. On the one hand, this makes the value of technology readiness less interesting to explore; on the other hand, the assessment of technology reliability depends on the technology readiness level, which requires a very high level of technology readiness.

The operability of the ship with the equipment is briefly mentioned, albeit not explicitly stated. This regards mostly the energy converters - it has been previously stated that by using a buffer the hydrogen carrier dehydrogenation is unlikely to be the limiting factor in the chain of supplying power to the ship. However, the energy converter is often a limiting factor, with gas turbines having start up times of seconds, internal combustion engines of minutes, and especially SOFCs not doing too well with power fluctuations at all. Despite these statements, this aspect is not examined in detail, as it is assumed that it will likely be addressed through an elaborate energy management system, combined with batteries for peak shaving. Not only does this guarantee meeting the operational profile, it also enhances the overall efficiency of the system.

Scalability is one of the values that can only be assessed with high TRL: knowledge about the supply chain (availability) and exact design of equipment (scalability of e.g. reactors) is required to assess this. Finally, bunkering and storage of hydrogen carriers is not necessarily straightforward; bunkering of hydrophilic and sticky powders that cannot come into contact with the air is a novelty in ship bunkering and part of a different research [183].

10.2.3 SAFETY AND SUSTAINABILITY VALUE SET

Safety and sustainability were both explored extensively in Chapter 9, which focused on a value conflict design approach to evaluating hydrogen carriers in maritime applications. Therefore, this section only summarises the key aspects most relevant to the overall comparison and interpretation of the results.

Safety has been evaluated from several perspectives; ranging from the integrity of the ship (practically in chapter 7 and more conceptually in chapters 6 and 9), safety of crew (both on the ship and at the port, discussed in most chapters in part 3, with a focus in chapter 8) and safety of the marine ecosystem. These values are all rather straightforward and often do not have double meanings or subvalues. Additionally, with risk analyses (for which the TRL of the substances and ship designs was not sufficiently mature), they can usually be well evaluated and compared. The main value missing here is one that has overlap with societal, namely the acceptance of the crew (and passengers) towards alternative fuels. The feeling of safety on board a ship is paramount; if the crew does not feel safe or does not trust the risk assessments, they will not sail on the ship. This perception should be mapped further in future research.

Sustainability has also been evaluated, although less in-depth. Only chapter 9 covers sustainability, which is approached as an extension of safety in the long term, encompassing material circularity, justice, economic impact and public health. These values were covered in less detail, and some values were missing as well. For example, economic impact is usually its own value set, as it encompasses a wide range of values (e.g. cost, availability of materials, availability of infrastructure, scalability, trade resilience). However, as the TRL is too low to assess the general economic impact, it was considered part of sustainability and estimated accordingly. Similarly, the effect of alternative fuels on global justice and intergenerational justice can be significant. This has two conclusions to it: firstly, justice itself is a value-set, as it consists of (at least) two separate values. Secondly, it should be examined in further detail whether hydrogen carriers are to be used, as the world may shift from an oil and gas-based energy distribution to a hydrogen carrier distribution system, providing ample opportunity to influence global and intergenerational justice.

10.3 BEST HYDROGEN CARRIER BASED ON POWER AND ENERGY DENSITY

Energy and power density are, in principle, relatively straightforward quantities to calculate and assess. The energy density depends not only on the intrinsic properties of the fuel but also on the overall system efficiency, including possible waste-heat integration to minimise losses. Chapter 3 describes the implementation of waste-heat recovery and the derivation of energy density and system efficiency from the overall configuration. Chapter 4 focuses on the additional components required when using hydrogen carriers, identifying the reactor as the most influential element. Finally, Chapter 5 compares the resulting energy and power densities across carriers.

Although the analyses in the first two chapters of this part may appear to identify a clear "best" option —typically, the system occupying the least space or mass — the definition of "best" quickly becomes ambiguous. As shown in Chapter 3, the density of the hydrogen carrier itself plays a decisive role: sodium borohydride (SB) has a relatively high energy density compared to ammonia borane (AB), making SB favourable for volume-limited vessels, whereas AB performs better in weight-limited applications. Even within the single criterion of energy density, therefore, the conclusion already depends on context.

When power density is considered, the influence of assumptions and state-of-the-art research becomes particularly pronounced. Dibenzyl toluene (DBT) exhibits very low power density, largely independent of the energy converter, due to its long dehydrogenation residence times. These could, in principle, be reduced through further technological development, but this remains uncertain. The key issue is precisely this uncertainty: the feasibility of DBT as a marine fuel depends critically on advancements that are still only potential.

When both power and energy density are compared on a broader scale (Chapter 5), it becomes clear that the preferred option depends strongly on ship type, operational profile, and whether the mass of spent fuel is included in the assessment—and to what extent. For instance, SB and AB produce heavier spent fuels, meaning that ships using them would return to port with greater displacement than when they departed. This characteristic is novel for the shipping industry, and strategies for managing such fuels remain underdeveloped. In this study, only the fuel mass itself is considered, which means that direct comparison with fully consumable fuels, such as ammonia or methanol, cannot yet provide a level playing field.

Furthermore, only four hydrogen carrier cases were analysed out of sixteen possible combinations. Other carriers might perform better in specific contexts or for particular operational profiles. The resulting diversity of options has both positive and negative implications: it broadens the design space and potential resilience of the energy system, but it may also slow decision-making, obscure comparability, and fragment technological development. Ultimately, even for metrics as ostensibly clear-cut as power and energy density, there appears to be no single "perfect" hydrogen carrier; the optimal choice remains conditional on context and priorities.

10.4 BEST HYDROGEN CARRIER BASED ON SAFETY AND SUSTAINABILITY

The IMO has set conventions and rules regarding safety, which have become increasingly more important since the sinking of the Titanic in 1912. The IMO conventions have several focus points; trying to ensure the safety of humans, both passengers and crew, as well as the safety of ecosystems and wildlife. However, chapters 8 and 9 show that safety (and sustainability) are widely varied and open for interpretation. These interpretations range from differences in what safety and sustainability entail, to assessment of hydrogen carriers based on these value-sets.

Chapter 6 tried to make a start with assessing the safety of hydrogen carriers, based on the values that IMO regards as part of safety. To assess the hydrogen carriers, they are compared to MDO. However, it becomes clear that just by looking at the hazards accompanying these alternative fuels, no conclusion can be drawn. Firstly, not enough data is available to accurately assess the hydrogen carriers - often times only the safety data sheets of either fuel or spent fuel are available and in certain cases (e.g. for AB) these are not even conclusive. Secondly, hazards are not sufficient, physical behaviour of substances matters strongly as well. There is a large difference between a toxic, invisible gas and a toxic, white, non-dusting powder. The powder is much more easy to avoid, as it does not spread itself easily and is clearly visible. In general, gases can be described as being more dangerous, with fluids in between and powders being most safe. Finally, the exact damage and toxicity levels differs; a high toxicity probability interval is more dangerous than a low one, even though both substances may receive the same hazard warnings. Drawing the conclusion that not one substance is the safest would be logical; however, chapter 6 shows that there is one single substance having substantially fewer hazards, while being in powder (spent fuel) or fluid (fuel) form; namely, NEC. Therefore, a cautious conclusion could be that NEC is the best option when considering the fuel's impact on human safety and the environment.

Additionally, the value of safety for the ship, the ship's integrity, can be influenced dually by use of alternative fuels in case of emergency scenarios. For example, the spent fuels of AB and SB are relatively inert (as discussed in chapter 7), resulting in possible impact dampening and fire reductions. The fuels, on the other hand, will likely enhance the impact or fire damage; is it considered better to have both of these on board as compared to something that is on the same level as MDO (which may burn in case of emergency as well). Additionally, this chapter showed that the information on safety data sheets is not focused on use on ships. This is obviously not expected either, but the chapter does show that especially regarding fuel spills many uncertainties exist. It was initially assumed that SB and AB might be dangerous during spills, as they allegedly react (violently) with (sea)water to produce hydrogen - however, AB does not appear to react with seawater at all, while SB reacts faster with seawater than with normal water (but the reaction rate at the temperature and pH of seawater is still relatively slow, so it is hard to estimate how dangerous it is). The cleaning up of spills in seawater, inevitably required when using hydrogen carriers on big scale as fuels, is also touched upon in this chapter. The chapter shows that clean up is not trivial at all and may, especially for LOHCs, with their non-biodegredability, be of great importance. Of course, it is not expected that all even remotely possible fuels are immediately investigated in such detail, but it does mean that additional research may be required to completely assess the influence of alternative fuels on ships - without all knowledge, how fair is it to make a choice regarding the best hydrogen carrier at all?

Finally, chapter 8 shows that, despite the importance of knowing the properties of all the alternative fuels, this is only part of what safety entails. Safety onboard is guided by much more aspects, often aspects that are hard to capture with a single number. Actually, it is advised not to put a single number on safety, as this usually undermines the trust the general public has in safety science. Furthermore, automation is encouraged for simple, repetitive tasks, but should not be used in complex tasks that are essential for the safe operation of a ship - the improvisational talents of humans are often required in emergency situations, and humans can only improvise correctly if they know the system sufficiently well. This already shows the shift from safe design towards safe operation - designing a ship completely foolproof is unlikely to be possible at all. However, the key to safe ships lies in their operation. Removing the victim-blaming culture, making sure everybody speaks he same language, and optimizing operations for humans will likely result in a safer ship. In short, the shipping industry should go from error-inducing to error-reducing, but this is not an easy solution. However, with a focus on safety during operation, the shipping industry can become significantly safer overall.

Finally, chapter 9 shows that it is possible to at least assess the safety and sustainability of alternative fuels on ships, under certain conditions. First, a specific set of values has to be decided to be used to assess. Choosing these values is not trivial and requires careful consideration. However, discussing and assessing these values is already a first step in the assessment of alternative fuels, and with argumentation it can become clear why which values are taken into account. Hydrogen carriers (and other alternative fuels) can then be assessed on each of these values. When desired, MDO can be used as a base scenario to compare fuels on each of these values with, however, it is of utmost importance to only compare fuels on one value at a time. When comparing them on all values, the weight of each of the values has to be assessed - what is deemed to be more important? This may also strongly be influenced by the operational profile and location of the ship. A ship sailing through cities may desire to protect the public health more than a ship that only sails on the deep seas, while a ship sailing through coral reefs may value the environmental impact more than another. However, when explicitly stating these values, why they are chosen on which occasion will shed light on the safest (and sustainable) hydrogen carrier. Despite not being able to single out one as best, well-thought choices can be made.

10.5 TIMELINESS

Timeliness: coming early or at the right time [413]

Timeliness — coming at the right time — may be the most critical quality hydrogen carriers need to possess. These technologies represent innovative solutions to the pressing challenge of identifying alternative fuels for the shipping industry. Although none of the hydrogen carriers examined are without limitations, they collectively offer a safer and more energy-dense alternative to many current fuel options, and they remain compatible with most hydrogen-based converters.

But the main question will be: are they in time? Their low TRL may be the primary factor hindering their usage; both now and in the long term. Ships are built in classes and remain in service for decades, which means that once an alternative fuel is selected, the surrounding design choices concerning energy converters, bunkering systems, storage solutions and logistics, tend to become fixed for many years. This long operational lifetime makes any fuel decision difficult to reverse.

The IMO targets of reaching zero GHG emissions by 2050 mean that ships must be designed or at least design-ready, for compliance today. At the same time, this moment of transition is unusually fragile. Climate policy and the geopolitical drive for energy autonomy are accelerating the pace of change, shifting decisions that once lay decades ahead into the present. This creates a rare window in which long-standing fuel choices are being reconsidered, but such windows close quickly. Once the industry settles on an alternative that is “good enough”, which ammonia or methanol may well prove to be and the sector may rapidly commit to that option for an entire generation of ships.

So, in the end, it may be that hydrogen carriers will not manage to be part of this design phase at all; their low TRL makes designers, shipowners, shipyards and companies hesitant to adopt them. Ultimately, the success of hydrogen carriers may depend less on their intrinsic performance than on their timely implementation.

11

CONCLUSION

> *End? No, it doesn't end here*
>
> Gandalf, *The Lord of the Rings: The Return of the King*

CHAPTER SUMMARY

This thesis investigated hydrogen carriers as alternative marine fuels to support the decarbonization of ships. Five promising carriers were identified and evaluated with respect to technical feasibility, safety, and sustainability. Energy and power density analyses showed that, although borohydride-based carriers such as sodium borohydride (SB) and ammonia borane (AB) exhibit high energy densities, no single carrier performs best across all criteria. Safety and sustainability assessments likewise revealed trade-offs rather than a universal optimum. The results highlight that the "best" hydrogen carrier depends on context, ship type, and operational priorities. Despite current technological immaturity, hydrogen carriers remain a promising pathway toward low-carbon shipping, warranting continued research, development, and early demonstration.

Hydrogen carriers are an alternative fuel option to reduce greenhouse gas emissions in the maritime industry. The maritime industry has several unique challenges to use these substances as fuels. This thesis aimed to find a suitable set of hydrogen carrier and energy converters to use as fuel on ships. Its first contribution was to find a set of hydrogen carriers that exhibit promising properties to use on ships. A literature review found five promising hydrogen carriers. These carriers are sodium borohydride (SB), ammonia borane (AB), potassium borohydride (KB), dibenzyltoluene (DBT) and n-ethylcarbazole (NEC). The next objective was to evaluate the energy and power density, which should be sufficient to use on ships (and preferably higher than pure hydrogen). Additionally, the hydrogen carriers should be safe. This thesis assessed the five carriers on these two characteristics. Soon, KB was disregarded, as it performed less favourably than SB across all evaluated properties. The other four have been evaluated across technical and safety properties. The technical properties were evaluated using models, while the safety properties were evaluated by using data from literature and own experiments. Combined, an overview of the possible combinations was assessed to find out whether a single hydrogen carrier and energy converter combination could be considered the best.

11.1 INSIGHTS FROM POWER AND ENERGY DENSITY PERSPECTIVE

To begin evaluating what may constitute the "best" hydrogen carrier from a technical perspective, this section examines the carriers' energy and power densities as key indicators of their practical feasibility on ships. The energy densities of the investigated hydrogen carriers for marine applications were thoroughly evaluated. By integrating waste heat, the total energy density of the endothermic hydrogen-releasing carriers, NEC and DBT, was maintained rather than reduced. Without this integration, their effective (gravimetric and volumetric) energy densities would decrease significantly, since part of the released hydrogen would otherwise need to be consumed to sustain the dehydrogenation reaction.

In contrast, the two borohydride-based carriers, SB and AB, achieve higher effective energy densities when applied on ships because they can use seawater, after purification, as an additional hydrogen source. This process increases the total hydrogen yield but also produces heavier spent fuels. The effect of this additional mass was not included in the present assessment, as the concept is still novel and its operational implications are not yet well understood. Overall, SB and AB showed very high energy densities, approaching those of marine diesel oil (MDO).

With regard to power density, several auxiliary components are required for system operation. Heat exchangers are necessary for waste-heat recovery, and hydrogen-release reactors enable the dehydrogenation process. Additional systems for residue management may also be needed, since the mixture of unreacted and spent fuel could potentially be processed further. However, because these aspects depend strongly on the specific reactor and catalyst design, they were not quantitatively considered in this study. The analysis indicates that reactor volume has the greatest influence on the total system size, whereas the required heat exchangers are comparatively compact.

When the power and energy densities were evaluated together, it became clear that no single hydrogen carrier is universally optimal. For different ship types—ranging from fishing vessels and inland barges to ocean-going freighters—different hydrogen carrier and energy-converter combinations proved most suitable. Each case therefore presents several viable options rather than one definitive best choice.

11.2 INSIGHTS FROM SAFETY AND SUSTAINABILITY PERSPECTIVE

Comparing alternative fuels, in general, and hydrogen carriers specifically on safety and sustainability values to find "the best" can quickly become biased. Safety and sustainability are value-sets consisting of many values and when trying to rank fuels, a rank in these values has to be decided upon. This decision can strongly influence the outcome, which is why this thesis only compared fuels on the same value. In this, there is belief that the journey is more important than the destination. The starting point of looking at values, deciding which values are important and can be evaluated is more important than the actual outcomes.

However, within the scope of one single value, it is possible to evaluate and compare the hydrogen carriers. Yet, this also results in a nuanced picture, where carriers may exhibit both positive and negative influences. For example, substances can positively influence long-term viability due to their carbon-neutral and recyclable nature. On the other hand, during a large scale spill they can have long-lasting effects on the environment, negatively influencing long-term viability.

These kind of dilemmas are important to realise and face, as there is in this case no single best carrier. Each of these hydrogen carriers have their negative and positive influences, on safety and sustainability, and a choice has to be made deliberate and with thought, depending on the specific situation and operational profile of the intended ship.

11.3 SCIENTIFIC CONTRIBUTIONS

This thesis addressed four scientific objectives. Each contribution addressed a distinct research gap, collectively advancing the understanding of hydrogen carriers as maritime fuels. The primary objective was to evaluate a broad range of hydrogen carriers in terms of their suitability for use on board ships. To achieve this, this thesis introduces a systematic classification of hydrogen carriers based on their chemical and physical characteristics. This classification enables group-wise assessment and efficient identification of promising candidates for maritime applications, reducing the effort required for preliminary screening.

The second objective was to evaluate the technical feasibility of integrating hydrogen carriers with different energy converters. An analytical model was developed to integrate waste heat and water, where applicable, to increase the overall energy density of the hydrogen carriers. This model was applied to assess the effective energy density of hydrogen carriers, which is comparable to that of diesel. The model also enables the assessment of other hydrogen carriers and energy converters due to its modularity.

The third objective was to assess the safety and sustainability of hydrogen carriers used in maritime applications. The systematic evaluation method developed is able to help assess and compare alternative fuels with a variety of technology readiness levels, including relatively new and unknown fuels. As the framework aims to help in decision making, ranking is excluded from it, yet values that influence the sustainability of an alternative fuel, which defines the long-term safety and usage possibilities, is included. This framework therefore provides a structured starting point for selecting alternative fuels based on safety and sustainability considerations.

Finally, the fourth objective was to identify the most suitable combinations of hydrogen carriers and energy converters for different ship types. By comparing and evaluating a large set of values, the most suitable hydrogen carrier can be defined, depending on the operational needs and layout of a certain ship type. However, the broader philosophical discussion showed that, of all these values, one likely outweighs all the others: timeliness. A hydrogen carrier introduced too late may never be widely adopted. Coming at the exact right time is thus of utmost importance, with many of the other values, including safety and energy density, having less importance.

11.4 FUTURE OUTLOOK

Before hydrogen carriers can be widely implemented in the maritime sector, considerable development work remains to be done. On the technical side, catalysts must be selected and optimized, and appropriate reactor concepts need to be designed and validated. The associated heat exchangers and spent fuel regeneration equipment also require further investigation, as the thermochemical behaviour of many hydrogen carriers can be complex and may not yet be fully understood.

From a safety standpoint, significant gaps exist in the available data. Many safety data sheets are incomplete, inconsistent, or entirely missing. Comprehensive experimental studies and standardized reporting will therefore be essential before these materials can be approved for large-scale use on ships.

Beyond these technical and safety challenges, successful deployment will also depend on strategic and organizational choices. Shipowners, operators, and classification societies will need to determine which values (such as safety, energy density or cost efficiency) take precedence when selecting a fuel.

Perhaps most importantly, progress will require decisive investment and early demonstration projects. The current low technology readiness level of hydrogen carriers makes them costly to develop, and delays may result in other alternative fuels, such as ammonia or methanol, capturing the market first. However, if research and pilot projects continue at pace, hydrogen carriers could emerge as a viable and versatile pathway toward reducing greenhouse gas emissions in shipping. Their potential justifies sustained attention and coordinated effort across academia, industry, and regulation.

11.5 ADMINISTRATIVE INFORMATION

11.5.1 SUPPLEMENTARY DATA AVAILABILITY

Table 11.1 lists references to datasets, models and code that, where applicable, support the results presented in this dissertation. Access to the source code developed for this research may be provided for academic and research purposes, subject to written approval from Delft University of Technology and the author of this dissertation.

Chapter	Type of data	DOI
3 & 5	Models and Excel data	10.4121/a1888538-f623-4df9-9217-538edd7e0917
4 & 5	Models and Excel data	10.4121/95ae4238-b9f1-4ba0-a40c-e661d1611cff
7	Experimental data sets	10.4121/5eaec65b-c728-413c-82ad-c3b722a57353

Table 11.1: Access to supplementary data

11.5.2 USE OF GENERATIVE AI

During the preparation of this work the author used ChatGPT in order to enhance clarity of sentences where necessary. After using this tool/service, the author reviewed and edited the content as needed and takes full responsibility for the content of the published article.

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BIBLIOGRAPHY

[1] S. McGrail, *Boats of the World: From the Stone Age to Medieval Times*. Oxford: Oxford University Press, 2009, ISBN: 9780198144687.

[2] J. Guthrie, *A History of Marine Engineering*. London: Hutchinson Educational Limited, 1971, ISBN: 0091082005.

[3] T. E. Ostervald, *Arrivée de londres à paris le 29 mars 1816 du bateau à vapeur « l'élise »*, Aquatint print, Sheet: 260 × 356 mm; plate: 220 × 284 mm. Credit: National Maritime Museum, Greenwich, London. Object ID: PAH0155. Royal Museums Greenwich, Collections Online. Accessed: 21 November 2025, 1814 (and 26 Mar 1816). [Online]. Available: `https://www.rmg.co.uk/collections/objects/rmgc-object-140102`.

[4] C. Naafs, 'De gouden driehoek centraal tijdens het tideman-symposium', *Marineblad*, 2025, Accessed: 26 November 2025. [Online]. Available: `https://www.marineblad.nl/artikel/de-gouden-driehoek-centraal-tijdens-het-tideman-symposium`.

[5] J. Korteweg, 'Bruno joannes tideman – a man of remarkably keen insight', *SWZ | Maritime*, 2025, Accessed: 26 November 2025. [Online]. Available: `https://swzmaritime.nl/news/2025/01/30/bruno-joannes-tideman-a-man-of-remarkably-keen-insight/`.

[6] K. Davids and J. Schokkenbroek, Eds., *The Transformation of Maritime Professions: Old and New Jobs in European Shipping Industries, 1850–2000* (Palgrave Studies in Economic History). Palgrave Macmillan, Cham, 2023, pp. xviii + 288, ISBN: 978-3-031-27211-0. DOI: `10.1007/978-3-031-27212-7`.

[7] W. M. Brown, 'The royal navy's fuel supplies 1898–1939: The transition from coal to oil', Ph.D. thesis, King's College London, 2003. [Online]. Available: `https://kclpure.kcl.ac.uk/portal/files/2932258/408161.pdf`.

[8] D. Micheli, S. Clemente and R. Taccani, 'Chapter 2 - energy systems on board ships', *Sustainable Energy Systems on Ships*, F. Baldi, A. Coraddu and M. E. Mondejar, Eds., Elsevier, 2022, pp. 27–78, ISBN: 978-0-12-824471-5. DOI: `10.1016/B978-0-12-824471-5.00008-6`.

[9] T. R. Walker et al., 'Chapter 27 - environmental effects of marine transportation', *World Seas: An Environmental Evaluation (Second Edition)*, C. Sheppard, Ed., 2nd Edition, Academic Press, 2019, pp. 505–530, ISBN: 978-0-12-805052-1. DOI: `10.1016/B978-0-12-805052-1.00030-9`.

[10] M. Asmussen and P. V. Ostaeyen, *How real-time emissions tracking can help decarbonize the maritime industry*, Accessed: 1 July 2025, 2025. [Online]. Available: `https://www.weforum.org/stories/2025/05/decarbonize-maritime-industry-real-time-emissions-tracking/`.

[11] NOAA Office of Response and Restoration / IncidentNews, *Incident map — incidentnews*, Accessed: 2025-10-09, National Oceanic and Atmospheric Administration, 2025. [Online]. Available: `\url{https://incidentnews.noaa.gov/map}`.

[12] N. H. Siang, *Singapore-flagged tanker and malta ship collide off tanah merah, 'light oil sheens' sighted*, Accessed: 2025-10-09; updated 1 Sep 2025, 06:45 PM, 2025. [Online]. Available: `https://www.channelnewsasia.com/singapore/tanah-merah-vessel-collision-marine-dynamo-flag-gangos-5326341`.

[13] International Maritime Organization, *2023 imo strategy on reduction of ghg emissions from ships*, [Accessed 27-09-2025], n.d. [Online]. Available: `https://www.imo.org/en/ourwork/environment/pages/2023-imo-strategy-on-reduction-of-ghg-emissions-from-ships.aspx`.

[14] DNV, *Energy-efficiency measures and technologies: Key solutions and strategies for maritime's decarbonization journey*, Published by DNV. Accessed: 23 July 2023, 2025. [Online]. Available: `https://www.dnv.com/maritime/publications/energy-efficiency-report-download/`.

[15] DNV, *Maritime forecast to 2050*, Published by DNV. Accessed: 10 October 2025, 2025. [Online]. Available: `https://www.dnv.com/maritime/maritime-forecast/`.

[16] E. Rivard, M. Trudeau and K. Zaghib, 'Hydrogen storage for mobility: A review', *Materials*, vol. 12, 12 2019, ISSN: 19961944. DOI: `10.3390/ma12121973`.

[17] X. Seykens et al., 'Hydrogen combustion concepts: Comparison of port fuel injection with spark ignition and high pressure direct injection (hpdi) – power density, efficiency, and emissions', *Proceedings of the 44th International Vienna Motor Symposium*, Vienna, Austria: ÖVK, 2023, ISBN: 978-3-9504969-2-5.

[18] L. van Biert et al., 'A review of fuel cell systems for maritime applications', *Journal of Power Sources*, vol. 327, pp. 345–364, 2016, ISSN: 03787753. DOI: `10.1016/j.jpowsour.2016.07.007`.

[19] L. V. Hoecke et al., 'Challenges in the use of hydrogen for maritime applications', *Energy & Environmental Science*, vol. 14, pp. 815–843, 2 2021. DOI: `10.1039/D0EE01545H`.

[20] C. J. McKinlay, S. R. Turnock and D. A. Hudson, 'A comparison of hydrogen and ammonia for future long distance shipping fuels', *RINA, Royal Institution of Naval Architects - International Conference on LNG/LPG and Alternative Fuel Ships*, 2020.

[21] S. Lee et al., 'Comparative energetic studies on liquid organic hydrogen carrier: A net energy analysis', *Renewable and Sustainable Energy Reviews*, vol. 150, 2021, ISSN: 18790690. DOI: `10.1016/j.rser.2021.111447`.

[22] B. Diesveld and E. D. Maeyer, 'Maritime fuel cell applications: A tool for conceptual decision making', *International Shipbuilding Progress*, vol. 67, no. 1, pp. 57–77, 2020. DOI: `10.3233/ISP-190275`.

[23] L. Li et al., 'Assessing the waste heat recovery potential of liquid organic hydrogen carrier chains', *Energy Conversion and Management*, vol. 276, p. 116 555, 2023. DOI: `10.1016/J.ENCONMAN.2022.116555`.

[24] P. Preuster et al., 'Solid oxide fuel cell operating on liquid organic hydrogen carrier-based hydrogen – making full use of heat integration potentials', *International Journal of Hydrogen Energy*, vol. 43, pp. 1758–1768, 3 2018. DOI: `10.1016/J.IJHYDENE.2017.11.054`.

[25] M. Niermann et al., 'Liquid organic hydrogen carrier (lohc) – assessment based on chemical and economic properties', *International Journal of Hydrogen Energy*, vol. 44, pp. 6631–6654, 13 2019, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2019.01.199`.

[26] K. Müller, S. Thiele and P. Wasserscheid, 'Evaluations of concepts for the integration of fuel cells in liquid organic hydrogen carrier systems', *Energy and Fuels*, vol. 33, pp. 10 324–10 330, 10 2019. DOI: `10.1021/acs.energyfuels.9b01939`.

[27] M. Otto et al., 'Optimal hydrogen carrier: Holistic evaluation of hydrogen storage and transportation concepts for power generation, aviation, and transportation', *Journal of Energy Storage*, vol. 55, pp. 2352–152, 2022. DOI: `10.1016/j.est.2022.105714`.

[28] M. Gambini et al., 'Feasibility study of lohc-sofc systems under dynamic behavior for cargo ships compared to ammonia alternatives', *International Journal of Hydrogen Energy*, vol. 81, pp. 81–92, 2024, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2024.07.224`.

[29] E. S. van Rheenen et al., 'Comparative energy analysis of hydrogen carriers as energy source on ships', *Journal of Marine Engineering & Technology*, vol. 0, no. 0, pp. 1–15, 2025. DOI: `10.1080/20464177.2024.2448057`.

[30] N. P. Santos, 'Hydrogen in the portuguese navy: A case study', *International Journal of Hydrogen Energy*, vol. 47, pp. 28 684–28 698, 66 2022, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2022.06.180`.

[31] A. Düll et al., 'Performance evaluation of kbh4 as energy carrier for shipping applications', *Chemie Ingenieur Technik*, vol. 94, no. 5, pp. 747–759, 2022. DOI: `10.1002/cite.202100193`.

[32] K. Machaj et al., 'Ammonia as a potential marine fuel: A review', *Energy Strategy Reviews*, vol. 44, p. 100 926, 2022, ISSN: 2211-467X. DOI: `10.1016/j.esr.2022.100926`.

[33] W. Zhang et al., 'Review of the state-of-the-art of alternative marine fuels: A viable approach to zero-carbon shipping', *Cleaner Logistics and Supply Chain*, vol. 16, p. 100 232, 2025, ISSN: 2772-3909. DOI: `10.1016/J.CLSCN.2025.100232`.

[34] E. Strantzali, G. A. Livanos and K. Aravossis, 'A comprehensive multicriteria evaluation approach for alternative marine fuels', *Energies 2023, Vol. 16, Page 7498*, vol. 16, p. 7498, 22 2023, ISSN: 1996-1073. DOI: `10.3390/EN16227498`.

[35] A. M. Moshiul, R. Mohammad and F. A. Hira, 'Alternative fuel selection framework toward decarbonizing maritime deep-sea shipping', *Sustainability 2023, Vol. 15, Page 5571*, vol. 15, p. 5571, 6 2023, ISSN: 2071-1050. DOI: `10.3390/SU15065571`.

[36] J. Hansson et al., 'Alternative marine fuels: Prospects based on multicriteria decision analysis involving swedish stakeholders', *Biomass and Bioenergy*, vol. 126, pp. 159–173, 2019, ISSN: 0961-9534. DOI: `10.1016/J.BIOMBIOE.2019.05.008`.

[37] C. Deniz and B. Zincir, 'Environmental and economical assessment of alternative marine fuels', *Journal of Cleaner Production*, vol. 113, pp. 438–449, 2016, ISSN: 0959-6526. DOI: `10.1016/J.JCLEPRO.2015.11.089`.

[38] N. Mandić et al., 'Multicriteria analysis of alternative marine fuels in sustainable coastal marine traffic', *Applied Sciences 2021, Vol. 11, Page 2600*, vol. 11, p. 2600, 6 2021, ISSN: 2076-3417. DOI: `10.3390/APP11062600`.

[39] Y. Wang, L. A. Wright and M. Bergman, 'A comparative review of alternative fuels for the maritime sector: Economic, technology, and policy challenges for clean energy implementation', *World*, vol. 2, pp. 456–481, 4 2021, ISSN: 2673-4060. DOI: `10.3390/WORLD2040029`.

[40] S.-P. Chen, J.-E. Li and Y.-X. Chen, 'Lifecycle cost-effectiveness analysis for greener alternative shipping fuels towards maritime energy sustainability', *npj Clean Energy 2025 1:1*, vol. 1, pp. 1–11, 1 2025, ISSN: 3059-2232. DOI: `10.1038/s44406-025-00006-4`.

[41] K. Kouzelis, K. Frouws and E. van Hassel, 'Maritime fuels of the future: What is the impact of alternative fuels on the optimal economic speed of large container vessels', *Journal of Shipping and Trade 2022 7:1*, vol. 7, pp. 1–29, 1 2022, ISSN: 2364-4575. DOI: `10.1186/S41072-022-00124-7`.

[42] T. Solakivi, A. Paimander and L. Ojala, 'Cost competitiveness of alternative maritime fuels in the new regulatory framework', *Transportation Research Part D: Transport and Environment*, vol. 113, p. 103 500, 2022, ISSN: 1361-9209. DOI: `10.1016/J.TRD.2022.103500`.

[43] Q. Wang et al., 'The use of alternative fuels for maritime decarbonization: Special marine environmental risks and solutions from an international law perspective', *Frontiers in Marine Science*, vol. 9, p. 1 082 453, 2023, ISSN: 22967745. DOI: `10.3389/FMARS.2022.1082453/BIBTEX`.

[44] Z. Yang et al., 'Evaluating alternative low carbon fuel technologies using a stakeholder participation-based q-rung orthopair linguistic multi-criteria framework', *Applied Energy*, vol. 332, p. 120 492, 2023, ISSN: 0306-2619. DOI: `10.1016/j.apenergy.2022.120492`.

[45] A. Foretich et al., 'Challenges and opportunities for alternative fuels in the maritime sector', *Maritime Transport Research*, vol. 2, p. 100 033, 2021. DOI: `10.1016/j.martra.2021.100033`.

[46] International Energy Agency, 'International shipping', *Paris*, 2021, Accessed on 22nd June 2022. [Online]. Available: `https://www.iea.org/reports/international-shipping`.

[47] J. Zheng et al., 'Current research progress and perspectives on liquid hydrogen rich molecules in sustainable hydrogen storage', *Energy Storage Materials*, vol. 35, pp. 695–722, 2021, ISSN: 2405-8297. DOI: `10.1016/J.ENSM.2020.12.007`.

[48] D. J. Durbin and C. Malardier-Jugroot, 'Review of hydrogen storage techniques for on board vehicle applications', *International Journal of Hydrogen Energy*, vol. 38, pp. 14 595–14 617, 34 2013, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2013.07.058`.

[49] U.S. Department of Energy, *Fuel cell technologies office multi-year research, development, and demonstration plan*, Accessed on 3rd June 2022, 2015. [Online]. Available: `https://www.energy.gov/eere/fuelcells/articles/hydrogen-and-fuel-cell-technologies-office-multi-year-research-development`.

[50] O. B. Inal and C. Deniz, 'Assessment of fuel cell types for ships: Based on multi-criteria decision analysis', *Journal of Cleaner Production*, vol. 265, pp. 673–684, 2020, ISSN: 09596526. DOI: `10.1016/j.jclepro.2020.121734`.

[51] R. Moradi and K. M. Groth, 'Hydrogen storage and delivery: Review of the state of the art technologies and risk and reliability analysis', *International Journal of Hydrogen Energy*, vol. 44, pp. 12 254–12 269, 23 2019, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2019.03.041`.

[52] K. T. Møller et al., 'Hydrogen - a sustainable energy carrier', *Progress in Natural Science: Materials International*, vol. 27, pp. 34–40, 1 2017, ISSN: 1002-0071. DOI: `10.1016/J.PNSC.2016.12.014`.

[53] Y. Kojima, 'Hydrogen storage materials for hydrogen and energy carriers', *International Journal of Hydrogen Energy*, vol. 44, pp. 18 179–18 192, 33 2019, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2019.05.119`.

[54] J. Abe et al., 'Hydrogen energy, economy and storage: Review and recommendation', *International Journal of Hydrogen Energy*, vol. 44, pp. 15 072–15 086, 29 2019, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2019.04.068`.

[55] J. Bellosta von Colbe et al., 'Application of hydrides in hydrogen storage and compression: Achievements, outlook and perspectives', *International Journal of Hydrogen Energy*, vol. 44, pp. 7780–7808, 15 2019, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2019.01.104`.

[56] K. van Kranenburg et al., 'E-fuels: Towards a more sustainable future for truck transport, shipping and aviation', TNO, Tech. Rep., 2020. [Online]. Available: `https://publications.tno.nl/publication/34636875/KDhcac/vankranenburg-2020-efuels.pdf`.

[57] P. Preuster et al., 'Solid oxide fuel cell operating on liquid organic hydrogen carrier-based hydrogen – making full use of heat integration potentials', *International Journal of Hydrogen Energy*, vol. 43, no. 3, pp. 1758–1768, 2018, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2017.11.054`.

[58] P. Gilbert et al., 'Assessment of full life-cycle air emissions of alternative shipping fuels', *Journal of Cleaner Production*, vol. 172, pp. 855–866, 2018, ISSN: 0959-6526. DOI: `10.1016/j.jclepro.2017.10.165`.

[59] B. P. Tarasov et al., 'Metal hydride hydrogen storage and compression systems for energy storage technologies', *International Journal of Hydrogen Energy*, vol. 46, pp. 13 647–13 657, 25 2021, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2020.07.085`.

[60] H. Q. Nguyen and B. Shabani, 'Review of metal hydride hydrogen storage thermal management for use in the fuel cell systems', *International Journal of Hydrogen Energy*, vol. 46, pp. 31 699–31 726, 62 2021, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2021.07.057`.

[61] K. Malleswararao et al., 'Experiments on a novel metal hydride cartridge for hydrogen storage and low temperature thermal storage', *International Journal of Hydrogen Energy*, 2022, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2022.03.097`.

[62] J. M. Brunel, 'Polysilanes: The grail for a highly-neglected hydrogen storage source', *International Journal of Hydrogen Energy*, vol. 42, pp. 23 004–23 009, 36 2017, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2017.07.206`.

[63] V. Kumar and E. Leitao, 'Properties and applications of polysilanes', *Applied Organometallic Chemistry*, vol. 34, 2020. DOI: `10.1002/aoc.5402`.

[64] T. Mitsudome et al., 'On-demand hydrogen production from organosilanes at ambient temperature using heterogeneous gold catalysts', *Scientific Reports 2016 6:1*, vol. 6, pp. 1–5, 1 2016, ISSN: 2045-2322. DOI: `10.1038/srep37682`.

[65] W. S. Han et al., 'Silane-based hydrogen storage materials for fuel cell application: Hydrogen release via methanolysis and regeneration by hydride reduction from organosilanes', *International Journal of Hydrogen Energy*, vol. 36, pp. 12 305–12 312, 19 2011, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2011.06.118`.

[66] T. Shimbayashi and K. Fujita, 'Metal-catalyzed hydrogenation and dehydrogenation reactions for efficient hydrogen storage', *Tetrahedron*, vol. 76, p. 130 946, 11 2020, ISSN: 0040-4020. DOI: `10.1016/J.TET.2020.130946`.

[67] E. Pawelczyk et al., 'Recent progress on hydrogen storage and production using chemical hydrogen carriers', *Energies*, vol. 15, no. 14, 2022, ISSN: 1996-1073. DOI: `10.3390/en15144964`.

[68] T. Shimonosono et al., 'Separation of hydrogen from carbon dioxide through porous ceramics', *Materials*, vol. 9, 11 2016. DOI: `10.3390/ma9110930`.

[69] W. Salim and W. S. Ho, 'Hydrogen purification with co2-selective facilitated transport membranes', *Current Opinion in Chemical Engineering*, vol. 21, pp. 96–102, 2018, ISSN: 2211-3398. DOI: `10.1016/J.COCHE.2018.09.004`.

[70] J. W. Makepeace et al., 'Reversible ammonia-based and liquid organic hydrogen carriers for high-density hydrogen storage: Recent progress', *International Journal of Hydrogen Energy*, vol. 44, pp. 7746–7767, 15 2019, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2019.01.144`.

[71] J. Chiefari and C. Hornung, 'Mobile hydrogen reformers as a novel approach to decarbonise the transport sector', *Current Opinion in Chemical Engineering*, vol. 34, p. 100 756, 2021, ISSN: 2211-3398. DOI: `10.1016/J.COCHE.2021.100756`.

[72] Hydrogenious, *Alma clean power, hydrogenious lohc technologies, hydrogenious lohc maritime announce jda*, Accessed on 30th March 2023, 2023. [Online]. Available: `https://hydrogenious.net/alma-clean-power-hydrogenious-lohc-technologies-hydrogenious-lohc-maritime-announce-jda/`.

[73] C. Lang, Y. Jia and X. Yao, 'Recent advances in liquid-phase chemical hydrogen storage', *Energy Storage Materials*, vol. 26, pp. 290–312, 2020, ISSN: 2405-8297. DOI: `10.1016/J.ENSM.2020.01.010`.

[74] P. C. Rao and M. Yoon, 'Potential liquid-organic hydrogen carrier (lohc) systems: A review on recent progress', *Energies*, vol. 13, 22 2020, ISSN: 19961073. DOI: `10.3390/en13226040`.

[75] Y. Sekine and T. Higo, 'Recent trends on the dehydrogenation catalysis of liquid organic hydrogen carrier (lohc): A review', *Topics in Catalysis*, vol. 64, pp. 470–480, 7-8 2021, ISSN: 15729028. DOI: `10.1007/s11244-021-01452-x`.

[76] G. P. Moss, P. A. S. Smith and D. Tavernier, 'Glossary of class names of organic compounds and reactivity intermediates based on structure (iupac recommendations 1995)', *Pure and Applied Chemistry*, vol. 67, no. 8-9, p. 1320, 1995. DOI: `doi:10.1351/pac199567081307`. [Online]. Available: `10.1351/pac199567081307`.

[77] D. Motta et al., 'Hydrous hydrazine decomposition for hydrogen production using of ir/ceo 2 : Effect of reaction parameters on the activity', *nanomaterials*, 2021. DOI: `10.3390/nano11051340`.

[78] NCBI, *Pubchem compound lcss for cid 222, ammonia*, Accessed on 28th March 2023, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Ammonia#datasheet=LCSS`.

[79] NCBI, *Pubchem compound summary for cid 9321, hydrazine*, Accessed on 15 March 2023, 2023. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Hydrazine`.

[80] H. W. Langmi et al., 'Hydrogen storage in metal-organic frameworks: A review', *Electrochimica Acta*, vol. 128, pp. 368–392, 2014, ISSN: 0013-4686. DOI: `10.1016/J.ELECTACTA.2013.10.190`.

[81] A. Zuttel et al., 'Hydrogen storage in carbon nanostructures', *International Journal of Hydrogen Energy*, vol. 27, pp. 203–212, 2 2002, ISSN: 0360-3199. DOI: `10.1016/S0360-3199(01)00108-2`.

[82] A. I. Bevan et al., 'Performance of a metal hydride store on the "ross barlow" hydrogen powered canal boat', *Faraday Discussions*, vol. 151, pp. 353–367, 2011, ISSN: 13596640. DOI: `10.1039/C0FD00025F`.

[83] U. B. Demirci, 'Ammonia borane: An extensively studied, though not yet implemented, hydrogen carrier', *Energies*, vol. 13, 12 2020, ISSN: 19961073. DOI: `10.3390/en13123071`.

[84] L. Laversenne et al., 'Hydrogen storage in borohydrides comparison of hydrolysis conditions of libh4, nabh4 and kbh4', *Journal of Thermal Analysis and Calorimetry*, vol. 94, 3 2008, ISSN: 13886150. DOI: `10.1007/s10973-008-9073-4`.

[85] T. Umegaki et al., 'Boron- and nitrogen-based chemical hydrogen storage materials', *International Journal of Hydrogen Energy*, vol. 34, 5 2009, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2009.01.002`.

[86] U. B. Demirci and P. Miele, 'Sodium tetrahydroborate as energy/hydrogen carrier, its history', *Comptes Rendus Chimie*, vol. 12, pp. 943–950, 9 2009, ISSN: 16310748. DOI: `10.1016/j.crci.2008.08.002`.

[87] P. Martelli et al., 'Stability and decomposition of nabh4', *Journal of Physical Chemistry C*, vol. 114, 15 2010, ISSN: 19327447. DOI: `10.1021/jp909341z`.

[88] Z. Xueping and L. Shenglin, 'Study on hydrogen storage properties of lialh4', *Journal of Alloys and Compounds*, vol. 481, pp. 761–763, 1-2 2009, ISSN: 09258388. DOI: `10.1016/j.jallcom.2009.03.089`.

[89] Z. Liu et al., 'Improved hydrogen storage properties and mechanisms of lialh4 doped with ni/c nanoparticles anchored on large-size ti3c2tx', *Journal of Alloys and Compounds*, vol. 931, p. 167 353, 2023, ISSN: 0925-8388. DOI: `10.1016/J.JALLCOM.2022.167353`.

[90] N. A. Sazelee and M. Ismail, 'Recent advances in catalyst-enhanced lialh4 for solid-state hydrogen storage: A review', *International Journal of Hydrogen Energy*, vol. 46, pp. 9123–9141, 13 2021, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2020.12.208`.

[91] C. Milanese et al., 'Solid state hydrogen storage in alanates and alanate-based compounds: A review', *Metals*, vol. 8, no. 8, 2018, ISSN: 2075-4701. DOI: `10.3390/met8080567`.

[92] L. Wang et al., 'Nanoconfined lithium aluminium hydride (lialh4) and hydrogen reversibility', *International Journal of Hydrogen Energy*, vol. 42, pp. 14 144–14 153, 20 2017, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2017.04.104`.

[93] N. A. Ali and M. Ismail, 'Modification of naalh4 properties using catalysts for solid-state hydrogen storage: A review', *International Journal of Hydrogen Energy*, vol. 46, pp. 766–782, 1 2021, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2020.10.011`.

[94] K. Suárez-Alcántara, J. R. Tena-Garcia and R. Guerrero-Ortiz, 'Alanates, a comprehensive review', *Materials*, vol. 12, no. 17, 2019, ISSN: 1996-1944. DOI: `10.3390/ma12172724`.

[95] T. Rüde et al., 'Benzyltoluene/perhydro benzyltoluene-pushing the performance limits of pure hydrocarbon liquid organic hydrogen carrier (lohc) systems', *Sustainable Energy & Fuels*, vol. 6, 2022. DOI: `10.1039/d1se01767e`.

[96] Y. Kwak et al., 'Hydrogen production from homocyclic liquid organic hydrogen carriers (lohcs): Benchmarking studies and energy-economic analyses', *Energy Conversion and Management*, vol. 239, p. 114 124, 2021. DOI: `10.1016/J.ENCONMAN.2021.114124`.

[97] G. E. Froudakis, 'Hydrogen storage in nanotubes & nanostructures', *Materials Today*, vol. 14, no. 7, pp. 324–328, 2011, ISSN: 1369-7021. DOI: `10.1016/S1369-7021(11)70162-6`.

[98] S. P. Shet et al., 'A review on current trends in potential use of metal-organic framework for hydrogen storage', *International Journal of Hydrogen Energy*, vol. 46, pp. 11 782–11 803, 21 2021, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2021.01.020`.

[99] O. K. Farha et al., ‘De novo synthesis of a metal organic framework material featuring ultrahigh surface area and gas storage capacities’, *Nature Chemistry 2010 2:11*, vol. 2, pp. 944–948, 11 2010, ISSN: 1755-4349. DOI: `10.1038/nchem.834`.

[100] P. Habibi et al., ‘Reversible hydrogen storage in metal-decorated honeycomb borophene oxide’, *ACS Appl. Mater. Interfaces*, vol. 13, p. 43 240, 2021. DOI: `10.1021/acsami.1c09865`.

[101] A. Jaiswal et al., ‘Alkali metals decorated silicon clusters (sinmn, n = 6, 10; m = li, na) as potential hydrogen storage materials: A dft study’, *International Journal of Hydrogen Energy*, vol. 47, pp. 1775–1789, 3 2022, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2021.10.228`.

[102] L. del Rosso, M. Celli and L. Ulivi, ‘Ice xvii as a novel material for hydrogen storage’, *Challenges*, vol. 8, 1 2017. DOI: `10.3390/challe8010003`.

[103] Y. Liu et al., ‘An ultralow-density porous ice with the largest internal cavity identified in the water phase diagram’, *Proceedings of the National Academy of Sciences of the United States of America*, vol. 116, pp. 12 684–12 691, 26 2019, ISSN: 10916490. DOI: `10.1073/pnas.1900739116`.

[104] L. J. Florusse et al., ‘Stable low-pressure hydrogen clusters stored in a binary clathrate hydrate’, *Science*, vol. 306, no. 5695, pp. 469–471, 2004. DOI: `10.1126/science.1102076`.

[105] L. Wang, M. Z. Quadir and K. F. Aguey-Zinsou, ‘Direct and reversible hydrogen storage of lithium hydride (lih) nanoconfined in high surface area graphite’, *International Journal of Hydrogen Energy*, vol. 41, pp. 18 088–18 094, 40 2016, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2016.07.073`.

[106] M. S. Salman et al., ‘The power of multifunctional metal hydrides: A key enabler beyond hydrogen storage’, *Journal of Alloys and Compounds*, vol. 920, p. 165 936, 2022, ISSN: 0925-8388. DOI: `10.1016/J.JALLCOM.2022.165936`.

[107] P. Muthukumar et al., ‘A critical review on design aspects and developmental status of metal hydride based thermal machines’, *International Journal of Hydrogen Energy*, vol. 43, pp. 17 753–17 779, 37 2018, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2018.07.157`.

[108] B. P. Tarasov et al., 'Metal hydride – graphene composites for hydrogen based energy storage', *Journal of Alloys and Compounds*, vol. 896, p. 162 881, 2022, ISSN: 0925-8388. DOI: `10.1016/J.JALLCOM.2021.162881`.

[109] S. Akbayrak and S. Özkar, 'Ammonia borane as hydrogen storage materials', *International Journal of Hydrogen Energy*, vol. 43, pp. 18 592–18 606, 40 2018, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2018.02.190`.

[110] H. Wu et al., 'Metal-catalyzed hydrolysis of ammonia borane: Mechanism, catalysts, and challenges', *International Journal of Hydrogen Energy*, vol. 45, pp. 30 325–30 340, 55 2020, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2020.08.131`.

[111] F. H. Stephens, V. Pons and R. T. Baker, 'Ammonia–borane: The hydrogen source par excellence?', *Journal of the Chemical Society. Dalton Transactions*, 25 2007, ISSN: 14779226. DOI: `10.1039/b703053c`.

[112] L. Ouyang et al., 'A recycling hydrogen supply system of nabh4 based on a facile regeneration process: A review', *Inorganics*, vol. 6, 1 2018, ISSN: 23046740. DOI: `10.3390/inorganics6010010`.

[113] H. N. Abdelhamid, 'A review on hydrogen generation from the hydrolysis of sodium borohydride', *International Journal of Hydrogen Energy*, vol. 46, pp. 726–765, 1 2021, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2020.09.186`.

[114] M. Rivarolo et al., 'Thermo-economic analysis of a hydrogen production system by sodium borohydride (nabh4)', *International Journal of Hydrogen Energy*, vol. 43, pp. 1606–1614, 3 2018, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2017.11.079`.

[115] U. B. Demirci et al., 'Sodium borohydride hydrolysis as hydrogen generator: Issues, state of the art and applicability upstream froma fuel cell', *Fuel Cells*, vol. 10, pp. 335–350, 3 2010, ISSN: 16156854. DOI: `10.1002/fuce.200800171`.

[116] SH2IPDRIVE, *Sh2ipdrive*, Accessed on 6th July 2023, 2023. [Online]. Available: `https://sh2ipdrive.com/`.

[117] L. LaVersenne and B. Bonnetot, 'Hydrogen storage using borohydrides', *Annales de Chimie: Science des Materiaux*, vol. 30, 5 2005, ISSN: 01519107. DOI: `10.3166/acsm.30.495-503`.

[118] C. Saka and A. Balbay, 'Fast and effective hydrogen production from ethanolysis and hydrolysis reactions of potassium borohydride using phosphoric acid', *International Journal of Hydrogen Energy*, vol. 43, pp. 19 976–19 983, 43 2018, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2018.09.048`.

[119] L. Li et al., 'Enhanced hydrogen storage properties of tin-lialh4 composite', *International Journal of Hydrogen Energy*, vol. 38, pp. 3695–3701, 9 2013, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2013.01.088`.

[120] M. Aziz, A. T. Wijayanta and A. B. D. Nandiyanto, 'Ammonia as effective hydrogen storage: A review on production, storage and utilization', *Energies*, vol. 13, p. 3062, 12 2020, ISSN: 19961073. DOI: `10.3390/en13123062`.

[121] A. Al-Enazi et al., 'A review of cleaner alternative fuels for maritime transportation', *Energy Reports*, vol. 7, pp. 1962–1985, 2021, ISSN: 23524847. DOI: `10.1016/J.EGYR.2021.03.036`.

[122] I. Lucentini et al., 'Review of the decomposition of ammonia to generate hydrogen', *Industrial and Engineering Chemistry Research*, vol. 60, pp. 18 560–18 611, 51 2021, ISSN: 15205045. DOI: `10.1021/acs.iecr.1c00843`.

[123] A. T. Wijayanta et al., 'Liquid hydrogen, methylcyclohexane, and ammonia as potential hydrogen storage: Comparison review', *International Journal of Hydrogen Energy*, vol. 44, pp. 15 026–15 044, 29 2019, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2019.04.112`.

[124] J. D. Ampah et al., 'Study on characteristics of marine heavy fuel oil and low carbon alcohol blended fuels at different temperatures', *Fuel*, vol. 310, p. 122 307, 2022, ISSN: 0016-2361. DOI: `10.1016/J.FUEL.2021.122307`.

[125] J. W. Carson and B. H. Pittenger, 'Asm handbook volume 7: Powder metal technologies and applications'. ASM International, 1998, ch. Bulk Properties of Powders, pp. 287–301.

[126] A. Valera-Medina et al., 'Ammonia for power', *Progress in Energy and Combustion Science*, vol. 69, pp. 63–102, 2018, ISSN: 03601285. DOI: `10.1016/J.PECS.2018.07.001`.

[127] M Murtomaa et al., 'On effects of ambient humidity on sodium borohydride powder', *Powder handling & processing*, vol. 11, 1 1999.

[128] P. Li et al., 'Deliquescence of nabh4 from density functional theory and experiments', *Industrial and Engineering Chemistry Research*, vol. 52, pp. 13 849–13 861, 38 2013, ISSN: 08885885. DOI: `10.1021/ie401742u`.

[129] W. Chen et al., 'Hydrolysis and regeneration of sodium borohydride (nabh4) a combination of hydrogen production and storage', *Journal of Power Sources*, vol. 359, pp. 400–407, 2017, ISSN: 0378-7753. DOI: `10.1016/J.JPOWSOUR.2017.05.075`.

[130] H. Zhong et al., 'An one-step approach towards hydrogen production and storage through regeneration of nabh4', *Energy Storage Materials*, vol. 7, pp. 222–228, 2017, ISSN: 2405-8297. DOI: `10.1016/J.ENSM.2017.03.001`.

[131] H. X. Nunes et al., 'Rehydrogenation of sodium borates to close the nabh4-h2 cycle: A review', *Energies*, vol. 14, 12 2021, ISSN: 19961073. DOI: `10.3390/en14123567`.

[132] H. Ritchie, M. Roser and P. Rosado, 'Energy', *Our World in Data*, 2022, https://ourworldindata.org/energy.

[133] NCBI, *Pubchem compound lcss for cid 4311764, sodium borohydride*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-borohydride#datasheet=LCSS`.

[134] U. Sanyal et al., 'Hydrolysis of ammonia borane as a hydrogen source: Fundamental issues and potential solutions towards implementation', *ChemSusChem*, vol. 4, pp. 1731–9, 2011. DOI: `10.1002/cssc.201100318`.

[135] J. O. Mandra, *Hull of the world's 1st inland hydrogen vessel heads for outfitting in the netherlands*, Accessed on 30th March 2023, 2023. [Online]. Available: `https://www.offshore-energy.biz/hull-of-the-worlds-1st-inland-hydrogen-vessel-heads-for-outfitting-in-the-netherlands/`.

[136] M. Wu et al., 'Analysis of heat conducting enhancement measures on the composite for hydrogen storage by incorporation of activated carbon with mofs', *International Journal of Hydrogen Energy*, vol. 48, pp. 3994–4005, 10 2023, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2022.10.245`.

[137] E. S. van Rheenen et al., 'Hydrogen carriers for zero-emission ship propulsion using pem fuel cells: An evaluation', *Journal of Marine Engineering & Technology*, pp. 1–18, 2023. DOI: `10.1080/20464177.2023.2282691`.

[138] N. Yamada and M. N. A. Mohamad, 'Efficiency of hydrogen internal combustion engine combined with open steam rankine cycle recovering water and waste heat', *International Journal of Hydrogen Energy*, vol. 35, no. 3, pp. 1430–1442, 2010, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2009.11.088`.

[139] R. Peters et al., 'Efficiency analysis of a hydrogen-fueled solid oxide fuel cell system with anode off-gas recirculation', *Journal of Power Sources*, vol. 328, pp. 105–113, 2016. DOI: `10.1016/J.JPOWSOUR.2016.08.002`.

[140] J. Yao et al., 'Design and multi-objective optimization of low-temperature proton exchange membrane fuel cells with efficient water recovery and high electrochemical performance', *Applied Energy*, vol. 324, p. 119 667, 2022, ISSN: 0306-2619. DOI: `10.1016/j.apenergy.2022.119667`.

[141] R. Gupta and K. Pant, 'Fundamentals and use of hydrogen as a fuel'. CRC press, 2008, pp. 2–32, ISBN: 978-1-4200-4575-8. DOI: `10.1201/9781420045772.ch1`.

[142] X. Wang, B.-G. Sun and Q.-H. Luo, 'Energy and exergy analysis of a turbocharged hydrogen internal combustion engine', *International Journal of Hydrogen Energy*, vol. 44, pp. 5551–5563, 11 2019. DOI: `10.1016/J.IJHYDENE.2018.10.047`.

[143] B. van Veldhuizen et al., 'The effects of fuel type and cathode off-gas recirculation on combined heat and power generation of marine sofc systems', *Energy Conversion and Management*, vol. 276, p. 116 498, 2023. DOI: `10.1016/j.enconman.2022.116498`.

[144] C. Tornatore et al., 'Ammonia as green fuel in internal combustion engines: State-of-the-art and future perspectives', *Frontiers in Mechanical Engineering*, vol. 8, p. 944 201, 2022. DOI: `10.3389/fmech.2022.944201`.

[145] T. B. Groom, J. R. Gabl and T. L. Pourpoint, 'Portable power generation for remote areas using hydrogen generated via maleic acid-promoted hydrolysis of ammonia borane', *Molecules*, vol. 24, no. 22, p. 4045, 2019, ISSN: 1420-3049. DOI: `10.3390/molecules24224045`.

[146] L. Zhao et al., 'Dynamic performance of an in-rack proton exchange membrane fuel cell battery system to power servers', *International Journal of Hydrogen Energy*, vol. 42, no. 15, pp. 10 158–10 174, 2017. DOI: `10.1016/j.ijhydene.2017.03.004`.

[147] M. M. E. Gohary and I. S. Seddiek, 'Utilization of alternative marine fuels for gas turbine power plant onboard ships', *International Journal of Naval Architecture and Ocean Engineering*, vol. 5, pp. 21–32, 1 2013. DOI: `10.2478/IJNAOE-2013-0115`.

[148] D. M. Rosado, S. R. Chavez and J. de Carvalho Jr, 'Determination of global efficiency without/with supplementary burning of a thermoelectric plant with combined cycle of natural gas.', *25th International Congress of Mechanical Engineering*, 2019. DOI: `10.26678/ABCM.COBEM2019.COB2019-0024`.

[149] Y. Wang et al., 'Pem fuel cell and electrolysis cell technologies and hydrogen infrastructure development – a review', *Energy Environ. Sci.*, vol. 15, pp. 2288–2328, 6 2022. DOI: `10.1039/D2EE00790H`.

[150] H. Nishikawa et al., 'High fuel utilization operation of pure hydrogen fuel cells', *International Journal of Hydrogen Energy*, vol. 33, no. 21, pp. 6262–6269, 2008, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2008.07.019`.

[151] K. Stark et al., 'Liquid organic hydrogen carriers: Thermophysical and thermochemical studies of carbazole partly and fully hydrogenated derivatives', *Industrial and Engineering Chemistry Research*, vol. 54, pp. 7953–7966, 32 2015. DOI: `10.1021/ACS.IECR.5B01841`.

[152] K. Muller et al., 'Liquid organic hydrogen carriers: Thermophysical and thermochemical studies of benzyl- and dibenzyl-toluene derivatives', *Industrial and Engineering Chemistry Research*, vol. 54, pp. 7967–7976, 32 2015, ISSN: 15205045. DOI: `10.1021/ACS.IECR.5B01840`.

[153] D. Teichmann et al., 'Energy storage in residential and commercial buildings via liquid organic hydrogen carriers (lohc)', *Energy Environ. Sci.*, vol. 5, pp. 9044–9054, 2012. DOI: `10.1039/C2EE22070A`.

[154] J. Zhang et al., 'Heat of reaction measurements of sodium borohydride alcoholysis and hydrolysis', *International Journal of Hydrogen Energy*, vol. 31, pp. 2292–2298, 15 2006. DOI: `10.1016/J.IJHYDENE.2006.02.026`.

[155] L. Ye et al., 'Measurement of specific heat capacity of nabo2(aq) solution and thermodynamic modeling of nabo2 + h2o, nabo2 + nacl + h2o, and nabo2 + na2so4 + h2o systems', *Journal of Chemical and Engineering Data*, vol. 65, pp. 2548–2557, 5 2020. DOI: `10.1021/ACS.JCED.9B01182`.

[156] L. Damjanović, S. Bennici and A. Auroux, 'A direct measurement of the heat evolved during the sodium and potassium borohydride catalytic hydrolysis', *Journal of Power Sources*, vol. 195, pp. 3284–3292, 10 2010. DOI: `10.1016/J.JPOWSOUR.2009.11.105`.

[157] C.-C. Chou and B.-H. Chen, 'Hydrogen generation from deliquescence of ammonia borane using ni–co/r-go catalyst', *Journal of Power Sources*, vol. 293, pp. 343–350, 2015, ISSN: 0378-7753. DOI: `10.1016/j.jpowsour.2015.05.091`.

[158] O. Komova et al., 'Destabilization of nh3bh3 by water during hydrothermolysis as a key factor in the high hydrogen evolution rates', *International Journal of Hydrogen Energy*, vol. 41, no. 39, pp. 17 484–17 495, 2016, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2016.07.163`.

[159] J. Andrieux et al., 'Revision of the nabo2–h2o phase diagram for optimized yield in the h2 generation through nabh4 hydrolysis', *International Journal of Hydrogen Energy*, vol. 37, no. 7, pp. 5798–5810, 2012, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2011.12.106`.

[160] Aspen Technology, Inc., *Aspen Exchanger Design & Rating (EDR)*, Accessed: 2 September 2025, 2025. [Online]. Available: `https://www.aspentech.com/en/products/engineering/aspen-exchanger-design-and-rating`.

[161] D. R. Lide, Ed., *CRC handbook of chemistry and physics, 81st edition*, en, 81st ed. Boca Raton, FL: CRC Press, 2000.

[162] S. Rassat et al., 'Thermal stability of ammonia borane: A case study for exothermic hydrogen storage materials', *Energy & Fuels*, vol. 24, 2010. DOI: `10.1021/ef901430a`.

[163] I. C. Kemp and J. Shiun Lim, 'Chapter 3 - key concepts of pinch analysis', *Pinch Analysis for Energy and Carbon Footprint Reduction (Third Edition)*, I. C. Kemp and J. Shiun Lim, Eds., Third Edition, Butterworth-Heinemann, 2020, pp. 35–61, ISBN: 978-0-08-102536-9. DOI: `10.1016/B978-0-08-102536-9.00003-5`.

[164] E. Rivard, M. Trudeau and K. Zaghib, 'Hydrogen storage for mobility: A review', *Materials*, vol. 12, no. 12, 2019, ISSN: 1996-1944. DOI: `10.3390/ma12121973`.

[165] R. De Saro, 'Thermal efficiency limits for furnaces and other combustion systems', *Journal of Thermophysics and Heat Transfer*, vol. 22, no. 3, pp. 532–537, 2008. DOI: `10.2514/1.28239`.

[166] S. Mukhopadhyay et al., 'Chapter 14 - application of soil quality indicators for the phytorestoration of mine spoil dumps', *Phytomanagement of Polluted Sites*, V. C. Pandey and K. Bauddh, Eds., Elsevier, 2019, pp. 361–388, ISBN: 978-0-12-813912-7. DOI: `10.1016/B978-0-12-813912-7.00014-4`.

[167] R Pawling, R Bucknall and A Greig, 'Considerations for future fuels in naval vessels', *Conference Proceedings of INEC*, 2022. DOI: `10.24868/10676`.

[168] A. Souflis-Rigas, J. Pruyn and A. Kana, 'Establishing the influence of methanol fuelled power propulsion and energy systems on ship design', *Proceedings of MOSES2023 conference*, 2023. DOI: `10.59490/moses.2023.658`.

[169] P. de Vos et al., 'Effective naval power plant design space exploration', *Proceedings of International Naval Engineering Conference and Exhibition*, 2022. DOI: `10.24868/10680`.

[170] P. Dimitriou and T. Tsujimura, 'A review of hydrogen as a compression ignition engine fuel', *International Journal of Hydrogen Energy*, vol. 42, no. 38, pp. 24 470–24 486, 2017, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2017.07.232`.

[171] Y. A. Cengel and A. J. Ghajar, *Heat and mass transfer: Fundamentals and applications*, 5th ed. New York, NY: McGraw-Hill Professional, 2014.

[172] K. Crapse and E. Kyser, 'Literature review of boric acid solubility data', Savannah River National Laboratory (SRNL), Tech. Rep., 2011. DOI: `10.2172/1025802`.

[173] W. M. Haynes, Ed., *CRC handbook of chemistry and physics, 92nd edition*, 92nd ed. Boca Raton, FL: CRC Press, 2011.

[174] D. Reay, C. Ramshaw and A. Harvey, 'Chapter 4 - compact and micro-heat exchangers', *Process Intensification*, ser. Isotopes in Organic Chemistry, Oxford: Butterworth-Heinemann, 2008, pp. 77–101, ISBN: 978-0-7506-8941-0. DOI: `10.1016/B978-0-7506-8941-0.00005-5`.

[175] R. K. Shah and D. P. Sekulić, *Fundamentals of Heat Exchanger Design*. John Wiley & Sons, 2003, ISBN: 978-0-471-32171-2.

[176] U. Sanyal et al., 'Hydrolysis of ammonia borane as a hydrogen source: Fundamental issues and potential solutions towards implementation', *ChemSusChem*, vol. 4, 2011. DOI: `10.1002/cssc.201100318`.

[177] H. S. Fogler, *Elements of Chemical Reaction Engineering*. Prentice Hall, 2016.

[178] R. Halseid, P. J. Vie and R. Tunold, 'Effect of ammonia on the performance of polymer electrolyte membrane fuel cells', *Journal of Power Sources*, vol. 154, no. 2, pp. 343–350, 2006, Selected papers from the Ninth Ulm Electrochemical Days, ISSN: 0378-7753. DOI: `10.1016/j.jpowsour.2005.10.011`.

[179] N. Brückner et al., 'Evaluation of industrially applied heat-transfer fluids as liquid organic hydrogen carrier systems', *ChemSusChem*, vol. 7, 2014. DOI: `10.1002/cssc.201300426`.

[180] Q. Li and H. Kim, 'Hydrogen production from nabh4 hydrolysis via co-zif-9 catalyst', *Fuel Processing Technology*, vol. 100, pp. 43–48, 2012, ISSN: 0378-3820. DOI: `10.1016/j.fuproc.2012.03.007`.

[181] N. Erat, G. Bozkurt and A. Özer, 'Co/cuo–nio–al2o3 catalyst for hydrogen generation from hydrolysis of nabh4', *International Journal of Hydrogen Energy*, vol. 47, no. 58, pp. 24 255–24 267, 2022, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2022.05.178`.

[182] X. Qiu et al., 'The release of hydrogen from ammonia borane over copper/hexagonal boron nitride composites', *RSC Adv.*, vol. 6, pp. 106 211–106 217, 108 2016. DOI: `10.1039/C6RA24000C`.

[183] M. van Benten, J. Padding and D. Schott, 'Circular bunkering for maritime vessels using sodium borohydride', *Renewable and Sustainable Energy Reviews*, vol. 223, p. 116 039, 2025, ISSN: 1364-0321. DOI: `10.1016/j.rser.2025.116039`.

[184] M. D. Kass, C. S. Sluder and B. C. Kaul, 'Spill behavior, detection, and mitigation for emerging nontraditional marine fuels', Oak Ridge National Laboratory, Tech. Rep., 2021.

[185] H. Chang et al., 'Consideration of potential technologies for ammonia removal and recovery from produced water', *Environmental Science & Technology*, vol. 56, no. 6, pp. 3305–3308, 2022. DOI: `10.1021/acs.est.1c08517`.

[186] Kemira Oyj, *Kemira sodium borohydride nabh$_4$: An effective reducing agent*, n.d. Accessed: 2025. [Online]. Available: `https://www.ecochem.com.co/pdf/Hydrifin\%20Brochure.pdf`.

[187] A. Ibrahim, M. Paskevicius and C. E. Buckley, 'Chemical compression and transport of hydrogen using sodium borohydride', *Sustainable Energy Fuels*, vol. 7, pp. 1196–1203, 5 2023. DOI: `10.1039/D2SE01334G`.

[188] J. Henderiks, *Personal communication with jurn henderiks, msc (product developer, hydroflexx)*, Private communication, 2025.

[189] E. S. van Rheenen et al., 'Solid hydrogen carriers as an alternative fuel and impact damper', *Proceedings of the International Naval Engineering Conference (INEC 2024)*, 2024. DOI: `10.24868/11165`.

[190] TCI America, *Safety data sheet: Borane - ammonia complex*, accessed 10 October 2024, 9211 N. Harborgate Street Portland, OR 97203 U.S.A., 2024. [Online]. Available: `https://www.tcichemicals.com/US/en/p/B5082`.

[191] Sigma-Aldrich Inc., *Safety data sheet: Borane-ammonia complex*, Safety Data Sheet, version 6.1, accessed 3 November 2025, 3050 Spruce St, St. Louis MO 63103, United States, 2025. [Online]. Available: `https://www.sigmaaldrich.com/NL/en/sds/aldrich/287717?userType=undefined`.

[192] Q. U. A. Yasin et al., 'Liquid organic hydrogen carriers for hydrogen storage: A review of chemistry, engineering design and economic feasibility', *Energy Conversion and Management: X*, vol. 29, p. 101 493, 2026, ISSN: 2590-1745. DOI: `https://doi.org/10.1016/j.ecmx.2025.101493`.

[193] E. Van Rheenen et al., 'Ship system design changes for the transition to hydrogen carriers', *International Marine Design Conference*, 2024. DOI: `10.59490/imdc.2024.894`.

[194] Y. Dong et al., 'Dehydrogenation kinetics study of perhydro-N-ethylcarbazole over a supported Pd catalyst for hydrogen storage application', *International Journal of Hydrogen Energy*, vol. 41, no. 20, pp. 8498–8505, 2016, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2016.03.157`.

[195] E. M. Moghaddam et al., 'Fixed bed reactors of non-spherical pellets: Importance of heterogeneities and inadequacy of azimuthal averaging', *Chemical Engineering Science: X*, vol. 1, p. 100 006, 2019, ISSN: 2590-1400. DOI: `10.1016/j.cesx.2019.100006`. [Online]. Available: `10.1016/j.cesx.2019.100006`.

[196] T. Sousa et al., 'A sodium borohydride hydrogen generation reactor for stationary applications: Experimental and reactor simulation studies', *Chemical Engineering Science*, vol. 84, pp. 70–79, 2012, ISSN: 0009-2509. DOI: `10.1016/J.CES.2012.08.001`.

[197] H. S. Fogler, 'Conversion and reactor sizing', *Elements of Chemical Reaction Engineering*, 5th ed. Boston, MA: Pearson Education, 2016, ch. 2, pp. 31–68, ISBN: 978-0133887518.

[198] N. Brückner et al., 'Evaluation of industrially applied heat-transfer fluids as liquid organic hydrogen carrier systems', *ChemSusChem*, vol. 7, pp. 229–235, 1 2014, ISSN: 1864564X. DOI: `10.1002/cssc.201300426`.

[199] H. S. Fogler, 'Catalysis and catalytic reactors', *Elements of Chemical Reaction Engineering*, 5th ed. Boston, MA: Pearson Education, 2016, ch. 10, pp. 399–493, ISBN: 978-0133887518.

[200] A. A. Shaikh, 'Industrial catalytic reactors', *Heterogeneous Catalysis*, Berlin, Germany: De Gruyter, 2020, ch. 7, pp. 89–110, ISBN: 9783110624861. DOI: `10.1515/9783110624861-007`.

[201] S Afandizadeh and E. Foumeny, 'Design of packed bed reactors: Guides to catalyst shape, size, and loading selection', *Applied Thermal Engineering*, vol. 21, no. 6, pp. 669–682, 2001, ISSN: 1359-4311. DOI: `https://doi.org/10.1016/S1359-4311(00)00072-7`.

[202] J. Lee et al., 'Development of dehydrogenation system for liquid organic hydrogen carrier with enhanced reaction rate', *Applied Sciences*, vol. 14, no. 13, 2024, ISSN: 2076-3417. DOI: `10.3390/app14135803`.

[203] J. Harmsen and R. Bos, *Multiphase Reactors: Reaction Engineering Concepts, Selection, and Industrial Applications*. De Gruyter, 2023, ISBN: 9783110713770. DOI: `10.1515/9783110713770`.

[204] J. Harmsen, 'Chapter 7 - scale-up of unit operations', *Industrial Process Scale-up*, J. Harmsen, Ed., Amsterdam: Elsevier, 2013, pp. 59–71, ISBN: 978-0-444-62726-1. DOI: `https://doi.org/10.1016/B978-0-444-62726-1.00007-9`.

[205] NPS Driven, *Hydrogen combustion engine*, Accessed: 2025-08-22, 2024. [Online]. Available: `https://www.npsdriven.com/wp-content/uploads/2024/05/NPSdriven\_H2ICE-leaflet\_A4\_202405v9HR.pdf`.

[206] ABC Engines, *Dual fuel and 100% hydrogen engines*, Accessed: 2025-05-01, n.d. [Online]. Available: `https://www.production.behydro.be/`.

[207] GE Vernova, *Hydrogen-fueled gas turbines*, Accessed: 14 February 2025, 2025. [Online]. Available: `https://www.gevernova.com/gas-power/future-of-energy/hydrogen-fueled-gas-turbines`.

[208] Rolls-Royce plc, *Hydrogen*, Accessed: 14 February 2025, 2025. [Online]. Available: `https://www.rolls-royce.com/innovation/net-zero/decarbonising-complex-critical-systems/hydrogen.aspx/1000`.

[209] L. Jiangsu Baolian Gas Co., *Water-cooled hydrogen fuel cell 50 kw / 60 kw for vehicle pem fuel cell system (water-cooled fuel cell)*, Accessed: 17 September 2025, 2025. [Online]. Available: `\url{https://szsince.en.made-in-china.com/product/vGrUYiLVgqkM/China-water-cooled-hydrogen-fuel-cell-50kw-60kw-for-vehicle-pem-fuel-cell-system-water-cooled-fuel-cell.html}`.

[210] Horizon Educational, *Hydrogen fuel cell stacks*, Accessed: 17 September 2025, 2025. [Online]. Available: `\url{https://www.horizoneducational.com/hydrogen-fuel-cell-stacks/c1024}`.

[211] H2Planet, *Greenhub 2 pro – turn-key fuel-cell genset series*, Accessed: 17 September 2025, 2025. [Online]. Available: `\url{https://www.h2planet.eu/en/landing_page/greenhub_2_pro_1}`.

[212] A. G. Elkafas et al., 'Fuel Cell Systems for Maritime: A Review of Research Development, Commercial Products, Applications, and Perspectives', *Processes*, vol. 11, no. 1, 2023, ISSN: 22279717. DOI: `10.3390/PR11010097`.

[213] K. Inman et al., 'Design of a proton exchange membrane portable fuel cell system for the 1st international association for hydrogen energy design competition', *International Journal of Hydrogen Energy*, vol. 36, pp. 13 868–13 874, 21 2011, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2011.04.213`.

[214] P. Shuhayeu et al., 'Investigating pem fuel cells as an alternative power source for electric uavs: Modeling, optimization, and performance analysis', *Energies 2024, Vol. 17, Page 4427*, vol. 17, p. 4427, 17 2024, ISSN: 1996-1073. DOI: `10.3390/EN17174427`.

[215] N. A. Qasem and G. A. Abdulrahman, 'A Recent Comprehensive Review of Fuel Cells: History, Types, and Applications', *International Journal of Energy Research*, vol. 2024, no. 1, p. 7 271 748, 2024, ISSN: 1099-114X. DOI: `10.1155/2024/7271748`.

[216] R. Burcher and L. J. Rydill, 'Submarine hydrostatics', *Concepts in Submarine Design* (Cambridge Ocean Technology Series), Cambridge Ocean Technology Series. Cambridge University Press, 1994, ch. 3, 25–51.

[217] International Maritime Organization, *Resolution mepc.281(70): Guidelines for the approval of alternative methods of compliance for the reduction of greenhouse gas emissions from ships*, Adopted on 28 October 2016, 2016. [Online]. Available: `https://wwwcdn.imo.org/localresources/en/KnowledgeCentre/IndexofIMOResolutions/MEPCDocuments/MEPC.281(70).pdf`.

[218] M. Dobberkau, R. Werner and F. Atzler, 'Methanol, the ice green maker', *Chemie Ingenieur Technik*, vol. 96, no. 9, pp. 1196–1202, 2024. DOI: `https://doi.org/10.1002/cite.202400021`.

[219] J. Zheng et al., 'Current research progress and perspectives on liquid hydrogen rich molecules in sustainable hydrogen storage', *Energy Storage Materials*, vol. 35, pp. 695–722, 2021, ISSN: 2405-8297. DOI: `https://doi.org/10.1016/j.ensm.2020.12.007`.

[220] Indian Register of Shipping, *Guidelines on methanol fueled vessels*, `https://www.irclass.org/media/7618/guidelines-on-methanol-fueled-vessels_rev4_dec-2024.pdf`, version Revision 4, Accessed: 2026-02-13, 2024.

[221] S. S. Rathore et al., 'Direct ammonia solid-oxide fuel cells: A review of progress and prospects', *International Journal of Hydrogen Energy*, vol. 46, no. 71, pp. 35 365–35 384, 2021, ISSN: 0360-3199. DOI: `https://doi.org/10.1016/j.ijhydene.2021.08.092`.

[222] Rijksdienst voor Ondernemend Nederland (RVO), 'Roadmap brandstoftransitie in de zeevaart', Rijksdienst voor Ondernemend Nederland (RVO), Den Haag, Netherlands, Technical report, 2024.

[223] K. Roelse, N. Dofferhoff and C. Westdijk, *Classificatie en kenmerken van de europese vloot en de actieve vloot in nederland*, Accessed 7 September 2025, 2002. [Online]. Available: `https://repository.tudelft.nl/record/uuid:3f04eec2-917e-4da3-bee2-e382762f7484`.

[224] Crowley Maritime Corporation, *Fishing vessels – engineering services portfolio*, Accessed 7 September 2025, 2025. [Online]. Available: `https://www.crowley.com/shipping/engineering-services/portfolio/fishing-vessels/`.

[225] Bord Iascaigh Mhara (BIM), *Improving fuel efficiency on fishing vessels (user friendly guide)*, accessed 7 September 2025, 2009. [Online]. Available: `https://bim.ie/wp-content/uploads/2021/02/Improving,Fuel,Efficiency,on,Fishing,Vessels,(User,Friendly,Guide).pdf`.

[226] Veerbootinfo.nl, *Veerbootinfo.nl – alle informatie over veerboten in nederland*, Accessed: 7 September 2025, 2025. [Online]. Available: `https://www.veerbootinfo.nl/`.

[227] Zero Emission Services, *Zespack*, Accessed:7 September 2025, 2025. [Online]. Available: `https://zeroemissionservices.nl/zespack-3/`.

[228] E. S. Van Rheenen et al., 'A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems', *Conference Proceedings of INEC*, 2022. DOI: `10.24868/10649`.

[229] D. Rothwell, *The Oxford Handbook of the Law of the Sea*. Oxford University Press, 2015, ISBN: 9780198715481. DOI: `10.1093/law/9780198715481.002.0003`.

[230] H. Tanaka et al., 'Hazard assessment of complex hydrides as hydrogen storage materials', *International Journal of Hydrogen Energy*, vol. 34, pp. 3210–3218, 7 2009, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2009.01.064`.

[231] D. Makarov et al., 'Hydrogen tank rupture in fire in the open atmosphere: Hazard distance defined by fireball', *Hydrogen*, vol. 2, pp. 134–146, 1 2021. DOI: `10.3390/hydrogen2010008`.

[232] NCBI, *Ghs classification*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/ghs/`.

[233] OSHA, *Hazard communication standard: Labels and pictograms*, Accessed on 12th November 2022, 2013. [Online]. Available: `https://www.osha.gov/sites/default/files/publications/OSHA3636.pdf`.

[234] M Markiewicz et al., 'Environmental and health impact assessment of liquid organic hydrogen carrier (lohc) systems-challenges and preliminary results', 2015. DOI: `10.1039/c4ee03528c`.

[235] NCBI, *Pubchem compound lcss for cid 3034397, 2,3-dibenzyltoluene*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/2_3-Dibenzyltoluene#datasheet=LCSS`.

[236] A. Caterbow and J. Hausmann, *The impact of hazardous chemicals on women*, WECF, accessed on 12th November 2022, 2016. [Online]. Available: `https://www.wecf.org/77912/`.

[237] Arkema, *Dibenzyltoluene*, Accessed on 12th November 2022, 2013. [Online]. Available: `https://www.arkema.com/files/live/sites/shared_arkema/files/downloads/socialresponsability/safety-summuries/hydrogen-peroxide-dibenzyltoluene-gps-2013-02-10-v0.pdf`.

[238] ECHA, *Dibenzylbenzene, ar-methyl derivative*, Accessed on 22th November 2022, 2022. [Online]. Available: `https://echa.europa.eu/nl/registration-dossier/-/registered-dossier/19786/6/2/1`.

[239] M. Markiewicz et al., 'Hazard assessment of quinaldine-, alkylcarbazole-, benzene-and toluene-based liquid organic hydrogen carrier (lohcs) systems', *Energy Environmental Science*, vol. 12, p. 366, 2019. DOI: `10.1039/c8ee01696h`.

[240] NCBI, *Pubchem compound lcss for cid 6836, 9-ethylcarbazole*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/9-Ethylcarbazole#datasheet=LCSS`.

[241] ECHEMI, *9-ethylcarbazole safety data sheets*, Accessed on 12th November 2022, 2013. [Online]. Available: `https://www.echemi.com/sds/n-ethylcarbazole-pid_Rock24510.html`.

[242] NCBI, *Pubchem compound summary for cid 66624952, 9-ethyldodecahydro-1h-carbazole*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/9-Ethyldodecahydro-1H-carbazole`.

[243] Amadis Chemical, *9-ethyldodecahydro-1h-carbazole*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://www.amadischem.com/proen/591108/`.

[244] ROTH, *Safety data sheet sodium borohydride 97%, extra pure*, SDB-4051-GB-EN.pdf:PDF. Accessed on 12th November 2022, 2022.

[245] CDH, *Potassium borohydride cas no 13762-51-1 material safety data sheet sds/msds*, Accessed on 12th November 2022, 2008. [Online]. Available: `https://www.cdhfinechemical.com/images/product/msds/92_1897241378_POTASSIUMBOROHYDRIDECASNO13762-51-1MSDS.pdf`.

[246] Y. Zhou et al., 'Volumetric and transport properties of aqueous nab(oh)4 solutions', *Chinese Journal of Chemical Engineering*, vol. 21, pp. 1048–1056, 9 2013, ISSN: 1004-9541. DOI: `10.1016/S1004-9541(13)60561-3`.

[247] NCBI, *Pubchem compound lcss for cid 145326, sodium metaborate*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-metaborate#datasheet=LCSS`.

[248] NCBI, *Pubchem compound lcss for cid 23701135, sodium metaborate dihydrate*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-metaborate-dihydrate#datasheet=LCSS`.

[249] NCBI, *Pubchem compound lcss for cid 123325, potassium metaborate*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Potassium-metaborate#datasheet=LCSS`.

[250] J. C. Slootweg, private communication, 2022.

[251] NCBI, *Pubchem compound lcss for cid 16211214, borax*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Borax#datasheet=LCSS`.

[252] NCBI, *Pubchem compound lcss for cid 5360545, sodium*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Sodium#datasheet=LCSS`.

[253] NCBI, *Pubchem compound lcss for cid 5462311, boron*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Boron#datasheet=LCSS`.

[254] NCBI, *Pubchem compound lcss for cid 24758, sodium hydride*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Sodium-hydride#datasheet=LCSS`.

[255] LGC, *Safety data sheet borol*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://static.cymitquimica.com/products/04/pdf/sds-A50000283MD.pdf`.

[256] NCBI, *Pubchem compound lcss for cid 5462222, potassium*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Potassium#datasheet=LCSS`.

[257] NCBI, *Pubchem compound lcss for cid 82127, potassium hydride*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Potassium-hydride#datasheet=LCSS`.

[258] NCBI, *Pubchem compound lcss for cid 132598553, ammonia borane*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Ammonia-borane#datasheet=LCSS`.

[259] NCBI, *Pubchem compound lcss for cid 223, ammonium*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Ammonium#datasheet=LCSS`.

[260] Y. Salama et al., 'The physicochemical and bacteriological quality and environmental risks of raw sewage rejected in the coast of the city of el jadida (morocco)', *Carphatian Journal of Earth and Environmental Sciences*, vol. 8, pp. 39–48, 2013.

[261] G. M. Marion et al., 'Ph of seawater', *Marine Chemistry*, vol. 126, pp. 89–96, 1-4 2011, ISSN: 03044203. DOI: `10.1016/J.MARCHEM.2011.04.002`.

[262] NCBI, *Pubchem compound summary for cid 16722522, aminoborane*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Aminoborane`.

[263] NCBI, *Pubchem compound summary for cid 139816, aminoboron*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Aminoboron`.

[264] P. Paetzold, 'Iminoboranes', *Advances in Inorganic Chemistry*, vol. 31, pp. 123–170, C 1987, ISSN: 0898-8838. DOI: `10.1016/S0898-8838(08)60223-8`.

[265] C. A. Thompson and L. Andrews, 'Reactions of b atoms with nh3 to produce hbnh, bnbh, and b2n', *J. Am. Chem. Soc*, vol. 117, p. 6331, 2 1995.

[266] NCBI, *Pubchem compound lcss for cid 138768, borazine*, Accessed on 28th March 2023, 2023. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Borazine#datasheet=LCSS`.

[267] R. H. Dolan, J. E. Anderson and T. J. Wallington, 'Outlook for ammonia as a sustainable transportation fuel', *Sustainable Energy and Fuels*, vol. 5, pp. 4830–4841, 19 2021, ISSN: 2398-4902. DOI: `10.1039/D1SE00979F`.

[268] NCBI, *Pubchem compound lcss for cid 887, methanol*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Methanol#datasheet=LCSS`.

[269] Neste, *Safety data sheet marine diesel oil dmb grade (mdodmb)*, Accessed on 12th November 2022, 2017. [Online]. Available: `https://www.neste.com/sites/neste.com/files/attachments/13999_marine_diesel_oileng.pdf`.

[270] A. Mjaavatten and D. K. Bjerketvedt, 'A hydrogen-air explosion in a process plant: A case history', 2005.

[271] R. Gerboni and E. Salvador, 'Hydrogen transportation systems: Elements of risk analysis', *Energy*, vol. 34, pp. 2223–2229, 12 2009, ISSN: 0360-5442. DOI: `10.1016/J.ENERGY.2008.12.018`.

[272] H. Dagdougui et al., 'Hydrogen logistics: Safety and risks issues', *Hydrogen Infrastructure for Energy Applications*, pp. 127–148, 2018. DOI: `10.1016/b978-0-12-812036-1.00007-x`.

[273] V. Molkov and J.-B. Saffers, 'Hydrogen jet flames', *International Journal of Hydrogen Energy*, vol. 38, no. 19, pp. 8141–8158, 2013, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2012.08.106`.

[274] H. J. Pasman and W. J. Rogers, 'Safety challenges in view of the upcoming hydrogen economy: An overview', *Journal of Loss Prevention in the Process Industries*, vol. 23, pp. 697–704, 6 2010, ISSN: 0950-4230. DOI: `10.1016/J.JLP.2010.06.002`.

[275] D. Baraldi et al., 'Numerical analysis of release, dispersion and combustion of liquid hydrogen in a mock-up hydrogen refuelling station', *Journal of Loss Prevention in the Process Industries*, vol. 22, pp. 303–315, 3 2009, ISSN: 0950-4230. DOI: `10.1016/J.JLP.2008.10.004`.

[276] H. D. Ng and J. H. Lee, 'Comments on explosion problems for hydrogen safety', *Journal of Loss Prevention in the Process Industries*, vol. 21, no. 2, pp. 136–146, 2008, Hydrogen Safety, ISSN: 0950-4230. DOI: `10.1016/j.jlp.2007.06.001`.

[277] S. Zhang and Q. Zhang, 'Effect of vent size on vented hydrogen-air explosion', *International Journal of Hydrogen Energy*, vol. 43, no. 37, pp. 17 788–17 799, 2018, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2018.07.194`.

[278] J. Yanez, M. Kuznetsov and A. Souto-Iglesias, 'An analysis of the hydrogen explosion in the fukushima-daiichi accident', *International Journal of Hydrogen Energy*, vol. 40, no. 25, pp. 8261–8280, 2015, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2015.03.154`.

[279] V. Vuorinen et al., 'Modelling aerosol transport and virus exposure with numerical simulations in relation to sars-cov-2 transmission by inhalation indoors', *Safety Science*, vol. 130, p. 104 866, 2020, ISSN: 0925-7535. DOI: `10.1016/j.ssci.2020.104866`.

[280] V. Vuorinen and K. Keskinen, 'Dnslab: A gateway to turbulent flow simulation in matlab', *Computer Physics Communications*, vol. 203, pp. 278–289, 2016, ISSN: 0010-4655. DOI: `10.1016/j.cpc.2016.02.023`.

[281] K. X. Li and J. Wonham, 'Maritime legislation: New areas for safety of life at sea', *Maritime Policy & Management*, vol. 28, no. 3, pp. 225–234, 2001. DOI: `10.1080/03088830110048880`.

[282] IMO, *International convention for the safety of life at sea (solas), 1974*, Accessed on 12th November 2022, 2019. [Online]. Available: `https://www.imo.org/en/About/Conventions/Pages/International-Convention-for-the-Safety-of-Life-at-Sea-(SOLAS),-1974.aspx`.

[283] UNTERM, *Safety*, Accessed on 12th November 2022, n.d. [Online]. Available: https://unterm.un.org/unterm/Display/record/IMO/NA?OriginalId=83476e19964244c08ce42b805157efcc.

[284] ILO, *Mlc, 2006: What it is and what it does*, Accessed on 12th November 2022, 2022. [Online]. Available: https://www.ilo.org/global/standards/maritime-labour-convention/what-it-does/lang--en/index.htm.

[285] MSC, *Msc/circ. 699 revised guidelines for passenger safety instructions, annex 1 guidelines for passenger safety instructions*, Accessed on 12th November 2022, 2022. [Online]. Available: https://puc.overheid.nl/nsi/doc/PUC_2593_14/1/.

[286] IMO, *Passenger ships*, Accessed on 12th November 2022, 2019. [Online]. Available: https://www.imo.org/en/OurWork/Safety/Pages/PassengerShips.aspx.

[287] IMO, *International code of safety for ship using gases or other low-flashpoint fuels (igf code)*, Accessed on 12th November 2022, 2019. [Online]. Available: https://www.imo.org/en/OurWork/Safety/Pages/IGF-Code.aspx.

[288] IMO, *Interim guidelines for the safety of ships using methyl/ethyl alcohol as fuel*, Accessed on 25th November 2022, 2020. [Online]. Available: https://www.ics.org.ir/IFleet/CLDFiles/News/ae228117-cd22-45d0-9470-b75d890fca6d_MSC.1-Circ.1621\%20-\%20Interim\%20Guidelines\%20For\%20The\%20Safety\%20Of\%20ShipsUsing\%20MethylEthyl\%20Alcohol\%20As\%20Fuel\%20(Secretariat).pdf.

[289] IMO, *Development of non-mandatory guidelines for safety of ships using ammonia as fuel*, Accessed on 25th November 2022, 2021. [Online]. Available: https://www.ics-shipping.org/wp-content/uploads/2021/07/MSC-104-15-9-Development-of-non-mandatory-guidelines-for-safety-of-ships-using-ammonia-as-fuel-Japan-Singapore-ICS-and....pdf.

[290] IMO, *International convention for the prevention of pollution from ships (marpol)*, Accessed on 12th November 2022, 2019. [Online]. Available: https://www.imo.org/en/About/Conventions/Pages/International-Convention-for-the-Prevention-of-Pollution-from-Ships-(MARPOL).aspx.

[291] IBIA, *Imo to develop guidelines for safe use of ammonia*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://ibia.net/2022/05/04/imo-to-develop-guidelines-for-safe-use-of-ammonia/`.

[292] IMO, *Imo goal-based standards*, Accessed on 12th November 2022, 2019. [Online]. Available: `https://www.imo.org/en/OurWork/Safety/Pages/Goal-BasedStandards.aspx`.

[293] H. Hoppe, 'Goal-based standards-a new approach to the international regulation of ship construction', *WMU Journal of Maritime Affairs*, vol. 4, pp. 169–180, 2 2005.

[294] IMO, 'Report of the maritime safety committee on its eightieth session', International Maritime Organization Maritime Safety Committee, Tech. Rep., 2005. [Online]. Available: `https://www.dco.uscg.mil/Portals/9/DCO\%20Documents/Marine\%20Safety\%20Center/Tonnage/Committee\%20Docs/MSC\_80-24\_Report\_of\_the\_MSC.pdf?ver=2017-06-20-121133-870Accessedon15thofNovember2022`.

[295] S.-m. Ha et al., 'Regulatory gaps between lng carriers and lng fuelled ships', *Journal of Marine Engineering & Technology*, vol. 21, no. 1, pp. 23–37, 2022.

[296] IMO, *Maritime safety committee (msc)*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://www.imo.org/en/MediaCentre/MeetingSummaries/Pages/MSC-Default.aspx`.

[297] MSC, *Interim guidelines for the safety of ships using fuel cell power installations*, Accessed on 12th November 2022, 2022. [Online]. Available: `https://www.mardep.gov.hk/en/msnote/pdf/msin2235anx1.pdf`.

[298] BV, *Nr671 ammonia-fuelled ships - tentative rules*, Accessed on 25th November 2022, 2022. [Online]. Available: `https://marine-offshore.bureauveritas.com/nr671-ammonia-fuelled-ships-tentative-rules`.

[299] LR, *Zero ready framework*, Accessed on 25th November 2022, 2022. [Online]. Available: `https://www.lr.org/en/latest-news/lr-launches-zero-ready-framework/`.

[300] S. Brosché, 'Women, chemicals and the sdgs gender review mapping with a focus on women and chemicals: Impact of emerging policy issues and the relevance for the sustainable development goals', 2020, Accessed on 13th November 2022. [Online]. Available: `https://ipen.org/sites/default/files/documents/ipen-gender-chemicals-report-v1_6dw-en.pdf`.

[301] US EPA, 'Hazards of ammonia releases at ammonia refrigeration facilities (update)', 2001, Accessed on 22nd June 2022. [Online]. Available: `https://www.epa.gov/sites/default/files/2013-11/documents/ammonia.pdf`.

[302] HNS-MS, *Ammonia anhydrous*, Accessed on 12th November 2022, 2017. [Online]. Available: `https://www.hns-ms.eu/result/21`.

[303] A. Kozlovski, 'Parity and the resolution of value conflicts in design', *Science and Engineering Ethics*, vol. 28, p. 22, 2022. DOI: `10.1007/s11948-022-00375-4`.

[304] A. Maertens, E. Golden and T. Hartung, 'Avoiding regrettable substitutions: Green toxicology for sustainable chemistry', *ACS Sustain Chem Eng.*, vol. 9, 23 2021. DOI: `10.1021/acssuschemeng.0c09435`.

[305] NOAA, *How much oil is on that ship?*, `https://response.restoration.noaa.gov/about/media/how-much-oil-ship.html`, [Online], 2016.

[306] M. F. Kirby and R. J. Law, 'Accidental spills at sea – risk, impact, mitigation and the need for co-ordinated post-incident monitoring', *Marine Pollution Bulletin*, vol. 60, no. 6, pp. 797–803, 2010. DOI: `10.1016/j.marpolbul.2010.03.015`.

[307] L. Schreiber et al., 'Long-term biodegradation of crude oil in high-arctic backshore sediments: The baffin island oil spill (bios) after nearly four decades', *Environmental Research*, vol. 233, p. 116 421, 2023. DOI: `10.1016/j.envres.2023.116421`.

[308] International Maritime Organization, *Protocol on preparedness, response and co-operation to pollution incidents by hazardous and noxious substances, 2000 (oprc-hns protocol)*, Accessed 10 December 2024, 2000. [Online]. Available: `https://www.imo.org/en/About/Conventions/Pages/Protocol-on-Preparedness,-Response-and-Co-operation-to-pollution-Incidents-by-Hazardous-and-Noxious-Substances-(OPRC-HNS-Pr.aspx`.

[309] International Oil Pollution Compensation Funds, *The hazardous and noxious substances convention*, Accessed 10 December 2024. [Online]. Available: `\url{https://www.hnsconvention.org}`.

[310] K. Purnell, *Are hns spills more dangerous than oil spills?*, Accessed 10 December 2024, 2009. [Online]. Available: `https://www.hnsconvention.org/wp-content/uploads/2018/08/whitepaper.pdf`.

[311] S. L. Floch et al., 'Environmental parameter effects on the fate of a chemical slick', *Air Quality - Monitoring and Modeling*, S. Kumar, Ed., IntechOpen, 2012, pp. 59–78. DOI: `10.5772/32950`.

[312] E. van Rheenen et al., 'Hazard identification of hydrogen-based alternative fuels onboard ships', *Sustainability*, vol. 15, 24 2023, ISSN: 2071-1050. DOI: `10.3390/SU152416818`.

[313] W. L. Jolly, *Modern Inorganic Chemistry*. New York: McGraw-Hill, 1985.

[314] M. Chandra and Q. Xu, 'Dissociation and hydrolysis of ammonia-borane with solid acids and carbon dioxide: An efficient hydrogen generation system', *Journal of Power Sources*, vol. 159, no. 2, pp. 855–860, 2006, ISSN: 0378-7753. DOI: `10.1016/j.jpowsour.2005.12.033`.

[315] Voyex, *Voyex website*, Accessed on 30th March 2023, 2023. [Online]. Available: `https://voyex.nl/`.

[316] A. Al-Kukhun, H. T. Hwang and A. Varma, 'Mechanistic studies of ammonia borane dehydrogenation', *International Journal of Hydrogen Energy*, vol. 38, pp. 169–179, 1 2013, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2012.09.161`.

[317] V. Kumar, B. Roy and P. Sharma, 'Kinetics of borazine formation from ammonia borane dehydrocoupling reaction through ab initio analysis', *International Journal of Hydrogen Energy*, vol. 44, pp. 22 022–22 031, 39 2019, ISSN: 03603199. DOI: `10.1016/J.IJHYDENE.2019.06.172`.

[318] J. Baumann, F. Baitalow and G. Wolf, 'Thermal decomposition of polymeric aminoborane (h2bnh2)x under hydrogen release', *Thermochimica Acta*, vol. 430, pp. 9–14, 1-2 2005, ISSN: 0040-6031. DOI: `10.1016/J.TCA.2004.12.002`.

[319] F Baitalow et al., 'Thermal decomposition of b–n–h compounds investigated by using combined thermoanalytical methods', *Thermochimica Acta*, vol. 391, pp. 159–168, 1-2 2002, ISSN: 0040-6031. DOI: `10.1016/S0040-6031(02)00173-9`.

[320] M. G. Hu, R. A. Geanangel and A. W. W. Wendlandt, 'The thermal deco,mposition of ammonia borane', *thermochimica Acta*, pp. 249–255, 1978.

[321] S. Frueh et al., 'Pyrolytic decomposition of ammonia borane to boron nitride', *Inorganic Chemistry*, vol. 50, pp. 783–792, 3 2011, ISSN: 00201669. DOI: `10.1021/ic101020k`.

[322] P. Patnaik, *Handbook of Inorganic Chemicals* (McGraw-Hill handbooks). McGraw-Hill, 2003, ISBN: 9780070494398.

[323] A. Karkamkar, C. Aardahl and T. Autrey, 'Recent developments on hydrogen release from ammonia-borane', *Material Matters*, vol. 2, 2 2007. DOI: `10.1016/B978-0-12-385142-0.00015-5`.

[324] J. E. House, 'Chemistry of nonmetallic elements i. hydrogen, boron, oxygen, and carbon', *Inorganic Chemistry*, pp. 465–516, 2020. DOI: `10.1016/B978-0-12-814369-8.00013-3`.

[325] NCBI, *Pubchem compound summary for cid 518682, boric anhydride*, Retrieved April 29, 2024, 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Boric-anhydride`.

[326] U. B. Demirci et al., 'Hydrogen release by thermolysis of ammonia borane nh3bh3 and then hydrolysis of its by-product [bnhx]', *Journal of Power Sources*, vol. 196, pp. 279–286, 1 2011, ISSN: 0378-7753. DOI: `10.1016/J.JPOWSOUR.2010.06.031`.

[327] X. Chen, J.-C. Zhao and S. G. Shore, 'Facile synthesis of aminodiborane and inorganic butane analogue nh3bh2nh2bh3', *J Am Chem Soc*, vol. 132, p. 17, 2010. DOI: `10.1021/ja104938v`.

[328] A. Nair et al., 'In situ generated aminodiborane as a reagent for deoxygenative reduction of carboxamides to amines', *Organic Chemistry Frontiers*, vol. 10, no. 2, 327–334, 2023, ISSN: 2052-4129. DOI: `10.1039/d2qo01717b`.

[329] H. Li et al., 'The effect of solvent properties on the hydrogen producing performance of catalytic liquid phase ammonia borane', *Fuel*, vol. 325, p. 124 849, 2022, ISSN: 0016-2361. DOI: `10.1016/j.fuel.2022.124849`.

[330] A. Brockman, Y. Zheng and J. Gore, 'A study of catalytic hydrolysis of concentrated ammonia borane solutions', *International Journal of Hydrogen Energy*, vol. 35, no. 14, pp. 7350–7356, 2010, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2010.04.172`.

[331] E. J. Prosen, W. H. Johnson and F. Y. Pergiel, 'Heat of reaction of diborane with water and the heat of formation of boric oxide', *Journal o Research of the National Bureau of Standard*, vol. 62, I 1959.

[332] K. Nagasawa, 'Borazines stable to hydrolysis', *Inorganic Chemistry*, vol. 5, pp. 442–445, 3 1966, ISSN: 1520510X. DOI: `10.1021/ic50037a024`.

[333] R. Singh, M. Singh and S. Gautam, 'Hydrogen economy, energy, and liquid organic carriers for its mobility', *Materials Today: Proceedings*, vol. 46, pp. 5420–5427, 2021, ISSN: 2214-7853. DOI: `10.1016/J.MATPR.2020.09.065`.

[334] S. Kumar et al., 'Study on the thermal decomposition of nabh4 catalyzed by zrcl4', *International Journal of Hydrogen Energy*, vol. 42, pp. 22 432–22 437, 35 2017, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2017.02.060`.

[335] T. S. Krolikowski, 'Violently sprayed sodium-air reaction in an enclosed volume', Argonne National Laboratory, Tech. Rep., 1968.

[336] L. S. Lebel and N. Girault, 'Aerosol generation from sodium pool fires: Learning from the 1980s-era emis experiments and modelling', *Nuclear Engineering and Design*, vol. 330, pp. 36–50, 2018. DOI: `10.1016/j.nucengdes.2018.01.030`. [Online]. Available: `10.1016/j.nucengdes.2018.01.030`.

[337] G. H. Bulmer and A. M. I. Fire, 'Fire safety considerations related to the large scale usage of sodium', *I.Chem.E. SYMPOSIUM SERIES*, vol. 33, 1972.

[338] M. J. van Setten et al., 'Thermodynamic stability of boron: The role of defects and zero point motion', *Journal of the American Chemical Society*, vol. 129, no. 9, pp. 2458–2465, 2007. DOI: `10.1021/ja0631246`.

[339] J. Chang, T. Zhang and N. Ge, 'Influence of pressure on the structure, mechanical and dynamic properties of boron-rich na2b30', *Journal of Solid State Chemistry*, vol. 296, p. 121 962, 2021, ISSN: 0022-4596. DOI: `10.1016/J.JSSC.2021.121962`.

[340] B. Albert, 'A new 'old' sodium boride: Linked pentagonal bipyramids and octahedra in na3b20', *Angewandte Chemie - International Edition*, vol. 37, pp. 1117–1118, 8 1998, ISSN: 14337851. DOI: `10.1002/(SICI)1521-3773(19980504)37:8<1117::AID-ANIE1117>3.0.CO;2-X`.

[341] B. Albert and K. Hofmann, 'Synthesis, characterization, and crystal structure of na3b20, determined and refined from x-ray and neutron powder data', *Zeitschrift für anorganische und allgemeine Chemie*, vol. 625, no. 5, pp. 709–713, 1999. DOI: `10.1002/(SICI)1521-3749(199905)625:5<709::AID-ZAAC709>3.0.CO;2-L`.

[342] A. Sermiagin et al., 'Mechanistic implications of the solvent kinetic isotope effect in the hydrolysis of nabh4', *International Journal of Hydrogen Energy*, vol. 47, 6 2022, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2021.11.040`.

[343] R. Retnamma, A. Q. Novais and C. Rangel, 'Kinetics of hydrolysis of sodium borohydride for hydrogen production in fuel cell applications: A review', *International Journal of Hydrogen Energy*, vol. 36, no. 16, pp. 9772–9790, 2011, European Fuel Cell 2009, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2011.04.223`.

[344] K. Hoeppner et al., 'Nabh4 hydrogen microreactor fabricated by microsystem technology', *Proceedings of PowerMEMS 2008+ microEMS 2008*, 2008, pp. 84–88.

[345] J. J. Kennedy, 'A review of uncertainty in in situ measurements and data sets of sea surface temperature', *Reviews of Geophysics*, vol. 52, no. 1, pp. 1–32, 2014. DOI: `10.1002/2013RG000434`.

[346] D. Wu and X. Qian, 'Experimental study on the thermal runaway of hydrogen peroxide with in-/organic impurities by a batch reactor', *Journal of Loss Prevention in the Process Industries*, vol. 51, pp. 200–207, 2018, ISSN: 0950-4230. DOI: `10.1016/j.jlp.2017.12.012`.

[347] NCBI, *Pubchem compound summary for cid 14798, sodium hydroxide*, Retrieved April 29, 2024, 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/14798`.

[348] V. Kochkodan, N. B. Darwish and N. Hilal, 'The chemistry of boron in water', *Boron Separation Processes*, pp. 35–63, 2015. DOI: `10.1016/B978-0-444-63454-2.00002-2`.

[349] G. Moussa et al., 'Borates in hydrolysis of ammonia borane', *International Journal of Hydrogen Energy*, vol. 38, pp. 7888–7895, 19 2013, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2013.04.121`.

[350] F. Sevim et al., 'Kinetic analysis of thermal composition of boric acid from thermogravic data', *Korean Journal of Chemical Engineering 23(5):*, vol. 23, pp. 736–740, 2006. DOI: `10.1007/BF02705920`.

[351] G. J. Kim and H. T. Hwang, 'Thermal hydrolysis of solid-state sodium borohydride for noncatalytic hydrogen generation', *Chemical Engineering Journal*, vol. 424, p. 130 445, 2021, ISSN: 1385-8947. DOI: `10.1016/J.CEJ.2021.130445`.

[352] S. Balci, N. A. Sezgi and E. Eren, 'Boron oxide production kinetics using boric acid as raw material', *Industrial and Engineering Chemistry Research*, vol. 51, pp. 11 091–11 096, 34 2012, ISSN: 08885885. DOI: `10.1021/ie300685x`.

[353] S. Lopatin et al., 'Thermodynamic properties of the na2o-bao-b2o3 glasses and melts', *Journal of Non-Crystalline Solids*, vol. 612, p. 122 353, 2023, ISSN: 0022-3093. DOI: `10.1016/j.jnoncrysol.2023.122353`.

[354] H. K. Atiyeh and B. R. Davis, 'Separation of sodium metaborate from sodium borohydride using nanofiltration membranes for hydrogen storage application', *International Journal of Hydrogen Energy*, vol. 32, no. 2, pp. 229–236, 2007, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2006.06.003`.

[355] N. Kabay and M. Bryjak, 'Boron removal from seawater using reverse osmosis integrated processes', *Boron Separation Processes*, pp. 219–235, 2015. DOI: `10.1016/B978-0-444-63454-2.00009-5`.

[356] R. L. Rasmussen, J. G. Morse and K. W. Morse, 'Main group elements', *Encyclopedia of Physical Science and Technology (Third Edition)*, R. A. Meyers, Ed., Third Edition, New York: Academic Press, 2003, pp. 1–30, ISBN: 978-0-12-227410-7. DOI: `10.1016/B0-12-227410-5/00398-7`.

[357] P. Patel et al., 'Computational analysis of the hydrogen dispersion in semi-confined spaces', *Process Safety and Environmental Protection*, vol. 176, pp. 475–488, 2023, ISSN: 0957-5820. DOI: `10.1016/j.psep.2023.06.019`.

[358] K. Muller et al., 'Experimental assessment of the degree of hydrogen loading for the dibenzyl toluene based lohc system', *International Journal of Hydrogen Energy*, vol. 41, pp. 22 097–22 103, 47 2016, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2016.09.196`.

[359] F. J. Millero and F Huang, 'The density of seawater as a function of salinity (5 to 70 g kg-1) and temperature (273.15 to 363.15 k)', *Ocean Sci*, vol. 5, pp. 91–100, 2009. DOI: `10.5194/os-5-91-2009`.

[360] NCBI, *Pubchem compound summary for cid 12544637, cid 12544637*, Retrieved April 29, 2024, 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/12544637`.

[361] U. B. Demirci, 'Impact of h.i. schlesinger's discoveries upon the course of modern chemistry on b-(n-)h hydrogen carriers', *International Journal of Hydrogen Energy*, vol. 42, pp. 21 048–21 062, 33 2017, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2017.07.066`.

[362] R. E. Chapin and W. W. Ku, 'The reproductive toxicity of boric acid.', *Environmental Health Perspectives*, vol. 102, no. suppl 7, pp. 87–91, 1994. DOI: `10.1289/ehp.94102s787`.

[363] NCBI, *Pubchem compound summary for cid 784, hydrogen peroxide*, Retrieved April 29, 2024, 2024. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/Hydrogen-Peroxide`.

[364] K. Wróbel, 'Searching for the origins of the myth: 80% human error impact on maritime safety', *Reliability Engineering & System Safety*, vol. 216, p. 107 942, 2021, ISSN: 0951-8320. DOI: `10.1016/j.ress.2021.107942`.

[365] C. Graham-Mclay, *Crew mistakes caused the sinking of a new zealand navy ship off samoan coast, inquiry finds*, Accessed 27 February 2025, 2024. [Online]. Available: `https://apnews.com/article/zealand-navy-ship-samoa-manawanui-sinking-military-dd9cccaa0739ef98f615cc4969a117b0`.

[366] Allianz, *Shipping safety - human error comes in many forms*, Accessed 27 February 2025, 2019. [Online]. Available: `https://commercial.allianz.com/news-and-insights/expert-risk-articles/human-error-shipping-safety.html`.

[367] International Maritime Organization, *Index of mepc resolutions and guidelines related to marIndex of MEPC Resolutions and Guidelines related to MARPOL Annex VI*, Accessed 27 February 2025, n.d. [Online]. Available: `\url{https://www.imo.org/en/OurWork/Environment/Pages/Index-of-MEPC-Resolutions-and-Guidelines-related-to-MARPOL-Annex-VI.aspx}`.

[368] C. Nuchturee, T. Li and H. Xia, 'Energy efficiency of integrated electric propulsion for ships – A review', *Renewable and Sustainable Energy Reviews*, vol. 134, p. 110 145, 2020, ISSN: 1364-0321. DOI: `10.1016/j.rser.2020.110145`.

[369] J. F. Hansen and F. Wendt, 'History and State of the Art in Commercial Electric Ship Propulsion, Integrated Power Systems, and Future Trends', *Proceedings of the IEEE*, vol. 103, no. 12, pp. 2229–2242, 2015, ISSN: 1558-2256. DOI: `10.1109/JPROC.2015.2458990`.

[370] P. Nema, R. K. Nema and S. Rangnekar, 'A current and future state of art development of hybrid energy system using wind and PV-solar: A review', *Renewable and Sustainable Energy Reviews*, vol. 13, no. 8, pp. 2096–2103, 2009, ISSN: 1364-0321. DOI: `10.1016/j.rser.2008.10.006`.

[371] A. D. Korberg et al., 'Techno-economic assessment of advanced fuels and propulsion systems in future fossil-free ships', *Renewable and Sustainable Energy Reviews*, vol. 142, p. 110 861, 2021, ISSN: 1364-0321. DOI: `10.1016/j.rser.2021.110861`.

[372] P. Swuste et al., *From Safety to Safety Science: The Evolution of Thinking and Practice*. Routledge, 2021, ISBN: 9781003001379. DOI: `10.4324/9781003001379`.

[373] H. Pasman and G. Reniers, 'Past, present and future of quantitative risk assessment (qra) and the incentive it obtained from land-use planning (lup)', *Journal of Loss Prevention in the Process Industries*, vol. 28, pp. 2–9, 2014, ISSN: 0950-4230. DOI: `10.1016/J.JLP.2013.03.004`.

[374] A. Basheer et al., 'Methodologies for assessing risks of accidents in chemical process industries', *J. Fail. Anal. Prev.*, vol. 19, no. 3, pp. 623–648, 2019.

[375] Committee for the Prevention of Disasters, *Guidelines for Quantitative Risk Assessment: Purple Book CPR 18E*. The Hague, Netherlands: Directorate-General for Social Affairs and Employment, 1999, Accessed on note = Accessed 27 July 2025, [Online]. Available: `https://publicatiereeksgevaarlijkestoffen.nl/documents/81474/1664357417-pgs3-1999-v0-1-quantitative-risk-assessment.pdf`.

[376] IMO, *Formal safety assessment*, Accessed 27 February 2025. [Online]. Available: `https://www.imo.org/en/OurWork/Safety/Pages/FormalSafetyAssessment.aspx`.

[377] P. Karvounis et al., 'Recent advances in sustainable and safe marine engine operation with alternative fuels', *Frontiers in Mechanical Engineering*, vol. 8, p. 994 942, 2022, ISSN: 22973079. DOI: `10.3389/FMECH.2022.994942/BIBTEX`.

[378] I. van de Poel and Z. Robaey, 'Safe-by-design: From safety to responsibility', *Nanoethics*, vol. 11, pp. 297–306, 3 2017, ISSN: 1871-4757. DOI: `10.1007/S11569-017-0301-X`. [Online]. Available: `https://pubmed.ncbi.nlm.nih.gov/29238409/`.

[379] B. Taebi, *Ethics and engineering* (Cambridge Applied Ethics), en. Cambridge, England: Cambridge University Press, 2021.

[380] M. R. Grech, T. J. Horberry and T. Koester, *HUMAN FACTORS in the MARITIME DOMAIN*. CRC Press, 2019, ISBN: 9780429355417. DOI: `10.1201/9780429355417`. [Online]. Available: `http://dx.doi.org/10.1201/9780429355417`.

[381] K. E. Weick and K. M. Sutcliffe, *Managing the Unexpected - Sustained Performance in a Complex World (3rd Edition)*. John Wiley & Sons, 2015, ISBN: 978-1-118-86241-4. [Online]. Available: `https://app.knovel.com/hotlink/toc/id:kpMUSPCWE1/managing-unexpected-sustained/managing-unexpected-sustained`.

[382] NSIA, 'Loss of propulsion and near grounding of viking sky, hustadvika, norway, 23 march 2019', Norwegian Safety Investigation Authority, Lillestrøm, Norway, Tech. Rep. Marine 2024/05, 2024, Report published by the Norwegian Safety Investigation Authority. [Online]. Available: `https://kudos.dfo.no/documents/82805/files/37867.pdf`.

[383] J. R. Chiles, *Inviting disaster*. London, England: HarperCollins, 2001.

[384] J. E. Skogdalen and J. E. Vinnem, 'Quantitative risk analysis offshore—human and organizational factors', *Reliability Engineering & System Safety*, vol. 96, pp. 468–479, 4 2011, ISSN: 0951-8320. DOI: `10.1016/J.RESS.2010.12.013`.

[385] M. Buitendijk, *Hapag-lloyd orders 24 ammonia-ready container ships*, Accessed 16 April 2025, 2024. [Online]. Available: `https://swzmaritime.nl/news/2024/11/08/hapag-lloyd-orders-24-ammonia-ready-container-ships/`.

[386] G. Njovu, *Ammonia-fueled vessels: Shipyard orders and new concepts*, Accessed 16 April 2025, 2019. [Online]. Available: `https://ammoniaenergy.org/articles/ammonia-fueled-vessels-shipyard-orders-and-new-concepts/`.

[387] D. P. Carlisle et al., 'Public response to decarbonisation through alternative shipping fuels', *Environment, Development and Sustainability*, vol. 26, no. 8, 20737–20756, 2023, ISSN: 1573-2975. DOI: `10.1007/s10668-023-03499-0`.

[388] J. Groeneweg, *Controlling the controllable: preventing business upsets*, fifth. Global Safety Group, 2002, ISBN: 90-6695-140-0.

[389] C. Perrow, *Normal Accidents: Living with High-Risk Technologies*. New York: Basic Books, 1984, ISBN: 0465051448.

[390] O. Turan et al., 'Can we learn from aviation: Safety enhancements in transport by achieving human orientated resilient shipping environment', *Transportation Research Procedia*, vol. 14, pp. 1669–1678, 2016, Transport Research Arena TRA2016, ISSN: 2352-1465. DOI: `10.1016/j.trpro.2016.05.132`.

[391] Ministry of Infrastructure and Water Management, *International safety management code (resolution a.741(18)) - netherlands regulatory framework (nerf) – maritime*, Accessed 15 July 2025. [Online]. Available: `https://puc.overheid.nl/nsi/doc/PUC_2410_14/6/`.

[392] United States Coast Guard, 'Report of the marine board of investigation into the sinking and loss of the steam ship El Faro (o.n. 561732)', United States Coast Guard, Tech. Rep., 2017, Report available from GISIS. [Online]. Available: `https://gisis.imo.org/Public/MCIR/Occurrence.aspx?Reference=C0010070&Form=InvestigationDocument`.

[393] E. O. Popa and A. Melnyk, 'Taking value conflicts seriously: Technological pluralism as an approach to hydrogen governance', *Energy Strategy Reviews*, vol. 59, p. 101 734, 2025, ISSN: 2211-467X. DOI: `10.1016/j.esr.2025.101734`.

[394] T. Notteboom, P. De Langen and W. Jacobs, 'Institutional plasticity and path dependence in seaports: Interactions between institutions, port governance reforms and port authority routines', *Journal of Transport Geography*, vol. 27, pp. 26–35, 2013, Institutions and the Transformation of Transport Nodes, ISSN: 0966-6923. DOI: `10.1016/j.jtrangeo.2012.05.002`.

[395] E. G. Carayannis and D. F. J. Campbell, 'Triple helix, quadruple helix and quintuple helix and how do knowledge, innovation and the environment relate to each other?: A proposed framework for a transdisciplinary analysis of sustainable development and social ecology', *International Journal of Social Ecology and Sustainable Development (IJSESD)*, vol. 1, no. 1, pp. 41–69, 2010. DOI: `10.4018/jsesd.2010010105`.

[396] D. Collingridge, *The social control of technology*. Open University Press, 1981, Available via WorldCat.

[397] J. Stilgoe, R. Owen and P. Macnaghten, 'Developing a framework for responsible innovation', *Research Policy*, vol. 42, no. 9, pp. 1568–1580, 2013. DOI: `10.1016/j.respol.2013.05.008`.

[398] R. von Schomberg and V. Blok, 'Technology in the age of innovation: Responsible innovation as a new subdomain within the philosophy of technology', *Philosophy & Technology*, vol. 34, no. 2, pp. 309–323, 2021. DOI: `10.1007/s13347-019-00386-3`.

[399] E. O. Popa et al., 'Moral impact of technologies from a pluralist perspective: Artificial photosynthesis as a case in point', *Technology in Society*, vol. 75, p. 102 357, 2023, ISSN: 0160-791X. DOI: `10.1016/j.techsoc.2023.102357`.

[400] Stratelligence and Dwarsverband, 'Vergelijking waterstofdragers: Multicriteria-analyse van leveringsketens in nederland', Ministerie van Klimaat en Groene Groei, Leiden, Nederland, Tech. Rep., 2024, Opgesteld in opdracht van het Ministerie van Klimaat en Groene Groei. Eindversie. [Online]. Available: `https://open.overheid.nl/documenten/600a920d-b0b9-4252-ad36-1555e37efca9/file`.

[401] International Maritime Organization, *List of imo conventions*, Accessed on February 2025, n.d. [Online]. Available: `https://www.imo.org/en/About/Conventions/Pages/ListOfConventions.aspx`.

[402] N. Akamangwa, ‘Environmental management at sea: What being ‘green’ means for seafarers’, *The World of the Seafarer: Qualitative Accounts of Working in the Global Shipping Industry*, V. O. Gekara and H. Sampson, Eds., Cham: Springer International Publishing, 2021, pp. 113–126, ISBN: 978-3-030-49825-2. DOI: `10.1007/978-3-030-49825-2_10`.

[403] Merriam-Webster, *Safety*, Accessed: 24 July 2025, n.d. [Online]. Available: `https://www.merriam-webster.com/dictionary/safety`.

[404] Merriam-Webster, *Sustainable*, Accessed: 24 July 2025, n.d. [Online]. Available: `https://www.merriam-webster.com/dictionary/sustainable`.

[405] P. Christmann and G. Lefebvre, ‘Trends in global mineral and metal criticality: the need for technological foresight’, *Mineral Economics*, vol. 35, no. 3-4, pp. 641–652, 2022, ISSN: 21912211. DOI: `10.1007/S13563-022-00323-5/TABLES/3`.

[406] G. M. Mudd, ‘Assessing the Availability of Global Metals and Minerals for the Sustainable Century: From Aluminium to Zirconium’, *Sustainability 2021, Vol. 13, Page 10855*, vol. 13, no. 19, p. 10 855, 2021, ISSN: 2071-1050. DOI: `10.3390/SU131910855`.

[407] B. Allan et al., ‘How the U.S. can stop losing the race for clean energy’, Carnegie Endowment for International Peace, Tech. Rep., 2025.

[408] International Energy Agency, ‘Securing Clean Energy Technology Supply Chains’, International Energy Agency, Tech. Rep., 2022, Accessed: 2025-07-27.

[409] S. Garrido Nuñez, D. L. Schott and J. T. Padding, ‘Optimization of operational parameters in the mechanochemical regeneration of sodium borohydride (nabh4)’, *International Journal of Hydrogen Energy*, vol. 97, pp. 640–648, 2025, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2024.11.360`.

[410] K. Volkart et al., ‘Multi-criteria decision analysis of energy system transformation pathways: A case study for switzerland’, *Energy Policy*, vol. 106, pp. 155–168, 2017, ISSN: 0301-4215. DOI: `10.1016/J.ENPOL.2017.03.026`.

[411] R. Schmidt-Scheele et al., ‘Sustainability assessments of energy scenarios: Citizens’ preferences for and assessments of sustainability indicators’, *Energy, Sustainability and Society*, vol. 12, pp. 1–23, 1 2022, ISSN: 21920567. DOI: `10.1186/S13705-022-00366-0/TABLES/5`.

[412] R. A. Estévez et al., 'Multi-criteria decision analysis for renewable energies: Research trends, gaps and the challenge of improving participation', *Sustainability 2021, Vol. 13, Page 3515*, vol. 13, p. 3515, 6 2021, ISSN: 2071-1050. DOI: `10.3390/SU13063515`.

[413] Merriam-Webster, *Timely*, "Timeliness" entry, n.d. [Online]. Available: `https://www.merriam-webster.com/dictionary/timeliness`.

[414] ChemicalBook, *Safety Data Sheet – Dibenzyltoluene*, Revision 1; CAS 26898-17-9; EINECS 248-097-0. Accessed 21 July 2025, 2025. [Online]. Available: `https://www.chemicalbook.com/msds/DIBENZYLTOLUENE.pdf`.

[415] European Chemicals Agency (ECHA), *ECHA substance information: Dibenzylbenzene, ar-methyl derivative, hydrogenated (ec 943-342-4)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.243.292/overview?searchText=943-342-4`.

[416] European Chemicals Agency (ECHA), *ECHA substance information: Dibenzyltoluene (ec 248-097-0, cas 26898-17-9)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.043.710/overview`.

[417] E. Spatolisano et al., 'Assessing opportunities and weaknesses of green hydrogen transport via LOHC through a detailed techno-economic analysis', *International Journal of Hydrogen Energy*, vol. 52, pp. 703–717, 2024, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2023.08.040`.

[418] M. Byun et al., 'Preliminary feasibility study for hydrogen storage using several promising liquid organic hydrogen carriers: Technical, economic, and environmental perspectives', *Energy Conversion and Management*, vol. 268, p. 116 001, 2022, ISSN: 0196-8904. DOI: `10.1016/J.ENCONMAN.2022.116001`.

[419] European Chemicals Agency (ECHA), *ECHA substance information: 9-ethylcarbazole (ec 201-660-4, cas 86-28-2)*, Accessed 21 July 2025. [Online]. Available: `https://echa.europa.eu/substance-information/-/substanceinfo/100.001.510`.

[420] Angene Chemical, *Safety Data Sheet – 9-Ethyldodecahydro-1H-carbazole*, `https://www.angenechemical.com/sds/146900-30-3.pdf`, Revision 2.0; CAS 146900-30-3. Accessed 21 July 2025, 2021.

[421] F. Asif et al., 'Performance analysis of the perhydro-dibenzyl-toluene dehydrogenation system—a simulation study', *Sustainability*, vol. 13, p. 6490, 11 2021, ISSN: 2071-1050. DOI: `10.3390/SU13116490`.

[422] P. Brack, S. E. Dann and K. G. Upul Wijayantha, 'Heterogeneous and homogenous catalysts for hydrogen generation by hydrolysis of aqueous sodium borohydride (NaBH4) solutions', *Energy Science & Engineering*, vol. 3, no. 3, pp. 174–188, 2015, ISSN: 2050-0505. DOI: `10.1002/ESE3.67`.

[423] S. M. Kwon et al., 'Development of a high-storage-density hydrogen generator using solid-state nabh4 as a hydrogen source for unmanned aerial vehicles', *Applied Energy*, vol. 251, p. 113 331, 2019, ISSN: 0306-2619. DOI: `10.1016/J.APENERGY.2019.113331`.

[424] B. G. Gang and S. Kwon, 'Design of an energy management technique for high endurance unmanned aerial vehicles powered by fuel and solar cell systems', *International Journal of Hydrogen Energy*, vol. 43, no. 20, pp. 9787–9796, 2018, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2018.04.049`.

[425] A. Schell et al., 'Modeling and control strategy development for fuel cell electric vehicles', *IFAC Proceedings Volumes*, vol. 37, no. 22, pp. 1–8, 2004, IFAC Symposium on Advances in Automotive Control 2004, Salerno, Italy, 19-23 April 2004, ISSN: 1474-6670. DOI: `10.1016/S1474-6670(17)30313-0`.

[426] R. Retnamma et al., 'Kinetic modeling of self-hydrolysis of aqueous NaBH4 solutions by model-based isoconversional method', *International Journal of Hydrogen Energy*, vol. 39, no. 12, 2014, ISSN: 03603199. DOI: `10.1016/j.ijhydene.2014.02.035`.

[427] European Chemicals Agency (ECHA), *ECHA substance information: Sodium borohydride (cas 16940-66-2, ec 241-004-4)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.037.262/overview?searchText=16940-66-2`.

[428] European Chemicals Agency (ECHA), *ECHA substance information: Boric acid (ec 233-139-2, cas 10043-35-3)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.030.114/overview`.

[429] C. Yüksel Alpaydın, S. K. Gülbay and C. Ozgur Colpan, 'A review on the catalysts used for hydrogen production from ammonia borane', *International Journal of Hydrogen Energy*, vol. 45, no. 5, pp. 3414–3434, 2020, Hydrogen Energy Technologies for Mitigating Global Warming, ISSN: 0360-3199. DOI: `10.1016/j.ijhydene.2019.02.181`.

[430] E. S. van Rheenen et al., 'Spill behaviour of hydrogen carriers as alternative fuels for ships', *Proceedings of the 10th World Congress on Civil, Structural, and Environmental Engineering (CSEE 2025)*, 2025. DOI: `10.11159/iceptp25.123`.

[431] M. Chandra and Q. Xu, 'Room temperature hydrogen generation from aqueous ammonia-borane using noble metal nano-clusters as highly active catalysts', *Journal of Power Sources*, vol. 168, pp. 135–142, 1 2007. DOI: `10.1016/J.JPOWSOUR.2007.03.015`.

[432] European Chemicals Agency (ECHA), *ECHA substance information: Ammonia (cas 7664-41-7, ec 231-635-3)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.138.215/overview?searchText=Ammonia`.

[433] R. Radonja, D. Bebić and D. Glujić, 'Methanol and ethanol as alternative fuels for shipping', *Promet - Traffic&Transportation*, vol. 31, pp. 321–327, 3 2019, ISSN: 0353-5320. DOI: `10.7307/PTT.V31I3.3006`.

[434] J. O. Mandra, *23 methanol-powered ships ordered since the start of 2024*, `https://www.offshore-energy.biz/23-methanol-powered-ships-ordered-since-the-start-of-2024/`, Accessed 21 July 2025; author based on Offshore-Energy listing, 2024.

[435] A.P. Moller - Maersk, *Maersk orders six methanol-powered vessels*, `https://www.maersk.com/news/articles/2023/06/26/maersk-orders-six-methanol-powered-vessels`, Accessed 21 July 2025, 2023.

[436] European Chemicals Agency (ECHA), *ECHA substance information: Methanol (cas 67-56-1, ec 200-659-6)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.000.599/overview?searchText=methanol`.

[437] NCBI, *Pubchem compound summary: Molecular hydrogen (h_2)*, Accessed 21 July 2025, 2025. [Online]. Available: `https://pubchem.ncbi.nlm.nih.gov/compound/783`.

[438] European Chemicals Agency (ECHA), *ECHA substance information: Hydrogen (cas 1333-74-0, ec 215-605-7)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.014.187/overview?searchText=1333-74-0`.

[439] T. Boot et al., 'In-situ hollow sample setup design for mechanical characterisation of gaseous hydrogen embrittlement of pipeline steels and welds', *Metals*, vol. 11, no. 8, p. 1242, 2021. DOI: `10.3390/met11081242`.

[440] European Chemicals Agency (ECHA), *ECHA substance information: Ultra-low sulfur diesel (cas 68334-30-5, ec 269-822-7)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.063.455/overview`.

[441] European Chemicals Agency (ECHA), *ECHA substance information: Fuel oil no. 4 (ec 270-673-5)*, Accessed 21 July 2025. [Online]. Available: `https://chem.echa.europa.eu/100.064.228/overview`.

[442] BP Australia Pty Ltd, *BP marine fuel oil safety data sheet*, SDS no. 3188928 (inferred); fuel for marine diesel engines. Accessed 21 July 2025, 2021. [Online]. Available: `https://bpmarinefuelssds.bp.com/ussds/amersdsf.nsf/AllFiles_AIR_BP_FUELS/968BF7351493A4FD80258CA80052B7F2/$File/3188928.pdf`.

[443] Fincantieri, *Zeus (zero emission ultimate ship)*, Accessed on 20 April 2023, 2023. [Online]. Available: `https://www.fincantierisi.it/innovation`.

[444] V. Raghuvanshi, *Indian lab teams up with france's naval group on submarine tech*, Accessed on 30 March 2023, 2023. [Online]. Available: `https://www.defensenews.com/industry/techwatch/2023/01/24/indian-lab-teams-up-with-frances-naval-group-on-submarine-tech/`.

[445] Interreg North-West Europe, *H2ships - system-based solutions for h2-fuelled water transport in north-west europe*, Accessed on 22nd June 2022, 2022. [Online]. Available: `https://www.nweurope.eu/projects/project-search/h2ships-system-based-solutions-for-h2-fuelled-water-transport-in-north-west-europe/`.

[446] Port of Amsterdam, *Start bouw innovatieve neo orbis met kiellegging*, Accessed on 30th March 2023, 2023. [Online]. Available: `https://www.portofamsterdam.com/nl/nieuws/start-bouw-innovatieve-neo-orbis-met-kiellegging`.

[447] B. G. Gang and S. Kwon, 'Design of an energy management technique for high endurance unmanned aerial vehicles powered by fuel and solar cell systems', *International Journal of Hydrogen Energy*, vol. 43, pp. 9787–9796, 20 2018, ISSN: 0360-3199. DOI: `10.1016/J.IJHYDENE.2018.04.049`.

[448] S. M. Kwon, S. Kang and T. Kim, 'Development of nabh4-based hydrogen generator for fuel cell unmanned aerial vehicles with movable fuel cartridge', *10th International Conference on Applied Energy*, vol. 158, Elsevier Ltd, 2019, pp. 1930–1935. DOI: `10.1016/j.egypro.2019.01.443`.

[449] T. Kim, 'Nabh4 (sodium borohydride) hydrogen generator with a volume-exchange fuel tank for small unmanned aerial vehicles powered by a pem (proton exchange membrane) fuel cell', *Energy*, vol. 69, pp. 721–727, 2014, ISSN: 03605442. DOI: `10.1016/j.energy.2014.03.066`.

[450] Østensjø Rederi, *Edda ferd*, Accessed on 30th March 2023, date unknown. [Online]. Available: `https://ostensjo.no/fleet/eddaferd/`.

[451] HYSILABS, *Hydrosil:h2 stored as liquids - patented solutions*, Accessed on 30th March 2023, 2023. [Online]. Available: `https://www.hysilabs.com/technology`.

[452] HYSILABS, *Hysilabs introduces hydrogen stored as liquids solutions*, Accessed on 22nd June 2022, 2022. [Online]. Available: `https://www.hysilabs.com/solutions`.

[453] S. Sluijters, *Presenting the first hydrogen powder generator*, Accessed on 30th March 2023, 2022. [Online]. Available: `https://www.electriq.com/blog-post/presenting-first-hydrogen-powder-generator`.

GLOSSARY

LATIN SYMBOLS

Symbol	**Description**
AVG	Average
cp	heat capacity at constant pressure
E	Energy
E loss	Lost energy
E_{tot}	Total Energy
Eout	Energy output
LHV_{H2}	Lower heating value
m	mass
$m_{carrier}$	mass flow of carrier
$\dot{m}$	mass flow
m_{h2}	mass hydrogen
$\dot{m}_{h2}$	mass flow of hydrogen
m_p	mass of power converter
m_w	mass of fuel
n	number of moles
P	Power
P′	Power density of single component
P″	Power density of whole system
P_{out}	Output power
P_{req}	Required power
Q	Heat
Q coolant	heat going to coolant

Symbol	Description
Q req	Required heat
Q wh	Available waste heat
Q_{hs}	Heat available in sink
Qfg	heat going to flue gasses
Qlocal	Local heat source
T	temperature, K
t	time
T_{local}	Local temperature, K
T_{max}	maximum temperature, K
W	Energy density of fuel
x	number

GREEK SYMBOLS

Symbol	Description
Δ	Difference between two values
η	Efficiency

ABBREVIATIONS

Term	Description
AB	Ammonia Borane, NH_3BH_3
BT	Benzyltoluene
DBT	Dibenzyltoluene
DoE	Department of Energy
ECHA	European Chemicals Agency
EDR	Exchanger Design & Rating
ETA	Event Tree Analysis

Term	**Description**
FG	Flue gas
FMEA	Failure Mode and Effects Analysis
FSA	Formal Safety Assessment
FTA	Fault Tree Analysis
GBS	Goal Based Standards
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
GHG	Greenhouse Gas Emissions
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
GT	Gas Turbine
H2	Hydrogen
HAZOP	Hazard and Operability Studies
HEX	Heat Exchanger
HFO	Heavy Fuel Oil
HNS	Hazardous and noxious substances
HT	High temperature
ICE	Internal Combustion Engine
IGC	The International Code of the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk
IGF code	International Code of Safety for Ships Using Gases or Other Low-flashpoint Fuels
IMO	International Maritime Organization
ISM	International Safety Management
KB	Potassium borohydride, KBH_4
LH2	Liquified Hydrogen
LNG	Liquid Natural Gas
LOHC	Liquid Organic Hydrogen Carrier
LT	Low temperature
MARPOL	International Convention for the Prevention of Pollution from Ships

Term	Description
MCDM	Multi-Criteria Decision Making
MDO	Marine Diesel Oil
MeOH	Methanol, CH_3OH
MLC	Maritime Labour Convention
MOF	Metal Organic Framework
MSC	Maritime Safety Committee
NEC	N-ethylcarbazole
NOx	Nitrogen Oxides
OPRC-HNS	Protocol on Preparedness, Response and Co-operation to pollution Incidents by Hazardous and Noxious Substances
PBT	Persistent, Bioaccumulative and Toxic Substances
PEMFC	Proton Exchange Membrane Fuel Cell
PH2	Pressurized Hydrogen
PHS	Polyhydrosiloxane
PMHS	Polymethylhydrosiloxane
PNEC	Predicted No-Effect Concentration
QRA	Quantitative Risk Assessment
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
SB	Sodium borohydride, $NaBH_4$
SOFC	Solid Oxide Fuel Cell
SOLAS	International Convention for the Safety of Life at Sea
SOx	Sulphur Oxides
THF	Tetrahydrofuran
TOL	Toluene
TRL	Technology Readiness Level
UN	United Nations
US	United States

A

GENERAL DATA ON HYDROGEN CARRIERS

This research is limited to four hydrogen carriers, namely dibenzyltoluene (DBT), n-ethylcarbazole (NEC), sodium borohydride (SB) and ammonia borane (AB). Occasionally four other fuels are also considered. These are ammonia, methanol and liquid hydrogen as alternative fuels and one common fuel, marine diesel oil. MDO is the current reference fuel in maritime operations and comparisons to MDO are made narratively where relevant.

A.1 LOHCS

A.1.1 DIBENZYLTOLUENE

DBT is a LOHC. It is circular, meaning there is a hydrogenated (full) and dehydrogenated (empty) version of DBT. DBT is an often-researched, oil-like substance, and its dehydrogenated version has been in use as a heat transfer fluid in commercial applications already [25], [152]. Because of its previous use as a heat transfer fluid, safety data sheets are available for the dehydrogenated version [414]. It has a boiling point of 397 °C and a high flashpoint of 189.8 °C [414]. The dehydrogenated version is also categorised as may be fatal when swallowed and enters the airways [415], while both versions of DBT are aquatic chronic [415], [416]. The hydrogenated version is also extremely viscous [152], however, is otherwise relatively safe; requiring no specific special first aid, fire protection or storage measures [416]. Releasing hydrogen from DBT costs heat, as it is an endothermic process [25]. The positive side effect is that there is no accidental release of hydrogen possible. Hydrogen is released at 280-310 °C [25]. A major negative property is its low energy density, of 6.2 wt% of hydrogen, and the large amount of energy required to release the hydrogen, reducing overall energy efficiency [25], [417].

The operational costs of DBT depend strongly on the cost of pure hydrogen [418], while the capital expenditure is defined by the costs of compressors [417].

A.1.2 N-ETHYLCARBAZOLE

NEC is the second LOHC considered, it has a relative high energy density (5.8 wt%), is easy to handle and can produce hydrogen relatively fast [25]. Another main advantage is its low dehydrogenation temperature, of 180 to 210 °C [25]. However, NEC is relatively little researched; the substance is not very mature, with research only starting in the early 2000s [25]. The capital expenditure of NEC is higher than DBT, likely because much less of it is produced each year [25], [418]. The dehydrogenated version of NEC is solid at temperatures below 68 °C, and has a flashpoint of 186 °C [25], [240]. It is toxic to the aquatic environment and should not be inhaled or touched [419]. The hydrogenated version of NEC is liquid at room temperatures and has a flashpoint of 146 °C [25]. Just like dehydrogenated NEC, it should not be swallowed or touched [420]. While dehydrogenated NEC is toxic for the environment, with an aquatic chronic toxicity of level 2, hydrogenated NEC does not appear to be toxic to the environment [419], [420]. Besides these properties, NEC does not require extreme pressures or temperatures during storage or processes.

A.1.3 ENDOTHERMIC RELEASE

Both LOHCs endothermically release hydrogen. The release mechanism for the LOHCs is very similar and is as follows:

$$\text{LOHC}^{+} + \text{Energy} \rightarrow \text{LOHC}^{-} + n\text{H}_2 \tag{A.1}$$

The significant difference is the temperatures at which they react and the heat required for dehydrogenation. DBT's dehydrogenation temperature lies between 553 and 593K; temperatures above 573K are required to reach full dehydrogenation, while DBT will start dissociating at temperatures above 563K. A temperature of 573K is chosen in the model, as this temperature is often used in experiments, and full dehydrogenation can be achieved without compromising the fluid too much [421]. The dehydrogenation process requires 558 kJ/mol of full LOHC [25]. The dehydrogenation temperature for NEC lies between 453 and 523K. The dehydrogenation process is much slower at lower temperatures. The model uses a temperature of 503K. The dehydrogenation process is fast at this temperature, without having high heating loads [179]. The hydrogenation process requires 318 kJ/mol of full LOHC [25]. [29] showed that, with an essential integration, a large part of the required heat could be supplied by the energy converter and heat available in the spent fuel, with similar results found by [24], who looked at a specific hydrogen carrier and energy converter. Figure 4.1 gives an overview of the specific components required for the hydrogen carrier to release hydrogen. After the carrier is transported from the tank, heat exchangers are used to preheat the carrier up to the dehydrogenation temperature. Part of this heat exchange already has to occur in the tank, as DBT is highly viscous; thus, preheating is required to get it out of the tank.

A.2 BORON-BASED CARRIERS

A.2.1 SODIUM BOROHYDRIDE

SB, $NaBH_4$, is a white powder, but can also exist as granulate. It has a high energy density of 10.8 wt%. Using SB on ships will require a specialized, circular bunkering system that is able to handle solid powders [183]. SB is a borohydride and releases hydrogen when in contact with water. A catalyst is needed to enhance this process, but there are many different types of catalysts available [113], [422]. This process goes as follows:

$$\mathrm{NaBH_4{+}(2{+}x)\ H_2O \rightarrow 4H_2 + NaBO_2 \cdot xH_2O} \tag{A.2}$$

The exact value of x depends on the operating parameters [159]. Equation A.2 shows that the original amount of hydrogen in sodium borohydride is doubled, as the hydrogen stored inside water is also freed, resulting in an energy density of over 21 wt%. It has previously been used as an energy source in unmanned aerial vehicles [423], [424] and even, albeit shortly, in cars [425]. However, for land-based applications, water storage is required, reducing the energy density. Using purified seawater means no additional water has to be stored on ships, effectively solving this low energy density issue. Another major issue of sodium borohydride is the regeneration process. Equation A.2 is exothermic, meaning that regeneration costs energy. Enhancing this process is part of active research [409]. Equation A.2 showcases another issue with sodium borohydride: self-hydrolysis is possible; e.g. when sodium borohydride comes into contact with water, hydrogen may be released. The speed of the reaction depends on the temperature and the pH of the water, with a higher temperature enhancing the reaction rate, whilst a higher pH reduces the reaction rate [426]. At low temperatures, of 20 °C, full conversion takes relatively long (several hours), reducing this problem. It is still an issue, however, just like the influence of sodium borohydride on the health of humans: it is acutely toxic (oral), corrosive to the skin, damaging to the eyes and may influence the reproducibility [427]. On the other side, sodium borohydride is not categorised as persistent [427]. Its spent fuel, boric acid, is often used, yet still the knowledge of the effects of boric acid on the reproducibility is limited, but boric acid is still assumed to be a health hazard [428].

A.2.2 AMMONIA BORANE

AB, NH_3BH, is a white, sticky powder. Similar to sodium borohydride, AB requires a specialized bunkering system designed to handle solid powders [183]. This system must facilitate the safe and efficient transfer of fuel to and from the vessel. It releases hydrogen through hydrolysis, but a catalyst is required for this [429]; self-hydrolysis is negligible [430]. Equation 2.1 shows this reaction:

$$H_3NBH_3 + 3H_2O \rightarrow NH_3 + B(OH)_3 + 3H_2 \tag{A.3}$$

Without a catalyst, AB is stable in the presence of water [430]. AB can have a very high energy density; the exact energy density depends on whether and how the ammonia produced is used. Although, AB has been relatively well researched, it has not been implemented yet [83]. The major issue with AB is the regeneration, which is closely related to the regeneration of sodium borohydride. Sodium borohydride is a intermediate product during the regeneration process, and the regeneration of AB is expensive and energy-intensive [83]. AB is thermally decomposed when temperatures are raised above 70 °C, releasing, amongst others, hydrogen and ammonia. This may be the reasoning behind the categorization of flammable solid [258]. Furthermore, AB is harmful if swallowed, causes skin and eye irritation and may cause respiratory irritation [258].

A.2.3 EXOTHERMIC RELEASE

AB and SB release hydrogen exothermically upon reacting with water, according to equations A.2 and A.3 These reactions are similar, requiring water and releasing equally or more hydrogen than initially stored in the molecule, as the process also releases hydrogen within theoccurs in the tank, as DBT is highly viscous; thus, preheating is required to remove it froml to the original molecule is possible but energy intensive due to the strong B-O bonds [111]. The exact composition of the spent fuel of SB (equation A.2) depends on the temperature of the reaction. At the optimal reaction temperatures of 333 to 353K, the composition is $NaBO_2.2H_2O$.

Equation A.3 shows the release mechanism of AB, which produces hydrogen and ammonia. Ammonia gas can be burned in a heat engine, for example, in a dual-fuel ammonia-hydrogen internal combustion engine. Additionally, it can be decomposed into N_2 and H_2, after which the H_2 can be used in a fuel cell. Finally, ammonia gas can be stored on board. Storage is not considered feasible because of the required safety regulations and additional space. The decomposition process is also disregarded, as this process is highly energy-intensive. Thus, in this study, similar to in [29], only dual-fuel options of ammonia and hydrogen gas are considered. Only the PEMFC cannot run on the ammonia-hydrogen dual-fuel of the four investigated energy converters.

Table A.1: Parameters of hydrogen carriers

Parameter	DBT	NEC	SB	AB
Theoretical energy density [MJ/kg]	7.44	6.98	25.56	23.52
Theoretical energy density [MJ/L]	7.0	6.63	27.34	14.4
Hydrogen yield per molecule of hydrogen carrier [mol/mol]	9	6	4	3
Molecular weight [g/mol]	290.54	207	37.8	30.8
Heat capacity fuel (incl. water if necessary [kJ/kgK]	1.96	2.04	4.54*	4.54*
Heat capacity spent fuel [kJ/kgK]	1.82	1.56	N.R.	N.R.
Dehydrogenation temperature [K]	573	503	353	353*
Dehydrogenation energy [kJ/mol Fuel]	558	318	-210	-156
Sources	[21] [96]	[151] [152] [153]	[154] [53] [155]	[176] [431]

Values denoted with * are estimated by the authors combined with data from Aspen as no precise information was available.
N.R. stands for 'Not required' as these values are not required in this calculation.
When a solution is mixed, the heat capacity of the solution is calculated

A.3 REFERENCE FUELS

A.3.1 AMMONIA

Ammonia is often mentioned as being a promising alternative fuel [19], [20], [120], [267]. It has a high energy density, can be used in internal combustion engines and fuel cells (even though purification is required for the latter), and is currently being produced on a large scale. Ammonia is often stored as a liquid, even though it is a gas at ambient temperature and pressure [267]. Thus, ammonia is often stored at slightly decreased temperatures (below -33 °C), or elevated pressures (above 10 bar) [267]. It is carbon-free, but combustion will result in the release of the pollutant NO_x, a pollutant [20]. Ammonia is categorised as a flammable gas, despite its high auto-ignition temperature of 651 °C [19], [78], [432]. Additionally, ammonia is toxic if inhaled and severely corrosive to the skin [432]. Because it is a toxic gas, it is often regarded as dangerous, as exposure at concentrations of over 1700 ppm can result in death within 30 minutes [267]. Equally, ammonia is extremely toxic to aquatic life [432], and is hard to clean up or detect, as it is very soluble in water [184].

A.3.2 METHANOL

Methanol is widely considered as an alternative fuel, with several full-scale ships in operation or production [19], [433], [434], [435]. It can be made in a green way, burns very clean and does not contain contaminants such as sulphur. A methanol engine will emit NO_x emissions, but only very little [37], [433]. A major technical disadvantage of methanol is its lubrication properties [37]. From a safety perspective, methanol has some disadvantages as well. It is a colourless liquid, with vapours slightly heavier than air [268]. It has a relatively low boiling point of around 65 °C and a low flashpoint of 9.7 °C [436]. Its auto-ignition temperature lies at 455 °C and all combined it is classified as a highly flammable liquid, yet non-explosive [268], [436]. Methanol is completely miscible in water and readily biodegradable, with a half-life of about 17 days [184], [436]. Even though it is unlikely to affect the environment, it does have effect on human health. It is toxic if inhaled, ingested or touched and causes damage to organs [268], [436].

A.3.3 LIQUID HYDROGEN

Hydrogen can be combusted or directly used in fuel cells [20]. It has a high gravimetric energy density but a very low volumetric energy density [16]. Hydrogen has no carbon content and can thus be emission-free when used in a fuel cell. However, burning hydrogen may release NO_x [20]. Hydrogen is an unscented, tasteless, non-toxic and invisible gas [437], [438]. It is also explosive, with a flammability range of 4 to 75% when mixed with air and an autoignition temperature of 500 °C [437]. Hydrogen may also cause embrittlement of materials [439]. Liquid hydrogen is kept at temperatures between 13.8 K and 33.2 K [16]. Hydrogen is classified as an extremely flammable gas, but is not toxic or corrosive [438]. When liquid hydrogen is released, it dissipates quickly, although it can freeze its surrounding area [184].

A.3.4 MARINE DIESEL OIL

Marine diesel oil (MDO) is a relatively light fuel oil. It is used especially in smaller vessels, auxiliary engines or emission reduction zones. It has a lower sulphur content than heavy fuel oil (HFO). In this research, we will mainly use MDO to compare. MDO (also known as No. 4 Fuel oil or Low Sulfur No. 4 Fuel oil) is a blend of several fuel oils and information can be conflicting [440], [441], [442]. We will use the blend as defined by BP [442]. MDO is a fluid at room temperature. As the exact composition of the blend differs, exact boiling and flash points are not given. However, the flash point should always be higher than 56 °C, and the autoignition temperature is higher than 225 °C, with a boiling point of above 462 °C [442] All combined, it is a flammable liquid and vapou [442]. MDO has effects on human health; it is harmful if inhaled, causes skin and eye irritation and should not be ingested. It may also cause drowsiness or cancer and possibly affect the unborn child [442]. The substance is not soluble in water and very toxic to aquatic life with long lasting effects [442].

B

ONGOING HYDROGEN CARRIER PROJECTS AND THEIR MARITIME RELEVANCE

This section gives an overview of ongoing and finished projects that use hydrogen carriers.Their relevance, potential limitations and future opportunities are also discussed.

B.1 METAL HYDRIDE FOR THE ROSS BARLOW CHANNEL BOAT

Metal hydrides, such as the one used in the Ross Barlow Channel boat are very suitable for these kinds of boats; boats that have rather short distances each year (≤1000km) at low speeds (≤5km/h). The Ross Barlow Channel Boat is 18 metres long and uses an $MgZn_2$ type metal hydride based on $TiMn_2$ [82]. Batteries are insufficient because these boats are not used often enough to avoid discharging [82]. As metal hydrides do not discharge over time and are safe, produce pure hydrogen and have a silent and emission-free operation, they have been used in this channel boat [82]. However, their practical energy density (≤2%) becomes a problem when larger distances need to be covered. Additionally, because the charging of the boat is slow (taking 2.5h to store 4kg of hydrogen), charging very often is not possible [82]. So metal hydrides are mainly suitable for boats that do not have to go far and operate too infrequently to use batteries or boats that need a bit more than batteries can deliver. It can be seen mainly as a range extender for boats that would

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The content of this chapter is based on the following article:
E. S. van Rheenen, J. T. Padding, J. C. Slootweg, and K. Visser, "Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation," J. Marine Engineering and Technology, vol. 23, no. 3, pp. 166–183, 2023. doi:10.1080/20464177.2023.2282691

otherwise be using batteries. Thus, for the normal operation of most ships, metal hydrides are insufficient.

B.2 METAL HYDRIDES FOR AIR-INDEPENDENT PROPULSION SYSTEM FOR U212 SUBMARINES

The U212 and U214 submarines (approximately 1500 tonnes and 56 metres) use a metal hydride system, developed by TKMS, for their air-independent propulsion [55]. This system can also be installed during retrofit of older submarines [55]. Submarines are one of the largest applications using metal hydrides [55]. Just like the Ross Barlow Channel Boat, it was decided that the range of submarines should be larger than that of conventional diesel-electric submarines. The metal hydride based air-independent propulsion system has metal hydrides as a base power source, with batteries supplying peak powers and even recharging when little power is required [55]. Because of the difference between submarines and channel boats, the reason behind choosing metal hydrides is different. For the submarines a large range of air-independent propulsion systems was researched and metal hydrides are chosen due to their low volume and relative simplicity. As metal hydrides have such a low hydrogen weight percentage, they had to be positioned in such a way as not to destabilize the submarine [55]. So, metal hydride powered submarines have a larger air-independent range than battery-powered submarines. The range of the metal hydride powered submarine is, however, limited by the weight of the metal hydrides, thus if an even larger range is required, metal hydrides would not be suitable anymore.

B.3 METAL HYDRIDES FOR HYDROGEN IN HYBRID SYSTEM OF ZEUS

Zeus (zero emission ultimate ship) is a 25 meters long and 100 tonnes heavy ship with a hybrid power system. It has a diesel-electric generator, a fuel cell and a battery system for its propulsion system [443]. The hydrogen for the fuel cell is stored in metal hydrides. Again, similar to the previous two uses of metal hydrides, the metal hydrides are used to extend the range the ship can sail, with the batteries supplying peak powers. For longer journeys, the diesel generators will provide the power [443]. The main difference between submarines and Zeus is the goal of the use of hydrogen. For Zeus, the goal is to be able to sail without any emissions, whereas for U212 submarines it is to stay undetected. However, the outcome is the same type of energy system, with a diesel engine to supply main power for longer journeys and the metal hydride and battery combination to sail for shorter periods of time (of up to 6 hours for the Zeus) [443].

B.4 SODIUM BOROHYDRIDE ON SUBMARINES IN INDIA

An alternative to using metal hydrides for air-independent propulsion is SB. The Indian navy had been planning to start retrofitting Kalvari-class (67metres, 1600 tonnes) submarines with SB as a power source for air-independent propulsion before 2025 [444]. Prototypes using sodium borohydrides have been tested and meet design requirements [444]. The main advantage of SB over metal hydrides is their higher gravimetric energy density. The volumetric energy density of SB is theoretically higher, but in practice, it is more likely to be similar to metal hydrides because of the need for a dehydrogenation reactor. The overall SB system is also more complicated to use. As they have a very similar volumetric energy density, only the weight of the hydrogen storage is reduced, which can be promising. Thus, submarines that want to sail larger ranges than practically possible with metal hydrides because of the weight, can possibly use SB as a hydrogen carrier. It also opens up more possibilities for the use of hydrogen carriers, besides the current use on submarines, as weight is often an issue.

B.5 H2SHIPS PILOT SHIP NEO ORBIS ON SODIUM BOROHYDRIDE

An example of the use of SB for other ships will be a pilot project of the H2Ships project: the 19.5 metres long Neo Orbis. The Neo Orbis will be an inland port vessel with SB as a power source [445]. The keel has been laid in January 2023, however, several delays have caused the ship to only set sail in 2025 [446]. Because of the distances and speeds the Neo Orbis will be sailing, metal hydrides and batteries are not an option. However, similar to the metal hydride system, the SB system will also be supplemented with a battery for peak shaving [445]. As the Neo Orbis will be operating in the harbour of Amsterdam and its adjacent areas, a safe and emission-free operation is important. This pilot project aims to demonstrate the feasibility of hydrogen in general, but also the use of hydrogen carriers such as SB as a safe storage of hydrogen.

B.6 SODIUM BOROHYDRIDE UAV

For unmanned aerial vehicles (UAV), weight is of utmost importance, which limits the use of lithium batteries [423, 447]. The high energy density combined with the safe handling makes SB a promising storage method for UAVs as well [423, 447]. An additional advantage is not having to control the temperature or pressure, which is not the case for pressurized or liquid hydrogen [423, 447]. Because of this, there is quite some research on SB as hydrogen supplier for UAVs. Some studies use acids [423], instead of catalysts, to gain more control and speed up the process. It is also said that use of catalysts may cause an unsteady flow of hydrogen [448], however other studies do not suggest this [447]. Next to catalysts, to reduce onboard required space, volume exchange tanks have been tested, which remained stable during the flight [449]. So, the works on using SB to store hydrogen is interesting, because of the system integration and volume and weight limitations. Unfortunately, because of the complex and heavy and bulky hydrogen release process, SB is not commercially used for hydrogen storage on UAVs [449]. Thus, additional research into the release mechanism and the dehydrogenation reactor is required.

B.7 SH2IPDRIVE

Contrary to the other projects, which are all rather concrete, the SH2IPDRIVE project is still very much in the research phase regarding hydrogen carriers. Research on hydrogen carriers within SH2IPDRIVE mainly focuses on SB, particularly on the dehydrogenation process, regeneration process and handling process of this substance. A second point of research within the hydrogen carrier group is the development of a new LOHC by Voyex [315]. The third and final point of research is on the integration of these two hydrogen carriers within ships. Results of the SH2IPDRIVE project are expected in the coming years. The project plan foresees application of borohydride and LOHC technology in a modular unit, to be placed on ships or other platforms.

B.8 HYDROGENIOUS AND ALMA CLEAN POWER PILOT PROJECT WITH LOHC AND SOFC SYSTEM

Hydrogenious is a company that has developed a hydrogen oil, based on benzyl toluene. As hydrogen release from benzyl toluene and other LOHCs is endothermic, they are planning to integrate the LOHC system with a solid oxide fuel cell [72]. Alma Clean Power will provide the SOFC. The 100kW integrated system pilot will be tested on board the Edda Ferd, an offshore supply vessel [72]. The Edda Ferd is a ship which already has different types of tanks for storage of liquids like marine gas oil, methanol and special products [450]. This is advantagious for the use of the LOHC onboard, as there is not only liquid tank space available, but also knowledge about other chemical substances than the conventional fuels. This pilot project will be interesting as it makes use of heat integration between an LOHC and SOFC, increasing the efficiency of the total system, which will give relevant data for the effective energy density of LOHCs in combination with SOFCs. Additionally the system will be tested out on the open seas, because the Edda Ferd is an offshore supply vessel. So, the behaviour of the dehydrogenation reactor under the different movements a ship is susceptible to on open seas will most likely provide very relevant information for reactor design.

B.9 HYDROSIL BY HYSILABS FOR LONG TERM STORAGE AND USE ON SHIPS

HySilabs has developed the organosilane HydroSil, a liquid, earth friendly molecule which releases hydrogen exothermically [451]. They promote HydroSil for onboard applications, long-term storage and green hydrogen transportation [452]. A 15kW release reactor should be finished soon and they aim for 10 large release systems and charging plants, as well as 100 smaller release systems and one massive charging plant by 2030 [451].

B.10 ELECTRIQ GLOBAL

Electriq Global is a company using KB as a hydrogen carrier. They have already produced a pilot power plant, which demonstrates the use of KB as a hydrogen supplier for a crane [453]. Electriq Global aims to produce KB in large quantities starting in 2025 [453]. It is currently unclear where the powder will be used and how it will be regenerated, but using KB as a hydrogen carrier to fuel a ship is not disregarded.

LIST OF PUBLICATIONS

JOURNAL PUBLICATIONS

1. E. S. van Rheenen, J. T. Padding, J. C. Slootweg, and K. Visser, "Hydrogen carriers for zero-emission ship propulsion using PEM fuel cells: an evaluation," J. Marine Engineering and Technology, vol. 23, no. 3, pp. 166–183, 2023. doi:10.1080/20464177.2023.2282691
   Awarded with IMaRESTs Denny Medal
2. E. S. van Rheenen, E. Scheffers, J. Zwaginga, and K. Visser, "Hazard Identification of Hydrogen-Based Alternative Fuels Onboard Ships," Sustainability, vol. 15, no. 24, 2023, Art. no. 16818. doi:10.3390/su152416818
3. E. S. van Rheenen, J. T. Padding, A. A. Kana, and K. Visser, "Comparative energy analysis of hydrogen carriers as energy source on ships," J. Marine Engineering and Technology, 2025. doi:10.1080/20464177.2024.2448057
4. E. S. van Rheenen, A. A. Kana, K. Visser, and J. T. Padding, "Energy and Power Density as Key Metrics for Assessing Hydrogen Carriers as Alternative Fuels in Maritime Applications," under review at Energy Conversion and Management: X, 2025
5. E.S. van Rheenen, K. Visser, A.A. Kana, and O.E. Popa, "A Value-Conflict Design Approach to Evaluating Hydrogen Carriers for Maritime Use: Safety and Sustainability in Focus," under review at Maritime and Transport Research, 2025

CONFERENCES

1. E. S. van Rheenen, J. T. Padding, A. A. Kana, and K. Visser, "A review of the potential of hydrogen carriers for zero emission, low signature ship propulsion systems," in Proceedings of the International Naval Engineering Conference and Exhibition (INEC), IMarEST, Delft, the Netherlands, 2022. doi: 10.24868/10649

2. E. S. van Rheenen, E. Scheffers, J. Zwaginga, and K. Visser, “Hazard Identification of Hydrogen-Based Alternative Fuels Onboard Ships,” presented at the World Conference on Transport Research (WCTR), Montreal, Canada, 2023.
3. E. S. van Rheenen, J. T. Padding, and K. Visser, “A 0D Model for the Comparative Analysis of Hydrogen Carriers in Ship’s Integrated Energy Systems,” Proceedings of the 4th International Conference on Modelling and Optimisation of Ship Energy Systems (MOSES), Delft, the Netherlands, 2024. doi: https://doi.org/10.59490/moses.2023.669
4. E.S. van Rheenen, “Integration of hydrogen carriers as alternative power source onboard ships,” presented at Ephyc, Ghent, Belgium, 2024.
5. E. S. van Rheenen, J. T. Padding, A. A. Kana, and K. Visser, “Ship system design changes for the transition to hydrogen carriers,” in Proceedings of the 15th International Marine Design Conference (IMDC), Amsterdam, the Netherlands, 2024. doi: 10.59490/imdc.2024.894
6. E. S. van Rheenen, J. P. K. W. Frankemölle, and E. L. Scheffers, “Nuclear fusion as unlimited power source for ships,” in Proceedings of the 15th International Marine Design Conference (IMDC), Amsterdam, the Netherlands, 2024. doi: 10.59490/imdc.2024.880
7. E. S. van Rheenen, A. A. Kana, J. T. Padding, and K. Visser, “Solid hydrogen carriers as an Alternative Fuel and Impact Damper,” in Proceedings of the International Naval Engineering Conference (INEC), IMarEST, Liverpool, United Kingdom, 2024. doi: 10.24868/11165
   (Awarded with IMarEST’s Patron’s Award)
8. E. S. van Rheenen, K. Visser, A. A. Kana, and J. T. Padding, “Spill Behaviour of Hydrogen Carriers as Alternative Fuels for Ships,” in Proceedings of the 10th World Congress on Civil, Structural, and Environmental Engineering (CSEE), Avestia Publishing, Barcelona, Spain, 2025. doi: 10.11159/iceptp25.123
9. E.S. van Rheenen, C.L. Löffler, A.A. Kana, J.T. Padding, and K. Visser, “Integrating Safety Science into the design of future ships”, presented at Practical Design of Ships and other Floating Structures (PRADS), Ann Arbor, MI, USA, 2025. doi: 10.5281/zenodo.17305769.

NON-SCIENTIFIC PUBLICATIONS

NON-SCIENTIFIC ARTICLES

1. E.S. van Rheenen, “Low-emission, hydrogen-based, safe alternative fuels”, SWZ Maritime (2023)
2. Co-author in: Marcel van Benten, Timon Kopka en Annabel Broer, "How 11 Researchers Power Hydrogen in Maritime", SWZ Maritime (2025)

INVITED TALKS

1. E.S. van Rheenen, "Hydrogen carriers as a safe alternative fuel", presented at the KNVTS Lustrum Symposium, May 2023
2. E.S. van Rheenen, "Ship System Integration Research of Hydrogen Carriers", presented at the SH2IPDRIVE Hydrogen Carrier Seminar, Delft 2024
3. Panel Member at Symposium PartnerSHIP – From Tideman to Dutch Naval Design, 2025
4. E.S. van Rheenen, "Hydrogen-based alternative fuels for ships", presented at the EIRES Energy day, 2025

CURRICULUM VITAE

Erin van Rheenen was born on December 9th 1996, in Zeist, the Netherlands. She started high school at the Gymnasium Apeldoorn in 2008, in Apeldoorn and continued at the Baudartius Lyceum in Zutphen. During her high school years, she spent a year abroad at the Tikkurilan Lukio in Vantaa, Finland, and lived with a host family. She obtained her VWO degree from the Baudartius Lyceum in Zutphen in 2015. She continued her studies with a Bachelor's degree in Mechanical Engineering at UTwente, where she graduated with honours by following the specialised honours mathematics track. She spent several months in Norway to pursue a minor at the University of Stavanger. Her bachelor's thesis was on heat flows in a microbrewery, and she obtained her diploma in 2018. She moved to Eindhoven to continue her education at Eindhoven University of Technology. She completed a double degree in mechanical engineering (specialising in power and flow) and science and technology of nuclear fusion. During her master's program, she returned to Finland to complete an internship at Aalto University in Espoo. She obtained her master's degree in 2021. In 2022, she began her PhD at Delft University of Technology in the Ship Design, Production, and Operation group of the Maritime and Transport Technology section, within the Mechanical Engineering department. During her PhD, she became part of the Diversity & Inclusivity group of MTT. She also initiated a series of SH2IPDRIVE meetings at TU Delft to ensure the research at TU Delft remained aligned. In the meantime, she was an active volunteer at her local scout group, helping the Girl Scouts grow from 8 to 24 members. She also volunteered during elections at the local polling station, alongside her buddy Maud, who has a physical and mental disability, for Stichting Prokkel. Her research topic included understanding, integrating, and analysing the technological, safety, and sustainability aspects of alternative fuels, with a focus on hydrogen carriers, which led to this thesis.

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"Now I'm sitting here before the fire
The empty room, the forest choir
The flames have cooled, don't get any higher
They've withered now, they've gone
But I'm steady thinking, my way is clear
And I know what I will do tomorrow"
— Scrum, *Caledonia*

This thesis is the result of several years of research into the broadness of alternative fuels on ships. Now that I am at the end, it is time for the next chapter, but not before looking back at those who supported me in the past years.

First of all, I would like to thank Klaas. Without you, Klaas, none of this would have been possible. You have guided me through the years and helped me grow. You were not discouraged by my (small) obsession with the Titanic, but supported me in adding safety to my thesis. Your supervision, but perhaps even more importantly, your enthusiasm, have kept my spirits high. Your proverb of 'perfect is de vijand van goed genoeg' is something I will remember during the rest of my life. It is only fitting that the only personal figure in this thesis would be figure B.1.

Figure B.1: Klaas and Erin in Liverpool; registration port of the Titanic, homeplace of the Beatles and conference location of INEC 2024

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