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Review of green hydrogen technologies application in maritime transport

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ABSTRACT

Maritime transport contributes 90% to the international trade. However, it still relies heavily on fossil fuels to secure its energy needs, hence, emitting greenhouse gases. Consequently, the need for sustainable and clean fuel is crucial. This article reviews the possible shipboard methods for green hydrogen production, its storage and consumption by various marine propulsion systems. Solar and wind-based hydrogen production methods on board ships are bounded by their limited availability during the day. While recovery energy requires only a modification of the propulsion system to benefit from the energy excess and produce green hydrogen. The use of ammonia as hydrogen medium storage and hydrogen solid storage are promising options due to their matching characteristics to hydrogen properties. Internal combustion engines are widely used in maritime transport and are appropriate for fueling with hydrogen. Finally, life-cycle assessment studies demonstrate the benign environmental impact of green hydrogen despite its expensiveness.

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KEYWORDS
Green hydrogen production chain; ships; internal combustion engine; fuel cell; LCA

Introduction

Sea transportation has many advantages (e.g., operational flexibility, reliability, lower cost, and energy-efficiency) over other forms of transport, making it an important pillar of the international economy (IEA 2021; UNCTAD 2017). Furthermore, different studies and reports have confirmed that the maritime transport consists of around 93,000 ships of the world commercial fleet, thus contributing to a rise of 150% in freight transport since 1990 as well as the sharing of up to 90% of the world trade (Baldi et al. 2020; Deniz and Zincir 2016; UNCTAD 2017). The propulsion of 95% of the civil ships is secured by diesel motors (Yuan et al. 2020). Hence, causing the emission of around 2.9% of carbon dioxide (CO_2) in 2018 (International Maritime Organization (2020); Commission 2022) which is expected to increase to about 12–18% by 2050 (Buhaug et al. 2009; Smith et al. 2014; Yang and Zhang 2019; Yuan et al. 2020), while the global emission of nitrogen oxides (NO_x) and sulfur oxides (SO_x) has already reached 15% and 13%, respectively, in 2012 (Fan et al. 2018; Inal and Deniz 2020). Consequently, despite the economic advantages of sea transportation, it is responsible for climate change and global warming, which are not only affecting the human health but also the fauna and flora (Alnes, Eriksen, and Vartdal 2017; Nuchturee, Tie, and Xia 2020). Researchers such as (Chen et al. 2021; Kamil et al. 2022) have reported in their studies that ships account for about 70% of the emissions at a distance of less than 400 km from the coast.

Since 2011, the International Maritime Organization (IMO) has adopted and published various energy-efficiency restrictions and strategies in order to force the maritime industry to radically reduce its greenhouse gases (GHG) emissions. These measures are reflected in numerous regulations such as the International Convention for the Prevention of Pollution from Ships (MARPOL) (Geertsma et al. 2017; Smith et al. 2014; Moreno-Gutiérrez et al. 2019; Ling-Chin and Roskilly 2016; Smith et al. 2014). The Ship Energy Efficiency Management Plan (SEEMP) and the Energy Efficiency Design Index (EEDI) which became effective in 2013 form parts of the Annex VI of MARPOL to control ships' effectiveness (Ling-Chin and Roskilly 2016; Moreno-Gutiérrez et al. 2019; Smith et al. 2014). The calculation and validation of EEDI as well as the SEEMP elaboration guidelines are published independently.

The IMO has adopted a new Resolution MEPC.304(72), on the 13 of April 2018, emphasizing the obligations of the strategies taken as they initially aim to minimize the carbon intensity brought by the international navigation activity by 40% on the horizon of 2030 and reach 70% by 2050 compared to a 2008 benchmark, as well as reducing the absolute GHG emissions by half by 2050 with the view to completely eliminate them (IEA 2021; IMO, International Maritime Organization 2018). The IMO has warned of the possibility that by 2050 the GHG emissions will reach 250% if there is a lack of policy mechanisms to implement serious and quick actions to achieve the Paris Agreement aims (Smith et al. 2014; IEA 2020). Practically, the IEA reported that in 2019, there was no use of zero or low-carbon fuels for marine transportation, while it is intended to reach at least 3% of the total energy consumption by 2030 and rise to the third of it on the horizon of 2050 (IEA 2020).

As part of the measures taken to cut off the emissions, the IMO outlined, on the 1st of January 2020, new SO_x limit regulations known as IMO 2020. This regulation became

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effective and was amended to the annex VI of the MARPOL on the 1st of March 2020. The "IMO 2020" requires all ships operating outside designated emission control areas (ECAS), to use fuel oils with a sulfur content not exceeding 0.50% m/m (mass by mass) (seven times lower than the previous limit of 3.50% m/m). In addition, ships operating in ECAS are already subject to a strict limit of 0.10% m/m. These measures are expected to significantly reduce global SO_x emissions. On the other hand, in order to force ships to comply strictly with IMO regulations regarding SOx emissions, the Marine Environment Protection Committee (MEPC 78) has designated the entire Mediterranean Sea as part of the Emission Control Area in 2022 ((IMO) 2020).

On the 1st of November 2022, the IMO added another amendment to the MARPOL Annex VI by implementing the Energy Efficiency Existing Ship Index (EEXI) and the Carbon Intensity Indicator (CII) certification (IMO, International Maritime Organization 2022b). These two requirements will enter into force on the 1st of January 2023 (Czermański et al. 2022; IMO, International Maritime Organization 2022c). The EEXI is a mandatory indicator for all ships to evaluate their energy efficiency and ensure that they meet the minimum energy efficiency standards. The data collected will be used to initiate the first annual reporting operational CII that is expected to be completed in 2023 allowing the CII ratings to be determined and given in 2024 (IMO, International Maritime Organization 2022a).

The marine industries have been engaged in the IMO restrictions by adopting efficient measures and applying innovative technologies in order to improve their existing energy systems while reducing their emissions part. Nevertheless, these actions seem inefficient and insufficient, and it is necessary to switch to free-carbon fuels to reach the objectives on time (Nuchturee, Tie, and Xia 2020). According to McKinlay et al. (McKinlay, Turnock, and Hudson 2020), heavy fuel oil (HFO) and liquefied natural gas (LNG) are the most common marine fuels. They are mature and economically advantageous. However, although LNG is a clean fuel compared to HFO (Zhuo and Wang 2022), the methane leakage of LNG during the transportation and midstream storage stages is still highly environmentally risky (Jiaxin, Liu, and Sun 2021). Madsen et al. (Madsen et al. 2020) specified in a recent study that even a 50% reduction of vessels using diesel as fuel will not solve the emissions problem, and they encourage a total transition from fossil-fuel alternatives. Consequently, a new eco-friendly and sustainable fuel and energy carrier for marine transportation is instantly required (Acar and Dincer 2014; Yuan et al. 2020).

Among the existing renewable energy sources so far, solar and wind power are considered to be the most environmentally friendly to deal with GHG emissions for marine use (Yuan et al. 2020). However, these renewables still have limits and cannot be used for all vessel types (Diab, Lan, and Ali 2016). For instance, solar energy is bounded by the presence of solar radiation (which is not available all day and every day), as well as by the hull structure that cannot carry the entire installation, while wind energy is limited by wind direction and strength (Diab, Lan, and Ali 2016; Nasirudin, Chao, and Ketut Aria Pria Utama 2017; Nuchturee, Tie, and Xia 2020; Yilmaz, Ozturk, and Selbas 2020). These disadvantages make it difficult to rely only on these renewables without the recourse to other complementary energy systems to meet all ships' energy needs (Nuchturee, Tie, and Xia 2020). Thus, achieving an emission-free maritime transport requires a cost-effective hydrogen economy (Dincer 2012).

Except for being one of the most plentiful chemical elements in the universe (e.g., the sun is predominated by hydrogen) and earth (e.g., water and all living matter), hydrogen has neither smell nor color and is considered as the simplest and lightest element (Dincer and Zamfirescu 2017). Moreover, hydrogen can switch quickly from high to low pressures (Bethoux 2020) and has a higher energy density per mass, which varies between a lower heating value (LHV) 120 MJ/kg and a higher heating value (HHV) 142 MJ/kg (Abdalla et al. 2018; Gambou et al. 2022; Miranda 2019; Ozturk and Dincer 2020; Sarafraz, Christo, and Reza Safaei 2022). Besides being used widely in chemical industry as a base component, hydrogen is also used for heating and it takes advantage of serving as an energy storage system (for instance, it can be stored in empty salt caves, underground gas and oil fields, and industrial reservoirs) and is an attractive eco-friendly combustible of the future when produced from renewable feedstocks (Donkers 2020; Hosseini and Abdul Wahid 2016; Sarafraz, Christo, and Reza Safaei 2022).

In order to justify hydrogen use, researchers such as (Aydin and Dincer 2022; Chen and Siu Lee Lam 2022; Osman et al. 2021) have performed and reviewed life-cycle assessment (LCA) analysis as it is the only tool to measure and evaluate the overall environmental impacts of such an energy vector. Consequently, hydrogen energy has proved to have a bright future combating environmental problems (climate change and global warming) (Abuşoğlu et al. 2017; Yilmaz, Ozturk, and Selbas 2020). Electricity is still seriously considered when it comes to heat supply, carbon-free transport, and industrial decarbonization, wherefore, many countries account hydrogen as the only carbon-free energy vector (Abad and Dodds 2020; Dincer and Zamfirescu 2017).

There are multiple articles in the open literature reviewing the production, storage, and distribution methods of hydrogen. For instance, Dutta (Dutta 2014; Tashie-Lewis and Godfrey Nnabuife 2021) has reviewed the production, storage, and utilization of hydrogen as an energy resource. The review has focused on the sustainable hydrogen production and its lightweight storage. Dincer and Acar (Dincer and Acar 2015) have reviewed the different renewable and nonrenewable production methods of hydrogen in addition to a life-cycle assessment analysis of the different methods. In addition to the hydrogen production chain, Abdalla et al. (Abdalla et al. 2018) have highlighted the key challenges of hydrogen in their review to make the use of hydrogen as an alternative energy possible. Bernard et al. (Tashie-Lewis and Godfrey Nnabuife 2021) have also reviewed the different methods of the production chain of hydrogen in the hydrogen economy. They also generally spotlighted the different applications for the transport sector. Laurens et al. (Hoecke et al. 2021) have presented different methods of hydrogen production and storage for maritime applications, they focused on hydrogen storage as it is the most challenging part, especially for this sector. Osman et al. (Osman et al. 2021) have also reviewed recent studies (2019–2021) of hydrogen production methods (renewable and nonrenewable) as well as their LCA. Moreover, they presented an overview of the hydrogen utilization in different sectors including maritime transportation. Inal et al. (Inal, Zincir, and Dere 2022) focused on the role of hydrogen as a pathway for decarbonization for the maritime sector, they reviewed the different storage methods of hydrogen on board ships and hydrogen utilization, however with regard to the hydrogen production methods, they addressed only some methods (from hydrocarbon fuels, biomass, and electrolysis) and did not focus on those to be adopted on board ships. Ishaq et al. (Ishaq, Dincer, and Crawford 2022) also reviewed some methods of hydrogen production from renewables comparing them to the nonrenewable methods. They focused on the challenges and opportunities of such an alternative fuel.

All the aforementioned research studies have presented a general review of the hydrogen production chain, as well as their application in various sectors. However, to the extent knowledge of this article's authors, there is a lack of reviews of the different methods for maritime transport, especially on board methods. Consequently, the novelty of this article lies in carrying out an analysis of the scope of application of H_2 in the maritime sector by reviewing the different green hydrogen production chain methods (from its production to its consumption by the propulsion system) specifically on board ships. This review will serve as an accurate reference stating only the clean methods of the production chain of green hydrogen on board ships together with an LCA analysis.

This article will first define the different hydrogen classes currently known in the literature (section **2**), and subsequently, it will review the possible methods agreed so far by researchers for the production of green hydrogen (section **3**), its storage (section **4**) and its consumption (section **5**) to identify the appropriate methods of the production chain for on board bunkering. Finally, section **6** will review the life-cycle assessment of green hydrogen to ensure that it is an environmentally effective alternative fuel.

Hydrogen classes designation

Currently, the presence of natural hydrogen gas is still under investigation as many research studies such as (Abdalla et al. 2018; Bethoux 2020; Touili et al. 2020) still believe that hydrogen is always bounded with other molecules (e.g., water), cannot be easily found on earth and is not yet considered as a primary source of energy (Acar and Dincer 2014; Bethoux 2020). However, other research studies like (Bethoux 2020; Miranda 2019) have already proved the presence of natural hydrogen, which is first detected in subsea, then wells, and in craton formation in specific regions around the world (e.g., Mali, Brazil, California, Iceland, Russia, and Sicily). More wells are likely to be discovered all over the world under the hypothesis that in the old geological era, continents were tied to each other (Bethoux 2020). The origin of this natural hydrogen is not yet clear and understandable. Therefore, efforts and projects (e.g., sen4H2 launched in 2019 by the European Space Agency (ESA)) are highly encouraged to discover natural hydrogen roots, which can change the manner of using hydrogen from not only an energy vector but also a primary energy source; hence, reducing the hydrogen cost in comparison to when it is extracted (Bethoux 2020).

Pending confirmation and further investigation in this regard, it is commonly known that hydrogen is predominantly extracted from fossil fuels or produced using renewable and nuclear energy through different processes (Abdalla et al. 2018). Depending on the generation method adopted, there are mainly three different hydrogen classes, namely; **(i) Grey hydrogen**, also known as brown or black hydrogen, constitutes 95% of the hydrogen produced in the world (Taibi et al. 2018) and is extensively consumed by the industrial sector (Renssen 2020). Grey hydrogen is made from fossil fuels, particularly natural gas (NG) (49%), through a steam methane reforming (SMR) process based on a reaction between NG and steam, which subsequently produces hydrogen and CO_2 (Abdin et al. 2020; Furat, Anda, and Shafiullah 2020; Renssen 2020; Sarafraz et al. 2019). Although this process is the least CO_2 emitter, which makes it the most commonly used among other thermochemical processes, it is still harmful to the environment as each tonne of hydrogen produced is responsible for 9 tonnes of CO_2 emitted (Bethoux 2020; Donkers 2020). By decarbonizing gray hydrogen using carbon sequestration technologies (viz. Carbon Capture, and Storage (CCS)), we obtain the so-called **(ii) blue/low carbon hydrogen** (Bethoux 2020; Donkers 2020). Unlike gray and blue hydrogen, **(iii) Green hydrogen** low-carbon relies on renewable and sustainable feedstocks by using the electricity generated to split water into oxygen and hydrogen (Donkers 2020); hence, being the perfect gas and fuel of the future to tackle environmental problems and human toxicity.

In 2019, CertifHy launched the first European – Wide guarantee of origin scheme that consists of establishing two hydrogen labels (low carbon, not low carbon) taking into consideration the hydrogen origin (renewable, nonrenewable) and the GHG intensity (CertifHy 2019). The benchmark threshold limit corresponds to 91 gCO_2eq/MJH_2 for each MWh of hydrogen produced, which is the value of the best available technology (BAT) referring to the NG-SMR process (Noussan et al. 2021; Abad and Dodds 2020; CertifHy). As illustrated by the hydrogen labels according to CertifHy guarantee of the origin scheme in Figure 1, the first label (not low carbon) ties in with any hydrogen between the best available technology limit and the 60% (34.6 gCO_2eq/MJH_2) reduction of GHG intensity, while any other hydrogen below the 60% reduction is labeled as low-carbon (CertifHy 2019; Abad and Dodds 2020; Noussan et al. 2021).

Green hydrogen production methods

The detailed description of hydrogen production methods is widely presented in the open literature such as in research held by (Dincer 2012; Dincer and Zamfirescu 2017). Consequently, this section will only outline the possible production processes to be used in the maritime sector.

Figure 2 shows the two general paths needed to extract gH_2 through green energy sources (Dincer 2012). However, in the case of ships' refueling, the only viable on board sources are solar, wind, and waste recovery energy. Hence, we will

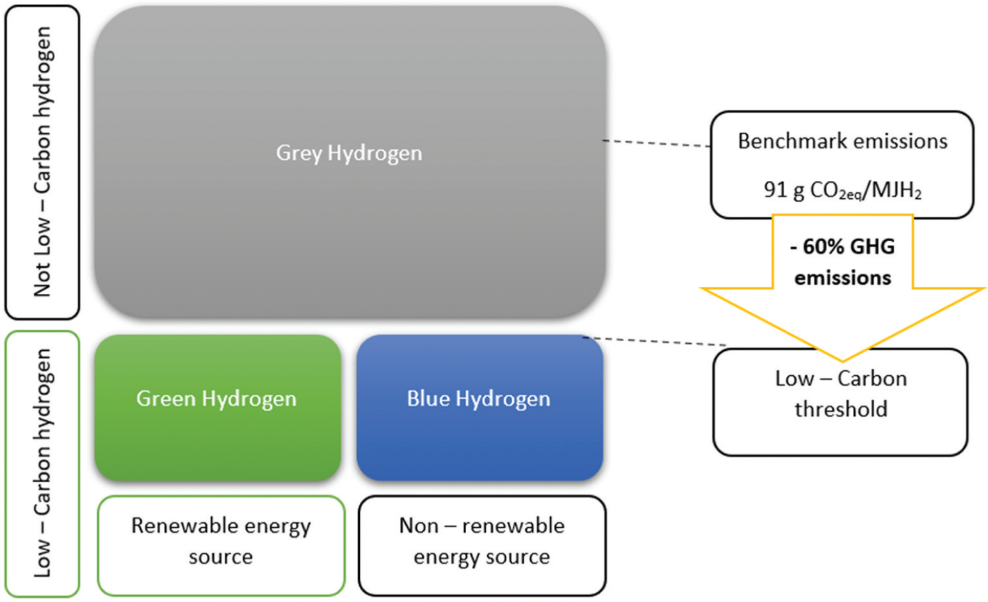

Figure 1. Hydrogen labels according to CertifHy guarantee of origin scheme (CertifHy 2021).

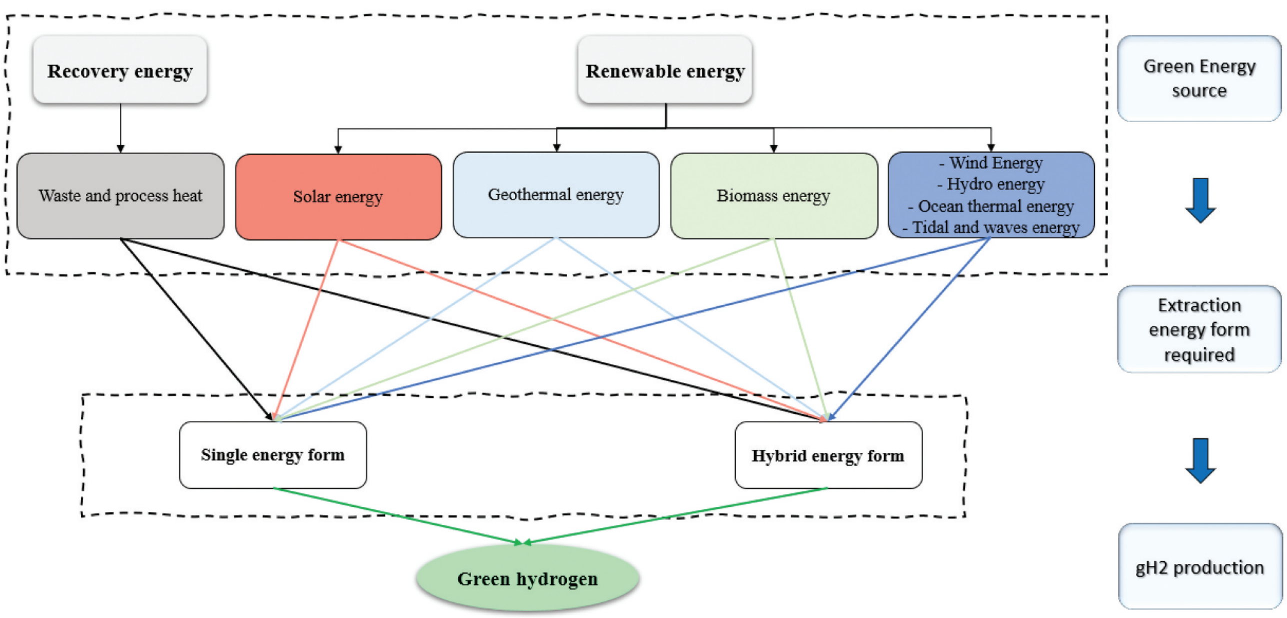

Figure 2. Extraction energy forms pathways for gH_2 production (Dincer 2012).

exclude the other energies from this review as outlined in Figure 3. Single energy forms refer to thermal, electrical, and photonic energy, while hybrid energy forms are a combination of these energies and are as follows: electrical + thermal, and electrical + photonic (Dincer 2012).

Energy sources on board ships

Before addressing the hydrogen production methods, this subsection is dedicated to briefly summarize the different possible energy sources (renewable, recovery) on board marine vessels.

Renewable energy sources on board ships

Solar and wind energy are the two possible sources to benefit from on board marine vessels. Solar energy can be used for photovoltaic (PV) generation systems by converting solar radiation into electricity, and the excess energy is stored in batteries (Pan et al. 2021). Due to the power generation limitation (100 W to few kW) of PV systems (caused by their low energy conversion efficiency and energy density), they can only be used as a main source in small and medium scale marine vessels, and an auxiliary source in large-scale vessels (Pan et al. 2021). PV systems can be used in three different modes: stand-alone, grid-connected, or hybrid. The stand-alone mode is widely used in most solar-powered marine

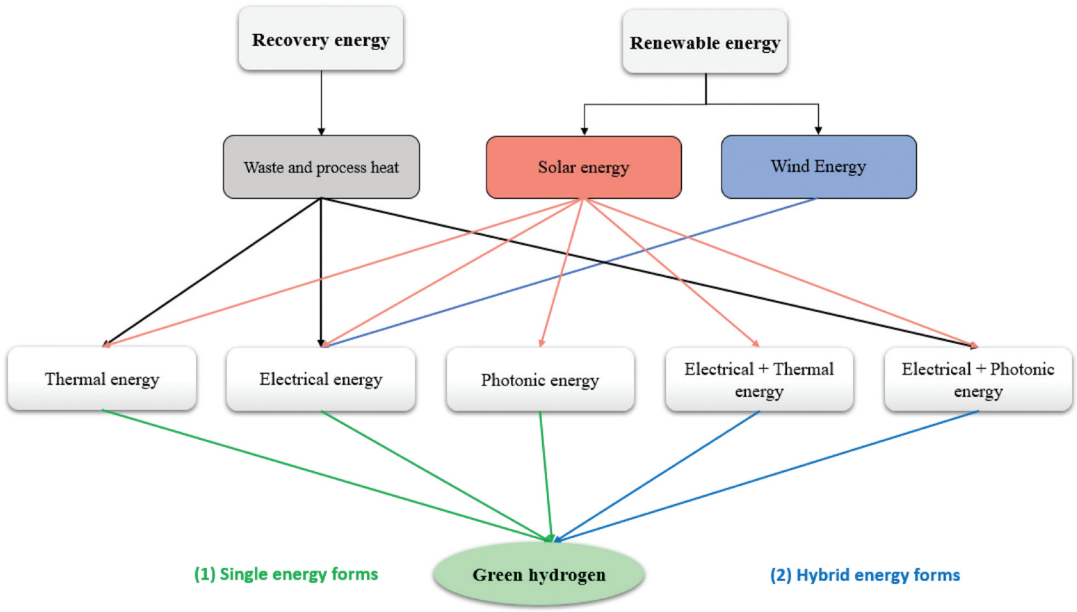

Figure 3. Single and hybrid extraction energy forms for gH_2 production on board vessels. (1) Single energy forms, (2) Hybrid energy forms.

vessels, although it is expensive and less efficient than the two other modes (Pan et al. 2021).

Unlike on-shore wind power systems, the offshore systems are more suitable for electricity generation as the friction affecting the wind speed is less and the energy losses are reduced (Pan et al. 2021; Talluri et al. 2016). There are mainly two methods to make use of the wind energy for the maritime sector: wind power generation and wind-assisted ship propulsion (WASP) (Pan et al. 2021). The wind power generation is governed by the choice of the wind turbine type, which is a crucial criterion. The vertical and horizontal axis wind turbines (respectively, VAWT and HAWT) are the two types of turbines used (Pan et al. 2021; Pope, Dincer, and Naterer 2010). VAWTs are more advantageous on board ships as they are cheap, stable, less complex, and easy to operate (Doulgeris et al. 2012; Pan et al. 2021). Ship sails in the WASP are distinguished from the traditional ones as they are connected and controlled by computers to assist the ship power generation. SAWP uses many different types of sails, such as: Skysails, softsails, Walker wingsails (aerofoils), flettner rotor sails, triangular sails, and rectangular sails (Pan et al. 2021). These types are widely defined in the open literature.

Recovery energy sources on board ships

Although the energy efficiency of marine engines can achieve 50%, the engine lost more than half of its energy to the environment in the form of heat during the fuel ignition process (Konur, Colpan, and Omur 2022; Senary et al. 2016; Singh and Pedersen 2016). The waste heat source depends on the ship type. For instance, the cold waste heat of LNG in the case of LNG-powered ships, and the waste heat from the cargo oil pump turbine (COPT), hydraulic-type cargo pump, or from the boiler/economizer in the case of tanker ships (Konur, Colpan, and Omur 2022, 2022). Another source of waste heat on board a ship is the auxiliary machinery, however the amount of the heat wasted is very low compared to the heat from the propulsion system (Konur, Colpan, and Omur 2022).

In general, the most attractive waste heat sources for an ocean-ongoing ship are the waste incinerator, the engine exhaust gas, the scavenge air (compressor outlet), and the engine-cooling water (Senary et al. 2016; Singh and Pedersen 2016). The temperature range of wasted heat of each source determines its quality (high, medium, and low) as shown in Table 1, hence its energy efficiency, which varies proportionally (Senary et al. 2016; Singh and Pedersen 2016).

The temperature range and its corresponding quality of the different waste heat sources are summarized in Table 2:

A single marine diesel engine wastes heat from different streams and each stream is characterized by a different quantity/quality (Singh and Pedersen 2016). The main engine stream sources with their corresponding waste heat quantity are presented in Table 3 (Singh and Pedersen 2016). A large amount of heat is dissipated from the exhaust gas, followed by the air cooler, jacket water, and lubricating oil, while only a small quantity is wasted as heat radiation.

Table 1. Heat energy quality and its corresponding temperature range (Singh and Pedersen 2016).

Quality	Temperature range (ºC)
High	≥650
Medium	232–649
Low	≤232

Table 2. The main waste heat source temperature range, and quality on board a ship (Singh and Pedersen 2016).

Waste heat source	Temperature (ºC)	Quality
Waste incinerator	850–1200	High
Engine exhaust gas	200–500	Medium
Scavenge air	100–160	Low
Engine cooling water	70–125	Low

Table 3. Waste heat sources from the engine streams (Mondejar et al. 2018; Singh and Pedersen 2016).

Waste heat source	Quantity (%)
Engine exhaust gas	25.5
Air cooler	16.5
Jacket water	5.2
Lubricating oil	2.9
Heat radiation	0.6

Table 4. WHRS applications (Senary et al. 2016; Shu et al. 2013).

Application	Temperature range (ºC)
Steam Rankine cycle	530
Organic Rankine cycle	65
Absorption and adsorption refrigeration	120–140 (steam)
Dehumidification	80–85 (hot water)

Although the waste incinerator has the highest temperature range (high quality), the amount of heat wasted is very low compared to all other waste heat sources (Singh and Pedersen 2016). The engine exhaust gas belongs to the second temperature range has the biggest amount (more than half) of the heat wasted among all other sources (Chunwee, Tam, and Wetenhall 2022; Singh and Pedersen 2016). The high quantity and the exergy content of the exhaust gas makes it an attractive waste heat source (Olgun et al. 2022; Singh and Pedersen 2016).

As presented in Table 4, depending on the temperature range of WHRS, they are commonly used for power generation, refrigeration, and water desalination (Senary et al. 2016).

Waste heat recovery systems (WHRS) are energy saving methods as they avoid the energy loss to the environment by making use of it to improve the efficiency of the ship and reduce emissions (Olaniyi and Prause 2020; Senary et al. 2016) and thus meeting the IMO regulations regarding the EEXI and CII ranking (Chunwee, Tam, and Wetenhall 2022). In addition, WHRS reduces the fuel consumption and the engine reliability remains constant despite increasing the recoverable energy quantity of the exhaust gas as it does not affect the thermal load (Konur, Colpan, and Omur 2022; Senary et al. 2016). Therefore, WHRS helps in both the economic and environmental improvements of the ship. There are mainly three different configurations for the WHRS (Singh and Pedersen 2016):

- Only from the exhaust gas;
- Combination of exhaust gas and high temperature (HT) cooling water; Or
- Combination of all waste heat sources; this latter configuration increases the waste heat recovery to the maximum.

Single extraction energy forms

Thermal energy

As previously mentioned, the possible paths to extract thermal energy on board are solar or recovery energy. As depicted in Figure 4, gH_2 is produced directly by a thermolysis process, or indirectly via sub-processes from thermo-catalysis and thermochemical processes.

Unlike the thermochemical water splitting process, thermolysis dissociates steam directly without the need for additional reactions (El-Shafie, Kambara, and Hayakawa 2019). However, this process requires high temperatures (above 2500°C) (Abdin et al. 2020; Dincer 2012; Dincer and Acar 2015; Roeb, Agrafiotis, and Sattler 2015). Effective separation membranes are not yet developed to operate at very high temperatures (Acar and Dincer 2018). Therefore, Baykara (Baykara 2004) conducted a solar thermolysis experiment and concluded that to effectively separate H_2 and O_2 and avoid an explosion, it is recommended to quickly cool them down to 1500–2000°C, then use a Palladium membrane (Abdin et al. 2020; Acar and Dincer 2018; Dincer and Acar 2015). The main drawbacks of thermolysis are its elements toxicity, the materials' corrosion,

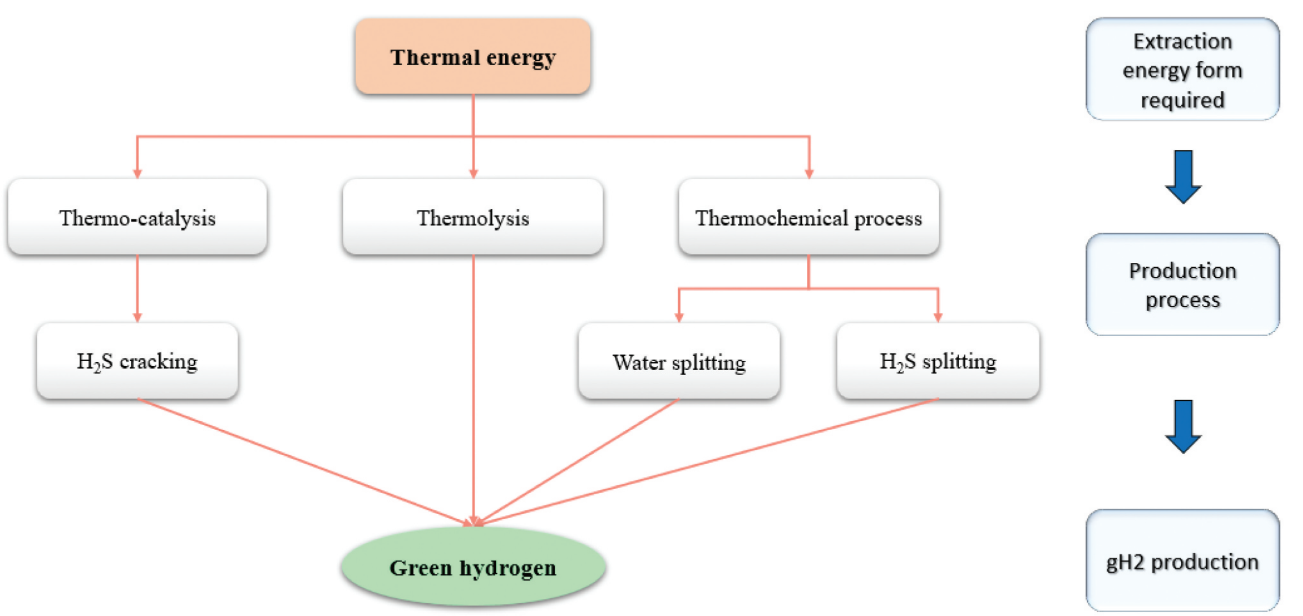

Figure 4. Green hydrogen production via thermal energy processes on board vessels.

and the production cost of hydrogen, which remains expensive (Acar and Dincer 2018; Dincer and Acar 2015; Nikolaidis and Poullikkas 2017).

Thermo-catalysis consists of cracking hydrogen sulfide (H_2S) either extracted from an industrial process or from the sea by using a high temperature powered from concentrated solar heat, industrial heat recovery, or flue gases. There is no commercial application of gH_2 production through this process yet (Dincer 2012).

Thermochemical water splitting (TCWS) is a process that dissociates water into H_2 and O_2 under closed multistep chemical cycles (Acar and Dincer 2018; Dincer and Zamfirescu 2016c; Dutta 2014). A thermal source (in our case, solar irradiation or energy recovered from flue gas) generates high-temperature heat driving the thermochemical cycles (Dincer 2012). To date, among at least 300 cycles, only few of them show promising results such as sulfur-iodine (S-I) and zinc-sulfur-iodine (Zn-S-I) cycles (Mehrpooya and Habibi 2020).

The main advantage of TCWS cycles lies in their dispensability of catalysts to start individual reactions during any step, their energy efficiency usually higher than 40%, all chemical elements used during the thermochemical cycle are recycled except water, which is the raw material for hydrogen production, as well as their operating temperatures (600–1200 K) (Acar and Dincer 2018; Dincer and Acar 2015). Nonetheless, TCWS still presents serious challenges in terms of H_2 production cost, corrosion, and their high-temperature needs (Acar and Dincer 2018; Mehrpooya and Habibi 2020).

Thermochemical hydrogen sulfide (H_2S) splitting is a process that still under R&D stage is based on using high-temperature heat from concentrated solar or industrial heat recovery in order to decompose H_2S into H_2 and sulfur (S) through cyclical reactions (Dincer 2012).

Electrical energy

Electrical energy is extracted mainly from renewable or recovery energy, resulting gH_2 production through electrolysis (Figure 5).

Electrolysis is the process of splitting water into H_2 and O_2 through an electrical energy (Aydin et al. 2021; Dincer and Zamfirescu 2016b; Nikolaidis and Poullikkas 2017; Proost 2020). The process is considered as "carbon-free" only when the electrical energy is extracted from eco-friendly resources, such as in our case; solar (photovoltaic power plants), autonomous or grid connected wind power plants, or thermodynamic cycles like Organic Rankine Cycle (ORC) powered by waste heat or flue gases (Dincer 2012; Dincer and Zamfirescu 2016b; Nikolaidis and Poullikkas 2017). The main reactions at the cell photocathode and photoanode are as follows (Abdalla et al. 2018; Nikolaidis and Poullikkas 2017):

$$\text{Anode}: 2p^{+} + H_2O \rightarrow 0.5O_2 + 2H^{+} \tag{1}$$

$$\text{Cathode}: 2e^{-} + 2H^{+} \rightarrow H_2 \tag{2}$$

$$\text{Global equation}: H_2O \rightarrow 0.5O_2 + H_2 \tag{3}$$

The high electrical energy needed during the electrolysis process and the high H_2 production cost resulting are behind

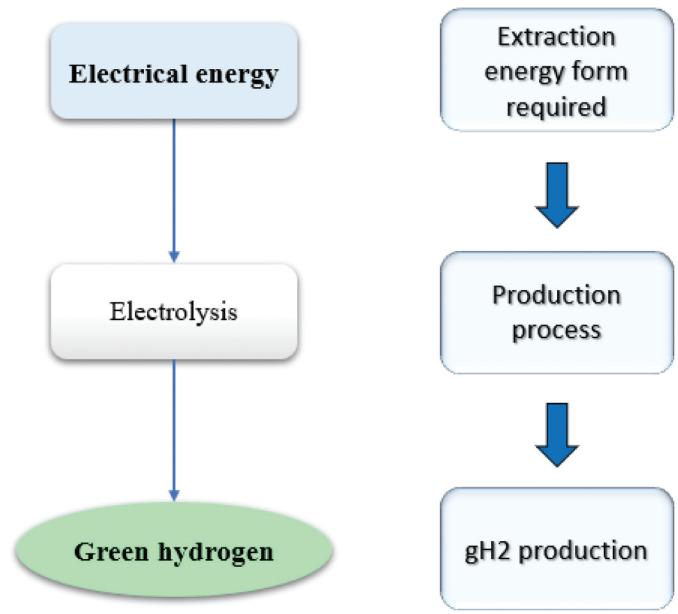

Figure 5. Green hydrogen production via electrical energy processes on board vessels.

the small quantity (4%) of hydrogen produced worldwide from this process, while the rest (96%) is still via fossil fuels (Nicita et al. 2020; Nikolaidis and Poullikkas 2017). However, electrolysis demonstrates a promising techno-economical future if governments encourage and subsidize it by applying carbon-tax policies (Abdin et al. 2020). Generally, the purity of H_2 from electrolysis is greater than 99% (Bethoux 2020; Ceran 2020; Dincer and Acar 2018; Dincer and Zamfirescu 2016b; Proost 2020).

There are three main low-temperature electrolysis technologies to be applied in the maritime sector according to the electrolyte used, namely, **(i)** Alkaline Electrolysis (AE), **(ii)** Direct Electrolysis of Seawater (DES), and **(iii)** Proton Exchange Membrane Electrolysis (PEME) (d'Amore-Domenech, Santiago, and Leo 2020).

(i) Alkaline electrolysis is the most developed technology and is considered as a key candidate for gH_2 large-scale production in the near future (Dincer and Acar 2018; d'Amore-Domenech, Santiago, and Leo 2020; Nicita et al. 2020). AE uses water at the cathode as feedstock and usually potassium hydroxide (KOH) or sodium hydroxide (NaOH) as a liquid electrolyte (Nicita et al. 2020; Dincer and Acar 2018; Dincer and Zamfirescu 2016b; d'Amore-Domenech, Santiago, and Leo 2020; Palhares, Vieira, and Damasceno 2018; Nikolaidis and Poullikkas 2017). The main characteristics of this technology are the operation temperature (60–90°C), the pressure is typically 30 bars, the efficiency varying between 50% and 65%, and a lifetime reaching 20 years (Dincer 2012; Dincer and Zamfirescu 2016b; d'Amore-Domenech, Santiago, and Leo 2020; Nicita et al. 2020). However, compared to other alternatives, the operation and maintenance of AE at sea is complicated as the electrolyte requires a periodic renewal due to the feed water impurities that pollute the electrolyte and plug the system (d'Amore-Domenech, Santiago, and Leo 2020).

(ii) Direct electrolysis of seawater is an AE process (Dincer and Zamfirescu 2016b) that directly uses seawater as both a feedstock and electrolyte (d'Amore-Domenech, Santiago, and Leo 2020). Thus, water purification and desalination are excluded from this process; however, the main disadvantage is the presence of chlorine (Cl_2), a toxic gas, that cannot be freed in the air (Dincer and Zamfirescu 2016b). DES operates at temperatures lower than 90°C (d'Amore-Domenech, Santiago, and Leo 2020). So far, this technology still does not have significant commercial applications (d'Amore-Domenech, Santiago, and Leo 2020).

(iii) Unlike AE, proton exchange membrane electrolysis introduces water into the anode and uses a solid polymer electrolyte (usually Nafion) (Buttler and Spliethoff 2018; Dincer and Acar 2018; d'Amore-Domenech, Santiago, and Leo 2020; Nicita et al. 2020; Nikolaidis and Poullikkas 2017). In addition, PEME is distinguished by its zero-gap engineering, which consists of gathering all required elements in a single Membrane-Electrode Assembly (MEA) optimizing space especially for small deck and requiring no maintenance; however, its components are the main reason for PEME's high cost (Donkers 2020; d'Amore-Domenech, Santiago, and Leo 2020). This technology operates at temperatures between 60°C and 80°C and a pressure up to 30 bars (d'Amore-Domenech, Santiago, and Leo 2020; Nicita et al. 2020). Compared to AE, PEME has a higher degradation rate, which affects its lifespan (d'Amore-Domenech, Santiago, and Leo 2020).

d'Amore-Domenech et al. (d'Amore-Domenech, Santiago, and Leo 2020) conducted different Multi-Criteria Decision-Making (MCDM) techniques such as Technique for Order of Preference by Similarity to Ideal Solution (TPOSIS), Simple Additive Weighting (SAW), Analytic Hierarchy Process (AHP), Choosing By Advantages (CBA), and Complex Proportional Assessment (COPRAS). The MCDM techniques ′ results (Figure 6) show that, among low-temperature electrolysis, PEME is the best technology for gH_2 production at sea followed by AE then DES.

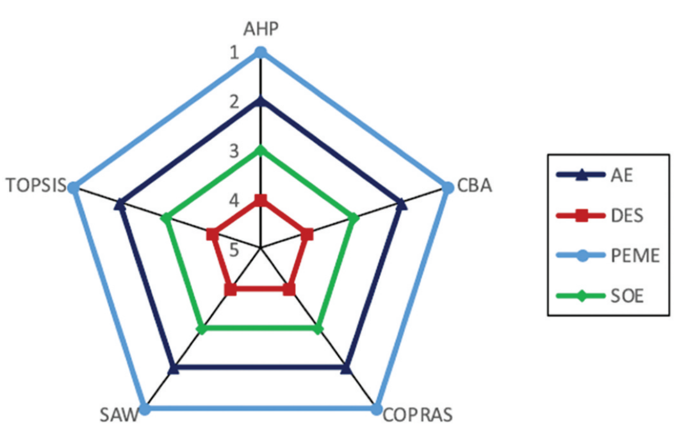

Figure 6. MCDM techniques applied on electrolysis technologies for maritime use (d'Amore-Domenech, Santiago, and Leo 2020).

Photonic energy

As shown in Figure 7 there are mainly three photonic energy-based production processes of gH_2, namely, PV-electrolysis, photocatalysis, and photo-electrochemical method.

PV-electrolysis consists of converting photonic energy to electricity through photovoltaic panels then to hydrogen via electrolysis (Acar and Dincer 2018; Dincer 2012). Although this H_2 production process still presents low efficiency with a cost at least 20 times higher than H_2 from fossil fuels, its efficiency is the highest among the other photonic-based processes (Acar and Dincer 2018; Dincer and Acar 2015).

Photocatalysis is one of the most environmentally benign methods for H_2 production (Aydin et al. 2021). This process does not require an intermediate electrical energy to convert photonic energy to hydrogen (Acar and Dincer 2018; Dincer and Acar 2015). In a recent review by (Abdin et al. 2020), they concluded that despite the fact that the photocatalysis process is still in the experimental phase, it already exhibits high efficiency with low cost compared to other H_2 production processes. Another disadvantage of this process lies in the recombination of excited electrons, which limits its performance (Aydin et al. 2021). Liu et al. (Liu et al. 2021) studied the different factors influencing hydrogen photoproduction and CO_2 photoreduction. Based on artificial intelligence (AI) analysis results, they concluded that the radiation intensity, the total organic carbon (TOC) concentration, and photocatalysts are the key parameters influencing the photocatalytic water splitting into hydrogen.

Photoelectrochemical (PEC) is one of the most renowned solar-based processes for water splitting, hence H_2 production (Dincer and Zamfirescu 2016d). However, this technology is still in early R&D stage (Dincer and Acar 2015) in order to improve its efficiency. There are four main PEC systems under investigation, two of them use powdered photoactive catalysts melted in water, while the other two use thin-film glass submerged in water (Acar and Dincer 2018). Some key features of PECs are their compactness, viz. the ability to incorporate together water electrolysis and solar absorption without any separation (Dincer 2012; Dincer and Acar 2015), and they can produce both energy carriers (electricity or hydrogen) (Dincer and Acar 2015).

According to Acar and Dincer (Acar and Dincer 2018), the main challenges of photonic-based hydrogen production processes are their low efficiency and high H_2 production cost. However, the development of advanced and innovative systems and materials will improve the efficiency/cost relationship in the near future (Acar and Dincer 2018; Dincer and Acar 2015). The production cost of hydrogen from PEC is 10 times more expensive than hydrogen from fossil fuel technologies (Dincer and Acar 2015).

Hybrid extraction energy form

Electrical + Thermal energy

The hybrid energy (electrical + thermal) is derived from solar and recovery energy. Green hydrogen is produced through two main processes as shown in Figure 8:

Unlike low-temperature electrolysis, high-temperature electrolysis consists of a solid oxide electrolysis cell (SOEC)

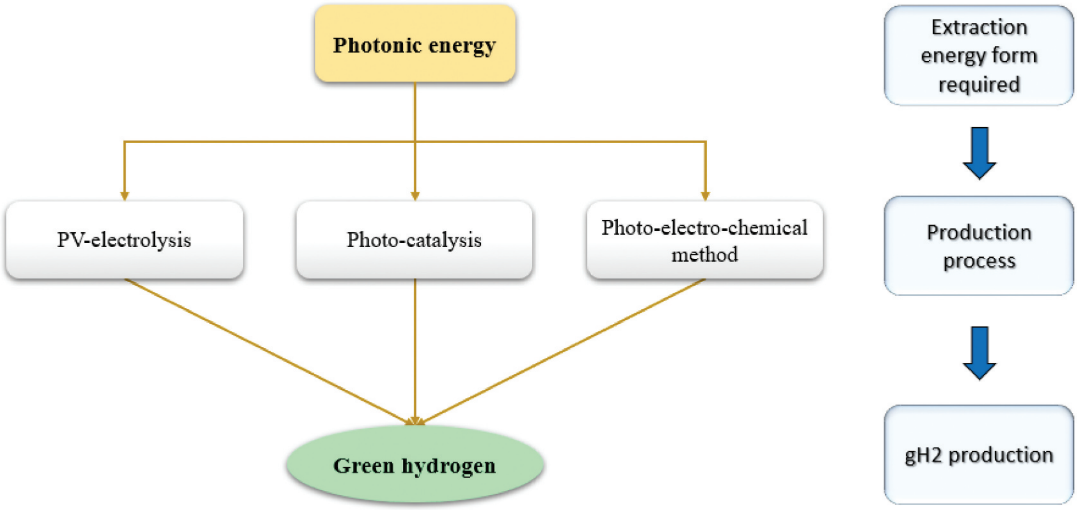

Figure 7. Green hydrogen production via photonic energy processes on board vessels.

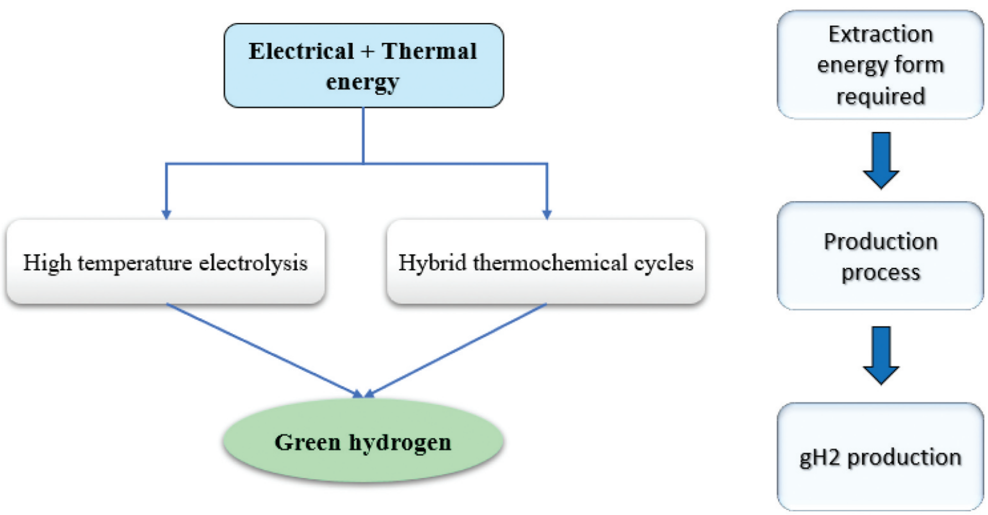

Figure 8. Green hydrogen production via electrical + thermal energy processes on board vessels.

using superheated steam as feedstock instead of water (d'Amore-Domenech, Santiago, and Leo 2020; Nikolaidis and Poullikkas 2017). Operating temperatures vary between 600 and 1000°C resulting in a high energy efficiency compared to other electrolysis technologies previously mentioned (Dincer and Acar 2018; d'Amore-Domenech, Santiago, and Leo 2020; Nicita et al. 2020). SOECs are able to generate electrolytic hydrogen on a large-scale (Dincer and Zamfirescu 2016b). The main challenge of using this technology at sea is the difficulty of finding high-temperature external sources to maintain a permanent operating temperature, which affects the system durability as well as the plant dynamics (Dincer and Acar 2018; d'Amore-Domenech, Santiago, and Leo 2020).

Unlike pure thermochemical cycles, hybrid thermochemical cycles require low temperatures (<1000°C) which expand gH_2 production materials and resources providing electrical and thermal energy needed (Dincer and Acar 2015). So far, the most recognized thermochemical cycles are Cu-Cl (Copper-Chlorine), HyS (hybrid sulfur), and Mg-Cl (Magnesium-Chlorine) (Dincer and Acar 2015; Dincer and Zamfirescu 2016c; El-Emam and Özcan 2019). These technologies are eco-friendly and characterized by their higher efficiency and exergy, among other hybrid alternatives as well as cost-effectiveness compared to fossil fuel and pure thermochemical processes (Dincer and Acar 2015; El-Emam and Özcan 2019).

Electrical +Photonic energy

A combination of an electrical-photonic energy extracted from solar results in the production of gH_2 through a photo-electrolysis process (Figure 9) (Dincer 2012). This process consists of a PEC composed of a semiconductor (solar energy absorption system) submerged in an electrolyte (water electrolysis system) (Abdalla et al. 2018). Water is considered as the only feedstock in this process (Dincer 2012; Nikolaidis and Poullikkas 2017). The cell absorbs solar photons and splits water into H_2 and O_2 via an electric field (Nikolaidis and Poullikkas 2017). Compared with other gH_2 production

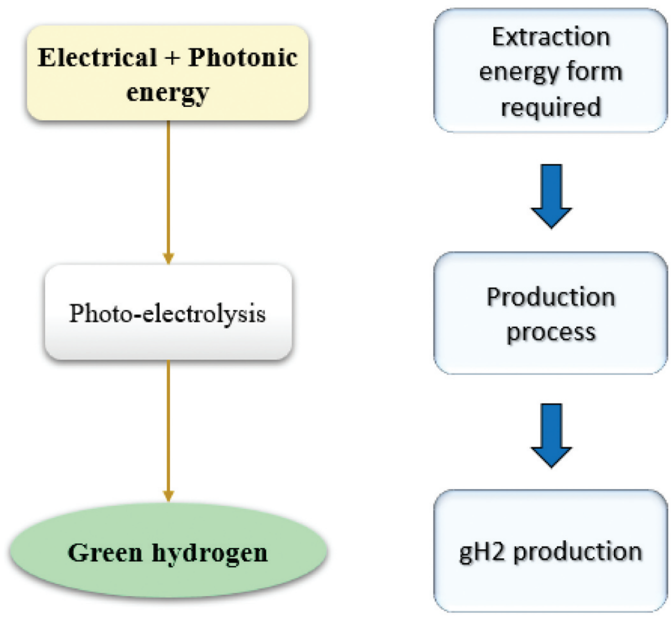

Figure 9. Green hydrogen production via electrical + photonic energy processes.

processes, photo-electrolysis has the most expensive hydrogen production cost (10.36 $/kg) and the lowest efficiency (0.06%) due to the ineffectiveness of the photocatalytic material (Abdalla et al. 2018; Nikolaidis and Poullikkas 2017).

Summary and conclusions of production methods

Table 5 summarizes the different possible methods to produce gH_2 on board marine transportation:

Figure 10 shows that, compared to the ideal case, electrolysis and hybrid thermochemical cycles rank the most energy-efficient technologies. While in terms of cost, thermochemical water splitting registers the highest rank followed by hybrid thermochemical cycles and electrolysis. However, processes derived from photonic and electrical-photonic energy have the lowest rank.

To date, few processes such as electrolysis and fossil fuel-based processes coupled with CCS are under investigation for the gH_2 production on board. Solar-based H_2 production processes are not 100% functional to produce gH_2 on board as the sun is not available all day, which will require storage, hence additional space. Meanwhile, wind-based processes depend on wind direction and strength. On the other hand, recovery energy consists simply of taking advantage of the energy excess to self-produce an environmentally benign hydrogen fuel (gH_2).

Green hydrogen storage methods

Storage is a fundamental stage in the hydrogen production chain (Dutta 2014; Lenivova 2020; McKinlay, Turnock, and Hudson 2020). Nevertheless, it presents challenges to be addressed expeditiously to transit toward an effective hydrogen economy (Abdalla et al. 2018; Dutta 2014; Gondal 2019;

Table 5. A summary of the main normalized gH_2 production methods selected for marine transportation (Dincer and Acar 2015).

Production process	Extraction energy	Feedstock	Green energy source	ExE	EE	Cost	Drawbacks	Benefits
Electrolysis	Electrical	Water	Recovery Solar Wind	2,50	5,30	7,34	• Expensive • Large-scale application critical challenge • Low system efficiency • Corrosion	• Emissions-free • Possibility of integration with FCs • Existing infrastructure
Thermolysis	Thermal	Water	Solar	4,00	5,00	6,12	• Corrosion • Elements' toxicity • Expensive • High temperatures	• Direct water decomposition
Thermochemical water splitting		Water	Recovery Solar	3,00	4,20	8,06	• Corrosion • Production cost • Need of high temperature	• Dispensability of catalysts • High energy efficiency • Elements' recyclability • Operation temperatures
PV-electrolysis	Photonic	Water	Solar	0,70	1,24	4,5	• Low efficiency • Expensive	• The highest photonic-based efficiency
Photo-catalysis		Water		0,10	0,20	5,19	• Maturity • Performance limitation	• Direct conversion from photonic energy to H2 • Low cost with high efficiency
Photo-electrochemical method		Water		0,15	0,70	0,00	• Low system efficiency • Power losses • Low volume production • Expensive materials and reactors	• Green • Low operation temperature
High temperature electrolysis	Electrical + Thermal	Water	Recovery Solar	2,60	2,90	5,54	• Durability • High-temperature need	• High energy efficiency • Large-scale application
Hybrid thermochemical cycles		Water		4,80	5,3	7,41	• An expensive hybrid option	• Low temperature comparing to pure thermochemical cycles • High efficiency • Cost-effective
Photo-electrolysis	Electrical + Photonic	Water	Solar	0,34	0,78	7,09	• Stability • Low efficiency • Expensive	NA
Ideal case				10	10	10		

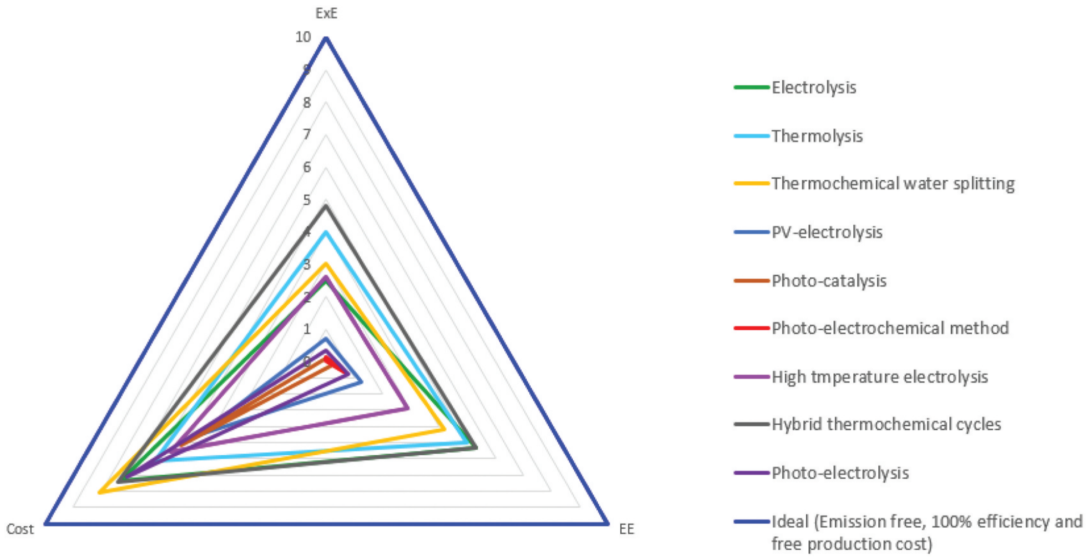

Figure 10. Standardised ranking comparison of H_2 production processes (Dincer and Acar 2015).

Qubeissi and El-Kharouf 2020; Rosen and Koohi-Fayegh 2016). In addition, if no serious precautions are taken, hydrogen presents serious risks (viz. flammability) when mixed with other substances (Atilhan et al. 2021; Dnv 2019; Furat, Anda, and Shafiullah 2020; Ríos 2020), especially in maritime use. Hydrogen is the lightest chemical element (Dincer and Zamfirescu 2016a, 2017; Rosen and Koohi-Fayegh 2016), it has the highest gravimetric energy density over other transportation fuels (viz. LNG, diesel, gasoline), however, it has the lowest volumetric density, which is the main reason behind its storage difficulties and costliness (Dincer and Zamfirescu 2016a; Dutta 2014; Gondal 2019; IAEA 2013; Lenivova 2020; Makridis 2017; McKinlay, Turnock, and Hudson 2020; Qubeissi and El-Kharouf 2020; Rosen and Koohi-Fayegh 2016). Depending on the storage methods and the fuel cargo needed, hydrogen requires huge tanks, developed storing materials, low temperatures, or high pressures (Dincer and Zamfirescu 2016a; IAEA 2013; Lenivova 2020; Makridis 2017; McKinlay, Turnock, and Hudson 2020; Qubeissi and El-Kharouf 2020; Rosen and Koohi-Fayegh 2016). Hydrogen is stored mainly according to three different states of matter: gas, liquid, or solid (Qubeissi and El-Kharouf 2020).

Gaseous storage

The gaseous state of hydrogen in nature eases its storage as a gas, however it imposes specific tanks particularly for marine storage purposes (McKinlay, Turnock, and Hudson 2020). Under ambient conditions, H_2 has a low volumetric density, which requires its compression before storage (Bethoux 2020). Compressed H_2 (CH_2) storage is the simplest and most commonly used method especially in refueling stations, mobile applications, and FC vehicles (Abdalla et al. 2018; Abdin et al. 2020; Lenivova 2020; Ogden et al. 2018; Rahul et al. 2012; Wang et al. 2021). CH_2 has already reached technology readiness levels (TRL) 8 to 9, which means that the system meets the performance requirements (completed, qualified, and proved) (Wang et al. 2021). According to Dincer and Zamfirescu (Dincer and Zamfirescu 2016a), the current technology development aims to increase the storage pressure of CH_2 from 30 MPa to 70 MPa and commercialize them in order to tote sufficient H_2 fuel (IAEA 2013). Although high-pressure cylinders are huge, they store only small quantities of H_2 and they are quite expensive (IAEA 2013; Korri 2018; McKinlay, Turnock, and Hudson 2020).

CH_2 can be stored in four different tank types (I, II, III, and IV), they vary mainly according to their weight and pressure resistance (Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017; IAEA 2013; Qubeissi and El-Kharouf 2020). Type IV is characterized by its lightweight (70% lighter than type I) and high-pressure resistance; however, it is costly (11$/liter) (Abdin et al. 2020; IAEA 2013; Qubeissi and El-Kharouf 2020). Thanks to the high-pressure resistance (35–70 MPa) of type III and IV, they are the best options for on-board hydrogen storage, however, safety as well as cost reduction must be taken into consideration (Bethoux 2020; IAEA 2013). For integration reasons, the on board storage at 70 MPa is adopted by the automotive industry despite its high cost (Bethoux 2020). In addition to the aforementioned storage tank types, a recent type (V) has been patented in 2014 which is characterized by having no liner (full composite); however, there are only few applications of this type due to its novelty (Hoecke et al. 2021). The working pressures of type V are estimated to be above 70 MPa (Hoecke et al. 2021).

Cryo-compressed H_2 (CcH_2) storage is a combination of CH_2 (at least 30 MPa) and liquified H_2 (20 K) (Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017; Julio et al. 2019a; Rivard, Trudeau, and Zaghib 2019). A cryo-compressed vessel is involved in the compressed hydrogen storage vessel; thanks to its design, it promises to increase the volumetric and gravimetric storage capacities at fixed volume and pressure while reducing costs and the H_2 boil-off rate, increasing the system

Table 6. Key metrics of CH_2, CcH_2, and LH_2 storage methods (Rivard, Trudeau, and Zaghib 2019; Wang et al. 2021).

Storage method	Temperature (K)	Pressure (Bar)	Volumetric energy density (kWh/l)
Compressed H_2	233–300	150–800	0.8 at 350 Bar and 1.4 at 700 Bar
Cryo-compressed H_2	33–77	150–350	2.6 at 38 K and 300 Bar
Liquid H_2	20–33	1–12.76	>2.3

safety as well as the storage density of the system (Abdalla et al. 2018; Julio et al. 2019a, 2019b; Rahul et al. 2012). The CcH_2 system has higher energy density compared to CH_2 storage and less energy losses than LH_2 as shown in Table 6 (Wang et al. 2021). The main limitation of this system is its strict insulation requirement (Wang et al. 2021). CcH_2 storage method is applied in large and medium scale as well as in international H_2 shipping (Wang et al. 2021).

Liquid storage

Liquefied H_2 (LH_2) is more advantageous than gaseous H_2 (GH_2) as it is characterized by a high energy storage and efficiency as well as a low weight (Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017; Qubeissi and El-Kharouf 2020). H_2 gas liquefaction increases its density to 70 kg/m^3 (Bethoux 2020; Rahul et al. 2012). Moreover, in order to reach a high purity level, hydrogen should be at its liquid state (IAEA 2013). Hydrogen liquefaction (cryogenic hydrogen) is reached at very low temperatures (20 K) (Abdalla et al. 2018; Abdin et al. 2020; Bethoux 2020; McKinlay, Turnock, and Hudson 2020; Rahul et al. 2012; Widera 2020). Hence, it requires expensive specific super-insulated tanks to endure the low temperature and an open storage system to meet the H_2 evaporation rate criteria (Abdalla et al. 2018; Dincer and Zamfirescu 2016a). The price per kg of hydrogen is exceeded by at least 30% due to the liquefaction (Dincer and Zamfirescu 2016a). However, the storage of huge quantities of LH_2 increases the system flexibility and reduces the storage cost (IAEA 2013). Commercial H_2 can be stored as a liquid in cylindrical or spherical cryogenic tanks (Qubeissi and El-Kharouf 2020). LH_2 is obtained mainly through three processes, namely, Helium – H_2 cycle, Precooled Linde – Helium process, and Claude process (Dincer and Zamfirescu 2016a). Although LH_2 attains an elevated mass–volume ratio (Fernández et al. 2020), one-third (~40%) of the energy input is lost in order to decrease the temperature beneath the critical point (33 K) (Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017; Fernández et al. 2020).

It is preferable to use LH_2 in transportation as it meets weight and volume requirements (IAEA 2013). For marine transportation, the bigger the ship, the bigger the fuel container needed (Wang et al. 2021). Unlike compressed gas, LH_2 reduces the fuel container size (for instance, at 150 bars, the volume is 6 times reduced) (Wang et al. 2021; Winnefeld et al. 2018). Nevertheless, due to the containers' thermal conductivity, LH_2 can only be used as a gas delivery medium for on-board storage (Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017). Practically, it has been proved that LH_2 cannot be stored for a long period of time and it is only devoted for small-scale applications requiring a low time constant (Abdin et al. 2020; Bethoux 2020).

H_2 liquefaction and LNG liquefaction are almost identical processes as they only differ in their critical refrigeration temperature (20 K and 113 K respectively) (Lenivova 2020). Therefore, despite the additional energy cost, vessels powered with LH_2 can also take advantage of the resulting boil-off issue from the difference between the ambient temperature and the low LH_2 temperature, by re-liquefying it (McKinlay, Turnock, and Hudson 2020; Wang et al. 2021). However, unlike LNG, LH_2 requires high safety restrictions as well as a high insulation (Lenivova 2020) which is the main reason behind the high cost of this technology, otherwise it would cost as much as LNG for vessels' refueling (Dnv 2018; Wang et al. 2021). LH_2 has the lowest storage price compared to compressed H_2 and CcH_2 (Wang et al. 2021). The volume of an LH_2 fuel storage tank on large commercial vessels would exceed 18,000 m^3 and 175,000 m^3 on an LNG of similar size (Wang et al. 2021). The data collected by (McKinlay, Turnock, and Hudson 2020) of long haul vessels sailing total 108 voyages over 38 months show that each ship voyage requires an energy of 9720 MWh maximum; hence, the volume needed to store LH_2 would exceed 6547 m^3 (Wang et al. 2021).

Fernández et al. (Fernández et al. 2017) studied three different H_2 storage systems (pressurized, cooled, and combined) on board LNG ships. Due to safety concerns, they concluded that the storage of combined H_2 is the best and cheapest method. Pressurized H_2 storage is excluded due to the high temperature and energy consumption demands, while the cooled H_2 storage requires high specific volume, both systems are risky for on board use.

Solid storage

One of the possible solid storages consists of absorbing and trapping H_2 in the crystalline structure of a metal hydride (MH) submitted to high pressures (Fernández et al. 2020; Rahul et al. 2012). Whether heating the MH or reducing its external pressure, it will release the H_2 stored (Fernández et al. 2020). This storage technology is characterized by its reliability as it increases the H_2 density with reasonable pressure and temperature without being hazardous (Fernández et al. 2020; Gkanas and Khzouz 2018; Qubeissi and El-Kharouf 2020). In addition, MH is a good H_2 fuel carrier in transport as it decreases the system volume and is cheap compared to LH_2 (Dvoynikov et al. 2021). However, considering the boil-off gas increase, storing H_2 in the MH is impractical inside LNG vessels (Fernández et al. 2020). Magnesium hydrides (MgH_2) and aluminum hydrides (AlH_3) are examples of MH used for H_2 storage. The kinetic desorption of AlH_3 as well as their high gravimetric and volumetric densities have recently encouraged their use for H_2 storage for FCs (Dincer and Zamfirescu 2016e). Magnesium-based films are also suitable for FC vehicles (Dutta 2014). MgH_2 are cheap, light, have high capacity, and their H_2 storage capacity is 7,6 wt% (Abdalla et al. 2018; Dutta 2014). The use of Mg in the auto industry is limited by its inactive kinetics (Dutta 2014). Unlike absorption systems, carrying adsorbed H_2 is risky despite its high storage density; this is because of the low volumetric and gravimetric H_2 densities compared to international regulations values (Fernández et al. 2020). Consequently, adsorption systems are ruled out from on board application (Fernández et al. 2020).

Chemical hydrides (e.g., ammonia-boron) depend on a physisorption and chemisorption processes to store high-density H_2, they are impractical due to the high temperature and energy activation requirements (Dincer and Zamfirescu 2016a; Rahul et al. 2012). Although liquid hydrides are a safe long-term H_2 storage alternative, the presence of chemicals inside cargo containers limits their safety and obstruct their on board use (Fernández et al. 2020). Hydrogen can also be stored in metal organic frameworks (MOF) via physisorption process (Abdalla et al. 2018; Abdin et al. 2020). They are adaptable nano-porous metals, and each MOF has a fixed pore size (Abdin et al. 2020; Rahul et al. 2012). This is an attractive technology as it provides larger areas for H_2 storage compared to other materials; it has high porosity, and the building blocks are changeable (Abdalla et al. 2018; Abdin et al. 2020; Rahul et al. 2012).

Hydrogen is stored in zeolites and glasses under high pressures and temperatures varying between 200°C and 400°C (Faye et al. 2017; Fernández et al. 2020). Zeolites and glasses are an expensive expanding technology that is still under development due to their narrow density storage (Fernández et al. 2020). This technology is unsuitable for on-board H_2 storage because of its large area requirement (Faye et al. 2017; Fernández et al. 2020).

The porous and lightweight characteristics of carbon nanotubes allow the adsorption of H2 under a pressure range (10–100 bars) and below ambient temperatures (Fernández et al. 2020). However, they cannot store a high H_2 capacity (Abdalla et al. 2018). Unlike carbon nanotubes, graphite particles (another carbon-based H_2 storing materials) are cheaper (Abdin et al. 2020; Fernández et al. 2020; Rusman and Dahari 2016).

Urea is a benign matter used as a form of H_2 storage (Dincer and Zamfirescu 2016a). It is widely used in the auto industry as a NO_x emissions reducer (Dincer and Zamfirescu 2016a). The main advantages of urea are its stability, transportation safety, and long-time H_2 storage ability (Dincer and Zamfirescu 2016a). H_2 can also be transformed benignly to methanol, ammonia or synthetic diesel in order to increase its storage density preventing its large-scale storage at natural state and making it a reliable fuel (Dincer and Zamfirescu 2016a). Unlike H_2, ammonia (NH_3) storage is cheaper, safer (easy smell detection), and its long-distance transportation is easier (Dvoynikov et al. 2021; Jiang and Xianzhi 2021; Wang, Meng, and Jiao 2022). Ammonia has the highest H_2 density (136 kg H_2/m^3) compared to hydrogen itself at both natural and liquid states (0.09 kg H_2/m^3 and 71 kg H_2/m^3 respectively) and to other fuels (e.g., LNG 106 kg H_2/m^3, Gasoline 118 kg H_2/m^3) (IAEA 2013; Jiang and Xianzhi 2021; Lenivova 2020; Wijayanta et al. 2019). In addition, ammonia has a significant storage density (603 kg/m^3). Thus, a great medium for H_2 storage (Dincer and Zamfirescu 2016a). NH_3 is absorbed by a metal ammine and then thermo-catalytically decomposed into H_2 and nitrogen (N) (Dincer and Zamfirescu 2016a; Dvoynikov et al. 2021). However, extracting H_2 is heat-consuming; therefore, to offset this heat, it can be recovered from an existing combustion process allowing an auto-cracking reaction of NH_3 (Dincer and Zamfirescu 2016a). Ammonia reduces NO_x emissions and, among other chemicals, is the only carbon-free hydrogen carrier (Lenivova 2020; McKinlay, Turnock, and Hudson 2020). Nevertheless, the gravitational energy density of ammonia is proportional to a vessel mass and affects its performances (Dvoynikov et al. 2021). In addition, the on-board application is logistically tricky and involves extra-infrastructure (McKinlay, Turnock, and Hudson 2020).

Taking into consideration the volumetric density of H_2, (Wang et al. 2021) focused in their review on LH_2 (−253°C) and CcH_2 (< −196°C) as they are more suitable for storage on board large ships. In addition, they pointed out that LH_2 storage is only used on board SF-BREEZE (a high-speed liner) (Markowski and Pielecha 2019), MH storage is dedicated to low power ships, while gaseous H_2 storage is the most used for the rest of FC vessels.

H_2 storage standards

Table 7 briefly presents some of the international and European standards and codes regarding H_2 storage under liquid and gaseous forms:

Summary and conclusions of hydrogen storage methods

Although hydrogen, in all its forms, has the lowest energy density among all transportation fuels, it is considered as the best fuel owing to different characteristics (clean burning, better performance, versatility, and sustainability) (Dincer and Zamfirescu 2016a; Halewadimath et al. 2022). In order to determine the best storage technology for each application, the following factors should be considered:

- The storage system key parameters: temperature and pressure (Fernández et al. 2020),
- The key metrics: volumetric and gravimetric densities, and technology cost (Moreno-Blanco et al. 2019b),
- The economic feasibility, technology availability, and limitations (on board, off board) (McKinlay, Turnock, and Hudson 2020).

Direct offshore hydrogen storage is impractical due to the high infrastructure requirements especially for large-scale applications (Bethoux 2020; Dincer and Zamfirescu 2016a; Gondal 2019). Furthermore, thermal management is a main technical issue for H_2 storage (Rahul et al. 2012) and its purification is a must before its storage (Dincer and Zamfirescu 2016a). However, thanks to the technological development, H_2 will compete with other fuels' prices in the near future (2025) (McKinlay, Turnock, and Hudson 2020). Despite the commercial maturity of CH_2 and LH_2, solid H_2 storage provides high

Table 7. European and international standards (Tronstad et al. 2017).

Standard/Code	Brief description	H_2 storage method
ISO/TR 15,916	• Risks and safety guidelines related to H_2 use (temperature, materials, H_2 embrittlement. . .)	Gaseous Liquid
PED. EN 1252–1:1998	• Materials used for storage containers, • Irrelevant to cryogenic tanks for LNG neither to cast materials and unalloyed materials.	Compressed gas
EN 1797:2001	• Compatibility between the gas and material used.	
EN 13,648 part 1, 2, and 3	• Extreme pressure safety and protection.	
ISO 15,399 Gaseous Hydrogen - Cylinders and tubes for stationary storage	• Covers volumes of 10000 l and pressures of 110 MPa	
EIGA code of practice IGC 15/06	• Tanks filling • H_2 compression • End-storage installation • H_2 purification	
IGC and IGF codes	• LH_2 storage on board vessels	Liquid

H_2 purity and safety and has the highest volumetric density (low pressure and volume requirements) (Abdin et al. 2020).

According to (Rivard, Trudeau, and Zaghib 2019), conducting a direct comparison between H_2 storage technologies is tricky as each one of them has distinguished features. Hence, Table 8 summarizes the different advantages and disadvantages of the available H_2 storage technologies, Table 9 presents some hydrogen storage methods' key metrics, while Table 10 reviews the technologies applied so far in the marine sector.

The first yacht powered with H_2 (2003).

[2] The first emission-free ship with H2 auto-production from seawater (2017).

On board green hydrogen consumption

Green-hydrogen fuel can be used on board ships to power internal combustion engines (ICE) (diesel, gas), fuel cells (FC), or hydrogen gas turbines (GT) (Ammar and Alshammari 2018; Hoecke et al. 2021; Sarafraz et al. 2019). Battery-electric (BE) propulsion systems are only compatible with large ferries (Korberg et al. 2021). Consequently, this review will focus more on FCs and ICEs. In order to choose the best propulsion system for ships, some major guiding elements should be considered, such as: sea spending time, fuel efficiency, and cost, as well as the whole propulsion system cost (Korberg et al. 2021). The operating principle of the aforementioned propulsion systems is extensively detailed in the open literature; therefore, this article will only review their main applications in the shipping industry.

Gas turbine engines operate under the Brayton cycle and are used as auxiliary power units in the shipping industry mainly in cruise liners (e.g., Queen Mary II) (Ammar and Alshammari 2018). The NO_x reduction techniques used in gas turbines powered by NG and petroleum products are impractical when these turbines are fueled by H_2 because of its combustion particularities (Ammar and Alshammari 2018; Tomczak et al. 2002). Therefore, current researches suggest the mix of H_2 with NG-blends whether in ICE or gas turbines in order to take advantage of H_2 usage (Ammar and Alshammari 2018).

Compared to conventional marine technologies, FCs are beneficial due to their silent operation mode, low-cost operating and maintenance, and have good low-exhaust emissions and low-load performance (Shakeri, Zadeh, and Bremnes Nielsen 2020). Moreover, FCs are distinguished by the absence of combustion (only electrochemical reactions (Shakeri, Zadeh, and Bremnes Nielsen 2020)) which minimizes the resulting pollutants (Ammar and Alshammari 2018; Keshavarzzadeh, Ahmadi, and Reza Safaei 2019). FCs predominantly use H_2 as their working-fuel and are classified according to the electrolyte type and operating temperatures into six different types as follows (Ammar and Alshammari 2018; Hoecke et al. 2021; Shakeri, Zadeh, and Bremnes Nielsen 2020):

- Low-temperature FCs (50 – 150°C)
- Alkaline electrolyte (AFC),
- Proton Exchange Membrane (PEMFC),
- Medium temperature FCs (around 200°C)
- Phosphoric acid (PAFC),
- High-temperature FCs (600 – 1000°C)
- Direct carbon (DCFC),
- Molten carbonate (MCFC),
- Solid oxide (SOFC).

Table 11 summarizes the different characteristics of FC technologies:

Although FCs are a mature technology in the road sector, they are presently operating only as a hybrid mode for ships' propulsion and an auxiliary power source in commercial naval ships (Ammar and Alshammari 2018; Seddiek, Elgohary, and Ammar 2015). Through 18 years (2000–2018), the total FC power installed in marine applications has reached 520 MW (Shakeri, Zadeh, and Bremnes Nielsen 2020). However, FCs are unable to meet large ships' power demand exceeding 10 of MW due to their output power limited to few MW (Xing et al. 2021); hence, they are currently dedicated only to small ships (up to 1 MW), while for large ships, they only deliver auxiliary power (Biert, Hart, and Mrozewski 2021). Consequently, FCs for the marine sector are still under continuous R&D (Hoecke et al. 2021; Shakeri, Zadeh, and Bremnes Nielsen 2020). Table 12 summarizes some examples of the current FC applications in the shipping propulsion sector (Shakeri, Zadeh, and Bremnes Nielsen 2020).

Welaya et al. (Welaya, El Gohary, and Ammar 2012) and Seddiek et al. (Seddiek, Elgohary, and Ammar 2015) stated in their studies that MCFC and PEMFC powered by high-hydrogen fuels (alcohols, NG) are the only commercially eligible technologies for on board-ships usage. According to a recent report by the Maritime Knowledge Centre (L van, Pieter't Hart, and Mrozewski 2021), low-temperature and high-temperature PEMFC as well as SOFC are the most

Table 8. H_2 storage technologies' benefits and drawbacks.

Storage method	Benefits	Drawbacks	Ref.
Compressed H_2 gas	• Available • Cheap • Industrial experience • Ease of operation at ambient T • Simple storage and recuperation	• Small H_2 pressure (<200 bars) • Low volumetric density • High T of H_2 release • High filling pressure • Energy consumer (9% of the stored energy for 70 MPa vessel) • High operating pressure • Pressure adjustment requirement • Expensive • Rapid loss of H_2 in accidents • Large physical volume • Safety issues: • Containment loss • Materials-blistering • Heating effect during filling • Energy losses estimated to 10%	(Abdalla et al. 2018; Abdin et al. 2020; Ayodele and Lange Munda 2019; Gondal 2019; IAEA 2013; Qubeissi and El-Kharouf 2020)
Liquified H_2	• High energy density • High energy storage • Low weight (3 times less than GH_2) • Storage efficiency • High liquid density • No purification needed: • H_2 purity (98%) • Suitable for direct use in FCs	• High energy consumer to reduce T below critical T (33K) • Evaporation losses • High energy requirement to keep low T • Expensive: • 75% of the cost due to the cryogenic tank • High production cost due to the high energy consumption • Safety issues: • Boil-off • Containment loss • Ice formation • T control to avoid overpressure. • Liquefaction energy requirement • Energy losses estimated to 40% • Time consumer • Energy consumer (25%–45% of the stored energy used only for liquefaction)	(Abdalla et al. 2018; Barthelemy, Weber, and Barbier 2017; Fernández et al. 2020; Gondal 2019; IAEA 2013; Korri 2018; Lenivova 2020; McKinlay, Turnock, and Hudson 2020; Qubeissi and El-Kharouf 2020; Rahul et al. 2012; Wijayanta et al. 2019)
Metal hydrides	• Reliable • Safer than LH_2 and CH_2 • Reduce by 3 times the system volume compared to LH_2 • Cheaper than LH_2 • High H_2 purity	• Expensive materials • Safety issues • Explosion • Toxicity • Boil-of gas • Containment loss. • Water reactivity and pyrophoric materials	(Abdalla et al. 2018; Dvoynikov et al. 2021; Fernández et al. 2020; Lenivova 2020; Qubeissi and El-Kharouf 2020)
Carbon nanotubes	• Large area • Lightweight • Chemical stability	• Expensive • High-risk transportation	(Fernández et al. 2020; Rusman and Dahari 2016)
Graphite particles	• Cheaper than carbon nanotubes	NA	(Fernández et al. 2020; Rusman and Dahari 2016)
Ammonia	• Easy long-distance transportation and storage • No need for expensive cryogenic tanks • H_2 stability • H_2 safety • High volumetric capacity • High volumetric density	• Toxicity • A stifling smell • Corrosivity	(Dvoynikov et al. 2021; Jiang and Xianzhi 2021; Lenivova 2020; Wang, Meng, and Jiao 2022)

promising FC technologies for marine applications, their main characteristics are summarized in Table 13 (Korberg et al. 2021; L van, Pieter‘t Hart, and Mrozewski 2021; Tronstad et al. 2017; van Biert et al. 2016). In addition to the aforementioned technologies, Xing et al. (Xing et al. 2021) also nominated MCFC and explained that the selection of the three technologies is due to their high power capacity, energy efficiency, and fuel impurity sensitivity. Currently, the most commonly used FC technologies in the marine sector are PEMFC and MCFC, respectively (Shakeri, Zadeh, and Bremnes Nielsen 2020). The high temperature of MCFC, SOFC, and PEMFC technologies puts them under continuous research. Even

Table 9. H_2 storage key metrics.

Storage method	Storage T (K)	Storage P (Bar)	Gravimetric energy density (MJ/kg)	Volumetric energy density (MJ/l)	Storage density (kg/m3)	Gravimetric H_2 content (wt%)	Volumetric H_2 content (kg-H2/m3)	Ref.
Hydrogen	NA	NA	142	0.013	0.09	NA	0.09	(IAEA 2013; Wang et al. 2021)
Compressed H_2	233–300	150–800	NA	2.88 at 350bar 5.04 at 700bar	NA	NA	NA	(Wang et al. 2021)
	NA	NA	NA	1.54 at 800bar		100	NA	(IAEA 2013)
	NA	NA	NA	1.11 at 500bar		100	NA	(IAEA 2013)
	298	690	120	4.5	39	100	42.2	(Andersson and Grönkvist 2019; Aziz, Tri Wijayanta, and Bayu Dani Nandiyanto 2020; Makepeace et al. 2019)
Cryo-compressed H_2	33–77	150–350	NA	9.36 at 38K and 300 bar	NA	NA	NA	(Wang et al. 2021)
Liquified H_2	20–33	1–12.76	NA	>8.28	NA	NA	NA	(Wang et al. 2021)
			NA	8.496 at 20K		100	NA	(IAEA 2013)
	NA	NA	142	9.9	71	NA	71	(IAEA 2013)
	20	1	120	8.49	70.8	100	70.8	(Andersson and Grönkvist 2019; Aziz, Tri Wijayanta, and Bayu Dani Nandiyanto 2020; Makepeace et al. 2019)
Ammonia	NA	NA	225	17.4	771	NA	136	(IAEA 2013)
	298	9.9	18.6	12.7	600	17.8	121	(Andersson and Grönkvist 2019; Aziz, Tri Wijayanta, and Bayu Dani Nandiyanto 2020; Makepeace et al. 2019)

Table 10. Hydrogen storage applications in ships (reproduced from (Wang et al. 2021)).

Category	Name	H2 storage method
Yachts and sport boats	Cobalt 233 Zet	3 H_2 containers of 350bar
	Yacht No.1[1]	6kg H_2 tanks at 300bar
	Riviera 600	High-pressure containers
	Energy observer[2]	8 tanks of carbon fiber and aluminum (62kg of H_2)
	Yacht XV 1	CH2 or MH with light composite containers
Pusher	RiverCell-Elektra	Six containers of 500bar holding 740kg CH_2
Underwater vehicles (AUVs)	URASHIMA	MH
	URASHIMA 2nd generation	
	IDEF	Pressurized H_2 gas bottle of 300bar and 50L
Fishing vessels	N/A	1 LH_2 container of 450L
Passenger vessels	Xperience NX	4 exchangeable H_2 gas containers with 200bar 30L H_2 gas in each
	Elding	High-pressure (350bar) containers
	Hydroville	12 H2 tanks of 205L at 200bar
	Hydra	MH
	Hydroxy 3000	Pressurized H_2 gas bottle of 200bar and 76L
	Ross Barlow	Fixed H_2 containers and solid H_2 store
	Tuckerboot	Exchangeable H_2 pressure containers
	Nemo H2	40kg H_2 in 8 cylinders at 350bar
	ALSTERWASSER	12 containers of 350bar 50kg H_2
	SF-Breeze	1200kg LH_2 container
Submarines	Class 212 A and 214	Lightweight outer hull and pressure hull

though these technologies help overcome carbon monoxide (CO) poisoning, they increase NO_x formation (Hoecke et al. 2021). The high-temperature of MCFC allows their hybrid integration with heat engines in marine applications and increases the engine efficiency (Shakeri, Zadeh, and Bremnes Nielsen 2020). However, the low-power density of MCFC and their slow start-up are the main drawbacks of this technology (Shakeri, Zadeh, and Bremnes Nielsen 2020). Although the power density of SOFC and MCFC is lower than of PEMFC, they are characterized by a higher energy efficiency thanks to the integration of waste heat recovery and reforming units (Xing et al. 2021). PEMFC efficiency is impacted by H_2 impurities (S, CO) and water management complexity (Shakeri, Zadeh, and Bremnes Nielsen 2020). Unlike ICEs, pure H_2 is mandatory for FCs (especially PEMFC) in order to increase their electrical efficiency and cut emissions, as the only by-product is water (Gianni, Bucci, and Marinò 2021; Olabi et al. 2020; Shakeri, Zadeh, and Bremnes Nielsen 2020; Tsujimura and Suzuki 2017). However, this requirement narrows PEMFC use (Hoecke et al. 2021). One solution is the use of high-temperature PEMFC, which has the same efficiency of low-temperature PEMFC; however, the high operating temperature will simplify water management and reduce H_2-impurity sensitivity (Shakeri, Zadeh, and Bremnes Nielsen 2020). PEMFCs are characterized by various simultaneous processes (chemical and physical) during energy conversion making it a complex technology and hence immature for large-scale commercialization (Ding et al. 2022). In order to overcome this issue and improve the PEMFC performances, (Ding et al. 2022) reviewed the application of machine learning (ML) tools

Table 11. Fcs characteristics (Xing et al. 2021; Tronstad et al. 2017; Baldi et al. 2020; van Biert et al. 2016; Rosli et al. 2017; Energy, Office of Energy Efficiency & Renewable 2021).

FC-type	Typical fuel	Operating Temperature (°C)	Power Capacity	Efficiency Electrical	Efficiency Overall	Drawbacks	Waste Heat Recovery	Relative Cost	Lifetime	Size
AFC	H_2	60–200	=<500 kW	50–60%	NA	CO_2 poisoning	NA	Low	Medium	Small
PEMFC		65–85	=<120 kW			CO + S poisoning				
HT-PEMFC		160–220			80%		HEx/ST	Medium		
PAFC	H_2, LNG and methanol	140–200	100–400 kW	40–55%					Good	Large
DMFC	Methanol	75–120	=<5 kW	20–30%	NA	methanol crossover	NA		Medium	Small
MCFC	H_2, methanol and hydrocarbons	650–700	120 kW–10 MW	50–55%	85%	S poisoning, cycling effects, long start-up time	HEx/ST	High	High	Large
SOFC		500–1000	=<10 MW	50–60%		S poisoning, cycling effects, mechanically fragile, long start-up time				Medium

Table 12. FC applications in the shipping propulsion sector (Markowski and Pielecha 2019; Shakeri, Zadeh, and Bremnes Nielsen 2020; Tronstad et al. 2017; van Biert et al. 2016; Xing et al. 2021).

Project	FC-type	Vessel-type	FC power rating	R&D partners	Fuel
FCSHIP	MCFC SOFC PEMFC	Passenger ferry	Up to 1 MW	DNV-GL	Hydrocarbons Hydrocarbons Hydrogen
Hydra	AFC	NA	6.9 kW	NA	Metal hydride
Hydrocell Oy			30 kW		
ZEMSHIP Alsterwasser	PEMFC	Passenger ferry	96 kW	Proton Motor	Hydrogen
Nemo H_2		Passenger ferry	60 kW	Alewijnse	
MARANDA		Research vessel	Two 82.5 kW (165 kW)	ABB and VTT	
Raicho Project for Next-Generation Water Transportation		Research vessel	30 kW	Tokyo University of Marine Science and Technology and Toshiba	
Hybrid Power Lab at NTNU		Laboratory scale demo	Two 30 kW (60 kW)	ABB, SINTEF Ocean, NTNU	
Elding		NA	10 kW	NA	
Hornblower Hybrid			32 kW		
Hydrogenesis			12 kW		
SF-BREEZE			120 kW		
Cobalt 233 Zet			50 kW		
MF Vågen	HT-PEMFC		12 kW		
RiverCell ELEKTRA			3 X 100 kW		

(an AI branch). These tools are cost and time effective compared to traditional trial-and-error methods. ML has been used in many areas including renewable energy and proved its accuracy and reliability in predicting the target output (Ding et al. 2022).

According to Shakeri et al. (Shakeri, Zadeh, and Bremnes Nielsen 2020), low-temperature FCs are safer, while high-temperature FCs are more efficient. DNV-GL set some safety rules regarding FCs' use on board ships such as the on board testing, fire safety, control monitoring, design principles, electrical system, and material requirements (Shakeri, Zadeh, and Bremnes Nielsen 2020). Moreover, DNV-GL classified those rules into two categories: FC (safety) refers to when FCs are used as an auxiliary source for the vessel propulsion power, while FC (power) refers to FCs as the prime source (Shakeri, Zadeh, and Bremnes Nielsen 2020).

The main disadvantages of FCs´ stack are their expensive cost, low lifetime, and low power capacity, which is unable to supply all the ship's power needs (Gianni, Bucci, and Marinò 2021; Hoecke et al. 2021; Kulagin and Grushevenko 2020; Shakeri, Zadeh, and Bremnes Nielsen 2020). FC efficiency and lifetime are affected by water and thermal managements as well as H_2-purity (Shakeri, Zadeh, and Bremnes Nielsen 2020). Moreover, the system overall efficiency is affected by the H_2-storage method efficiency (Shakeri, Zadeh, and Bremnes Nielsen 2020). As shown in Figure 11, for the same FC efficiency (45–60%) and electric power efficiency (95–98%), we note that the total system efficiency is higher in the case of CH_2 followed by LOHC and LH_2. Compared to other propulsion systems (ICE, GT, BE), the energy efficiency of FCs is higher (Ahmadi et al. 2020; Braga et al. 2014; Gianni, Bucci, and Marinò 2021; Hoecke et al. 2021; Kulagin and Grushevenko 2020; Xing et al. 2021). Furthermore, FCs are advantageous in terms of operability, safety, and reliability (Xing et al. 2021). However, they still need further improvements regarding their durability, power capacity, and economic cost (Xing et al. 2021). In addition, increasing FC operating temperature increases its electrical efficiency (Shakeri, Zadeh, and Bremnes Nielsen 2020).

Table 13. LT/HT PEMFC and SOFC are the main operating characteristics and parameters for marine applications (L van, Pieter't Hart, and Mrozewski 2021).

Characteristics	LT-PEMFC	HT-PEMFC	SOFC
Operating temperature (°C)	65–85	140–180	500–1000
Electrical efficiency (% LHV)	40–60	40–50	50–65
Fuel requirements	99.99% H_2	CO < 3%	S < 20 ppm
Gravimetric power density (W/kg)	125–750	25–150	8–80
Volumetric power density (W/L)	50–400	10–100	4–32
Stack lifetime (kh)	5–35	5–20	20–90
System lifetime		≥10 years with stack replacement	
Cold start-up time	<10 seconds	10–60 minutes	>30 minutes
Load transients (0 to 100%)	seconds	<5 minutes	<15 minutes
Current capital cost ($/kW)	1000–2500	3000–5000	3500–15000
Future capital cost ($/kW)	60–600	150–1500	500–2000
Future capital cost ($/kW)	6–7	5–6	4–5
Cooling medium	Liquid	Liquid	Air

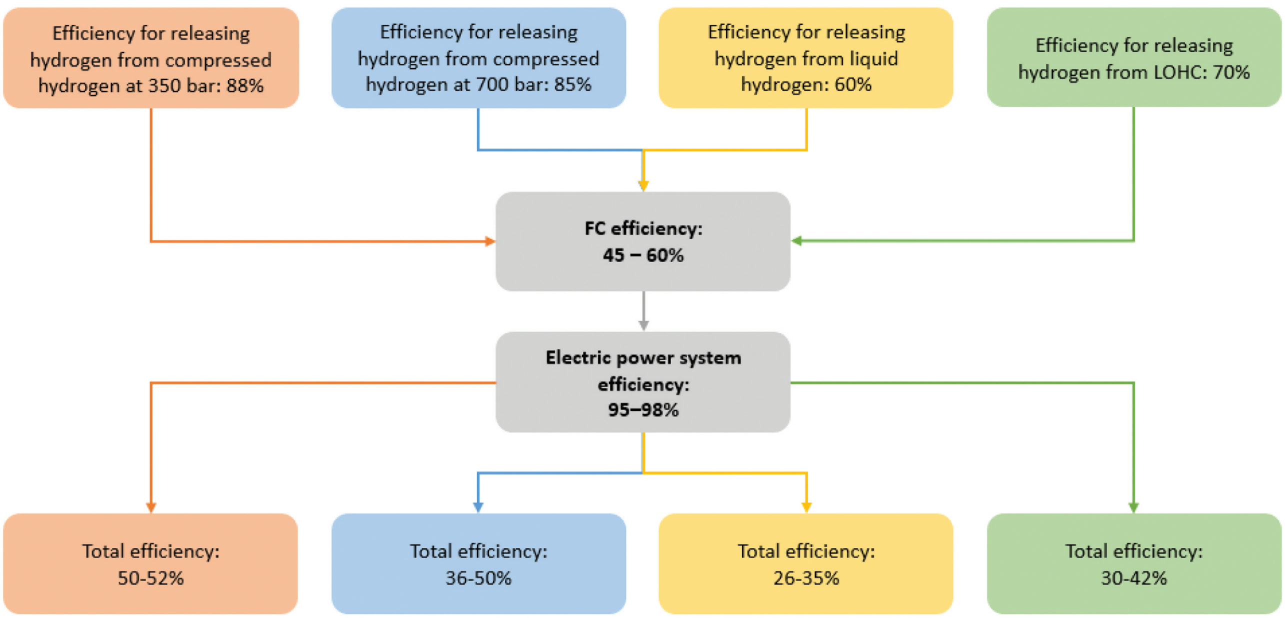

Figure 11. Total electric efficiency in function of H2 storage efficiency (Shakeri, Zadeh, and Bremnes Nielsen 2020).

ICEs are used in almost all ships (Prussi et al. 2021). According to Seddiek et al. (Seddiek, Elgohary, and Ammar 2015), at least 95% of marine power plants on board vessels rely on ICEs. They are generally fed with fuels derived from petroleum, which are responsible for GHG and local pollutants (i.e., particulate matters) (Prussi et al. 2021; Viana et al. 2020). In order to reduce these emissions and the cost of combustion engines, one solution is to replace diesel with green fuels (e.g., green hydrogen) (Ammar and Alshammari 2018; Prussi et al. 2021; Seddiek, Elgohary, and Ammar 2015). Both ICE and FC can be fed directly with H_2 rather than electro-fuels (Korberg et al. 2021). According to (Ammar and Alshammari 2018; Seddiek, Elgohary, and Ammar 2015), the use of LH_2 fuel for FCs and ICEs on board ships is the main focus for many research programs. However, unlike other propulsion systems (FC and GT), using H_2 in ICE (H2ICE) instead of diesel will only require some engine modification, which will optimize the cost (Ammar and Alshammari 2018; Korberg et al. 2021). For instance, an FC will require additional equipment (gearbox + electric engine) to convert its electrical power, while an ICE is capable of producing the mechanical power directly (Korberg et al. 2021).

The use of H2ICE reduces the engine torque and its output power while increasing its thermal efficiency (Ammar and Alshammari 2018; Seddiek, Elgohary, and Ammar 2015). Direct-burning of H_2 inside ICE liberates its internal energy (Olabi et al. 2020). H_2-fueled ICE goes through four phases: (1) pressure-boosted H2ICE, (2) liquid-H2ICE, (3) direct-injection H2ICE, and (4) H2ICE-electric hybrid (Seddiek, Elgohary, and Ammar 2015).

Diesel cycle engines and spark-ignition are the two appropriate ICEs for H_2 burning (Olabi et al. 2020). H_2 is combusted in diesel/gas engines either as a single fuel or combined with other fuels (Dimitriou and Tsujimura 2017; Hoecke et al. 2021). In the case of diesel cycle, H_2 must be mixed with other fuels since the cycle does not admit pure H_2 (Olabi et al. 2020). Although H_2 mixture with other fuels increases NO_x emissions and fuel consumption, it decreases CO and CO_2 emissions and increases the engine thermal efficiency (Alrazen et al. 2016; Koten 2018; Olabi et al. 2020). According to (Ammar and Alshammari 2018), catalytic reduction filters and exhaust gas recirculation are used to reduce the resulting NO_x from H2ICE.

Seddiek et al. (Seddiek, Elgohary, and Ammar 2015) discussed the different stages of H_2 production chain on board a RO/RO ship in the Mediterranean Sea and concluded that H2ICE and diesel-ICE have a similar combustion and compression pressure, while the main difference lies in H2ICE low fuel consumption, thermal efficiency, and average effective pressure. Moreover, in order to satisfy the hydrogen storage needs on board ships, H2ICE bunkering tanks should be increased by around double capacity of diesel and heavy fuel tanks (Seddiek, Elgohary, and Ammar 2015). The main drawback of H_2 use in ICE is its high auto-ignition which, unlike hydrocarbon-fuels, complicates its use as it influences the synchronized and efficient combustion in the engine cylinder (Hoecke et al. 2021). Other disadvantages are the intake temperature, the engine knocking, and the air fuel ratio (Seddiek, Elgohary, and Ammar 2015).

To date, the investment cost of H2ICE (four and two-stroke engines) is (470/700 €/kW) cheaper than PEMFC (LT and HT) (730 €/kW) and SOFC (1280 €/kW) (Baldi, Brynolf, and Maréchal 2019; Korberg et al. 2021). The cost of H_2 storage on board large ferries is 1.71€/kWh and 1.29€/kWh for general cargo, container ships, and bulk carriers, which is much cheaper than batteries (250 €/kWh). Moreover, hydrogen as a clean fuel has a longer lifespan (Korberg et al. 2021; GL 2019; CleanTech 2019; Alnes, Eriksen, and Vartdal 2017).

Four-stroke ICEs on cargo ships could be replaced by FCs systems if their efficiencies are enhanced 15% to 20% more than ICE (Korberg et al. 2021). However, for bulk carriers, FC may need substantial upgrades to replace two-stroke engines and make the technology-switch worthwhile (Korberg et al. 2021). According to (Korberg et al. 2021), from a TCO (Total cost of ownership) standpoint, if batteries and FCs fail to perform technologically and economically, despite fossil fuels' replacement, ICE would certainly remain a viable propulsion technology for the marine sector. It is estimated that a modern ship has a lifetime of about 25–30 years (Prussi et al. 2021). Consequently, ICEs are a good option as their lifetime is estimated to 30 years, double of FCs´ lifetime (15 years) (Korberg et al. 2021). Although ICEs are maintenance intensive compared to FCs (Shakeri, Zadeh, and Bremnes Nielsen 2020), they are still a more attractive alternative, especially when powered by cheap fuels, which dismiss FCs´ use (Korberg et al. 2021).

Life-cycle assessment of green hydrogen

In order to present tangible evidence on the use of green hydrogen as an alternative fuel for maritime transport, this review would not be complete without addressing and evaluating the environmental impacts of such fuel. In other words, to ascertain how green is green hydrogen (Osman et al. 2021). Life-cycle assessment is a fundamental tool that provides a detailed analysis of the emissions released throughout a process or a product lifetime in comparison with other suggested alternatives according to ISO 14,040 and ISO 14,044 requirements (Aydin and Dincer 2022; Chen and Siu Lee Lam 2022; Iannuzzi, Antonio Hilbert, and Eduardo Silva Lora 2021; Olabi et al. 2020; Osman et al. 2021; Palmer et al. 2021; Perčić et al. 2021). Detailed investigations about LCA are widely presented in the open literature. The authors will only present some research findings in the present review.

Generally, LCA consists of four major stages, namely, (i) goal and scope definition, (ii) life-cycle inventory data collection and analysis, (iii) life-cycle impact assessment, and (iv) results interpretation (Aydin and Dincer 2022; Chen and Siu Lee Lam 2022; Dincer and Acar 2015). The commonly studied environmental impacts are global warming potential (GWP), eutrophication potential (EP), photochemical oxidation (POP), abiotic depletion (ADP), ozone layer depletion potential (ODP), and acidification potential (AP) (Al-Qahtani et al. 2021; Chen and Siu Lee Lam 2022; Zhang et al. 2022).

Olabi et al. (Olabi et al. 2020)compared different LCA analyses and deduced that using clean and renewable feedstocks for hydrogen production is one of the most environmentally friendly technologies. For instance, hydrogen produced by solar thermal electrolysis and PV electrolysis emits 2.06 and 3.08 kg CO_{2eq}/kg H_2 respectively against 10.28 kg CO_{2eq}/kg H_2 from SMR and 11.59 kg CO_{2eq}/kg H_2 from gasification. Thus, emissions from SMR and gasification are more than triple the emissions from solar thermal and PV electrolysis. Furthermore, hydrogen produced by SMR emits 94% more GHG emissions than water electrolysis from wind energy (taking into consideration the 65% emissions during the wind power plant installation phase) (Olabi et al. 2020). Along the same lines as Olabi et al., Aydin and Dincer (Aydin and Dincer 2022) studied the LCA of clean hydrogen production by renewable (AE, PEME, and Cu-Cl cycle) and nuclear-based methods, and also assessed the potential environmental impacts of hydrogen from its production to consumption by fuel cell electric buses. Additionally, Aydin and Dincer dealt with different LCA studies that compared conventional and renewable hydrogen production methods such as (Bicer and Dincer 2017; Cetinkaya, Dincer, and Naterer 2012), (Xiaojin et al. 2017), and (El-Emam and Özcan 2019). All investigations agreed that hydrogen produced from renewables has less environmental impact than conventional methods (e.g., diesel). On the other hand, (Aydin and Dincer 2022) recommend focusing on the manufacturing materials when producing hydrogen by renewable methods.

Chen and Lam (Chen and Siu Lee Lam 2022) have carried out an LCA of two power systems in tugboats (diesel engine and PEMFC). They concluded that adopting hydrogen as a tugboat fuel significantly reduces the most worrying environmental impacts in the maritime sector (AP (45%), POP (50%), GWP (85%), and EP (54%)). In addition, the authors (Chen and Siu Lee Lam 2022) stated that the global warming impact of hydrogen-powered tugboats is due to the use of nonrenewable methods for hydrogen production, while there are no emissions at the operation stage. Therefore, they recommended the adoption of green hydrogen (from renewables) in the maritime industry in order to reduce the global warming impact caused as well as the other environmental impacts.

Zhang et al. (Zhang et al. 2022) conducted a comprehensive LCA of three coupling solar-based production methods of hydrogen (PEME + photothermal power generation (PT), PEME + PV power generation, and thermochemical water splitting using S-I cycle + PT). They concluded that overall S-I + PT has less environmental impacts (GWP, AP, EP, and

ODP) compared to other studied technologies, hence advantageous. In addition, as previously stated by other researchers, Zhang et al. also mentioned that emissions by renewable feedstocks for hydrogen production occur only during the production phase and not during the operation phase. Therefore, they recommend carefully choosing appropriate low-emission construction materials in order to successfully limit the overall environmental impact of the production system. On the other hand, for the three studied hydrogen production systems, environmental impacts are reduced by increasing the systems ′ lifetime (Zhang et al. 2022).

Perčić et al. (Perčić et al. 2021) compared the emissions released by a RO/RO passenger ship powered by a diesel system, a hydrogen system, and an electrical system with a Lithium-ion battery. They concluded that green hydrogen and electricity-powered ships reduce emissions by 91% and 47% of CO_{2eq} respectively compared to diesel system. (Yanfei and Taghizadeh-Hesary 2022) stated that according to different LCA studies conducted by (Ren, Zhou, and Xunmin 2020) and (Kannangara, Bensebaa, and Vasudev 2021), FC electric vehicles fueled with green hydrogen are better than BE vehicles in terms of CO_2 emissions. Although LCA has demonstrated the benign impact of green hydrogen in ships powered by FCs, the use of fossil fuel is still much cheaper according to the life-cycle-cost assessment (Perčić et al. 2022).

Conclusion

Green hydrogen is a promising clean fuel for the marine sector to cut its part of GHG emissions. Moreover, gH_2 is an advantageous option for ships to be energetically self-sufficient and avoid power shortage throughout a sea journey. For this reason, the different stages of the gH_2 production chain on board ships have been reviewed in the present article leading to the following conclusions:

- Solar-based H_2 production processes are not 100% functional to produce gH_2 on board as the sun is not available all day, which will require additional storage and space.
- Wind-based processes depend on wind direction and strength.
- Solar and wind energy technologies are used as standalone systems for small-scale ships, while in the case of large-scale ships they need to be connected to the grid or combined with other energy generation systems. Therefore, limiting the on board gH_2 production autonomy. Recovery energy consists simply of taking advantage of the energy excess to self-produce an environmentally benign hydrogen fuel (gH2). Making it a favorable and suitable energy source for on-board maritime vessels use.
- Electrolysis is still under investigation for the on board gH2 production. Considering H2 properties, solid storage is one of the appropriate options for on board use as it has the highest volumetric density, a high H2-purity, and is safer.
- Ammonia is also a viable H2 storage medium, for long-distance journeys, due to its H2 safety and stability as well as ease of transportation and storage.
- Ammonia is a promising solution to the H2 storage challenges and addressing a bottleneck in the production chain.
- FCs are a mature technology in the transport sector, they have a reduced lifetime and are unable to fully meet all ships' categories power demand as their output power is limited to only a few MW.
- ICEs are used in almost all ships and are currently the preferable propulsion technology as they are cheaper, have a higher lifetime, and the technology fuel-switch to H2 will only require some engine modification to optimize the overall cost. In addition, due to hydrogen R&D advancements, its prices are expected to drop in the few coming years, thus making it competitive with fossil fuels.
- Researchers agreed, through different LCA studies, that hydrogen produced from renewables has significantly less impact on the environment from production to consumption stages. Therefore, green hydrogen is a suitable fuel for maritime transport.
- The impact of manufacturing materials used by renewables should not be overlooked (for instance solar PV and wind-based production methods).

Finally, the authors recommend that special attention should be paid to financially supporting green hydrogen use in order to overcome the high-cost issue and accelerate its adoption by different sectors, in particular the maritime industry. In other words, stakeholders and policymakers must decide whether to prioritize the environment or saving money.

8. Nomenclature

ADP	Abiotic Depletion Potential
AE	Alkaline Electrolysis
AFC	Alkaline electrolyte Fuel Cell
AHP	Analytic Hierarchy Process
AI	Artificial intelligence
AP	Acidification Potential
BE	Battery-electric
BOG	Boil off gas
CBA	Choosing By Advantages
CcH_2	Cryo-compressed H_2
CCS	Carbon Capture, and Storage
CH_2	Compressed H_2
CH_4	Methane
CII	Carbon Intensity Indicator
CO	Carbon monoxide
CO_2	Carbone dioxide
DCFC	Direct carbon Fuel Cell
DES	Direct Electrolysis of Seawater
EE	Energy efficiency
EEDI	Energy Efficiency Design Index
EEXI	Energy Efficiency Existing Ship Index
EP	Eutrophication Potential
ESA	European Space Agency
ExE	Energy exergy
FC	Fuel cell
gH_2	Green hydrogen
GHG	Greenhouse gases
GT	Gas turbine

GWP	Global Warming Potential
H_2ICE	H_2 powered-ICE
H2S	Hydrogen Sulphide
HAWT	Horizontal axis wind turbines
HFO	Heavy Fuel Oil
HHV	Higher heating value
ICE	Internal combustion engine
IEA	International Energy Agency
IMO	International Maritime Organization
kW	Kilowatt
LCA	Life-cycle assessment
LH_2	Liquefied H_2
LHV	Lower heating value
LNG	Liquefied Natural Gas
MARPOL	International Convention for the prevention of pollution from ships
MCDM	Multiple-criteria decision-making
MCFC	Molten Carbonate Fuel Cell
MH	Metal hydride
MJ	Megajoule
ML	Machine learning
MOF	Metal organic frameworks
MW	Megawatt
NA	Not available
NG	Natural gas
NO_x	Nitrogen Oxides
ODP	Ozone layer Depletion Potential
ORC	Organic Rankine Cycle
PAFC	Phosphoric acid Fuel Cell
PEC	Photoelectrochemical
PEME	Proton Exchange Membrane Electrolysis
PEMFC	Proton Exchange Membrane Fuel Cell
POP	Photochemical Oxidation Potential
PV	Photovoltaic
R&D	Research and Development
RO/RO	Roll-On/Roll-Off ship
S	Sulphur
SAW	Simple Additive Weighting
SEEMP	Ship Energy Efficiency Management Plan
SMR	Steam Methane Reforming
SOEC	Solid Oxide Electrolysis Cell
SOFC	Solid Oxide Fuel Cell
SO_x	Sulphur Oxides
TCWS	Thermochemical water splitting
TOPSIS	Technique for Order of Preference by Similarity to Ideal Solution
TRL	Technology readiness levels
VAWT	Vertical axis wind turbines
W	Watt
WASP	Wind-assisted ship propulsion
WHRS	Waste heat recovery systems
wt%	weight percentage

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