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Review

Color-Coded Hydrogen: Production and Storage in Maritime Sector

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Abstract: To reduce pollution from ships in coastal and international navigation, shipping companies are turning to various technological solutions, mostly based on electrification and the use of alternative fuels with a lower carbon footprint. One of the alternatives to traditional diesel fuel is the use of hydrogen as a fuel or hydrogen fuel cells as a power source. Their application on ships is still in the experimental phase and is limited to smaller ships, which serve as a kind of platform for evaluating the applicability of different technological solutions. However, the use of hydrogen on a large scale as a primary energy source on coastal and ocean-going vessels also requires an infrastructure for the production and safe storage of hydrogen. This paper provides an overview of color-based hydrogen classification as one of the main methods for describing hydrogen types based on currently available production technologies, as well as the principles and safety aspects of hydrogen storage. The advantages and disadvantages of the production technologies with respect to their application in the maritime sector are discussed. Problems and obstacles that must be overcome for the successful use of hydrogen as a fuel on ships are also identified. The issues presented can be used to determine long-term indicators of the global warming potential of using hydrogen as a fuel in the shipping industry and to select an appropriate cost-effective and environmentally sustainable production and storage method in light of the technological capabilities and resources of a particular area.

Keywords: hydrogen production; maritime transport; renewable energy; color-coded hydrogen; decarbonization pathways

1. Introduction

Climate change and environment protection are currently two of the most important global issues. Therefore, significant efforts are being made to reduce the environmental footprint of industry and various modes of transportation as the main sources of air pollution [1–5]. International maritime transport is still mainly dependent on liquid marine fuels derived from crude oil as the primary source of energy for the various types of commercial and passenger vessels [6], which have a particularly large impact on the environment, accounting for an estimated 3% of global greenhouse gas emissions [7]. Near the coast, maritime transport can contribute up to 7% of PM_{10} and 14% of $PM_{2.5}$ pollutants to air pollution [8].

1.1. Emission Reduction Targets and Acts in Maritime Transport

In order to improve future environmental outlook, the International Maritime Organization (IMO) has set a target to reduce emissions associated with maritime transport by 50% by 2050 [9]. Shipping under the zero-emission policy considers three different but interrelated measures [10,11]. First is the consideration of newly designed ships towards zero-emission targets and the use of alternative fuels, taking into account operational performance and reliability while meeting existing safety requirements. Second is the sustainability of production and availability of alternative maritime fuels for shipping with respect to current and future needs. The third is the consideration of the new and

existing infrastructure needed to support zero-emission maritime transport. All newly built ships must be designed in accordance with the Ship Energy Efficiency Management Plan (SEEMP), taking into account the Energy Efficiency Design Index (EEDI) [12]. The EEDI can serve as a basis for comparison between ships, regardless of their type or size, but does not provide a fully valid measure of energy efficiency because it only evaluates a portion of the ship's energy system at a single operating point [13]. Although compliance with the EEDI can improve the overall energy efficiency of the maritime fleet, this approach only applies to newly built ships [14,15]. The operational life cycle of a ship varies according to its design but the typical expected lifespan is about 20 years [16–18]. This means that using EEDI as the sole measure to reduce carbon emissions cannot ensure that the maritime sector will fully meet the 2050 deadline set by the IMO [19]. The ageing of the marine fleet combined with the use of conventional fuel makes it difficult to meet increasingly stringent future environmental standards and regulations [20–25]. In order to comply with Sulphur Emission Control Areas (SECAs) established in the IMO 2020 regulation [26], emission control gas abatement systems, or sulphur scrubbers, have been introduced to assist in the removal of Sox and particulate matter from engine exhaust [27].

1.2. Altenative Fuels as a Pathway to Maritime Decarbonization

In addition to improving currently available systems, the decarbonization of marine fuels is also being considered. Due to stricter regulations, alternative fuels and biofuels such as biodiesel, vegetable oil, ammonia, methane, or similar hydrocarbons have become available for use in the marine sector [28–31]. Perspective energy sources for marine transport are shown in Table 1.

Table 1. Comparison of perspective energy carriers in marine transportation sector.

Energy Carrier	Gravimetric Energy Density [MJ/kg]	Volumetric Energy Density [MJ/m³]	CO_{2eq} Emissions [gCO_{2eq}/MJ]	Technological Maturity [1]	References
HFO	40.05–41.2	39,564–42,036	84.98	9	[32–34]
MDO/MGO	42.6	36,089	75–89.6	9	[35,36]
LNG	42–67.59	20,825	56–66.5	7,8	[32,35–40]
Methanol	19.9–22.7	16,000	31.3–99.57	2–8	[32,37,39,41–48]
Ammonia	18.6	12,700–22,500	18.73–46.19	4–7	[46,49–52]
Hydrogen	120–142	3389 (at 35 Mpa) 6779 (at 70 Mpa) 8000 (Liquid)	5.2	2–9	[39,53–59]

[1] According to technology readiness level guide [60,61].

Liquefied natural gas is considered the main alternative to marine fuel oil because it produces significantly lower carbon dioxide emissions and only small amounts of nitrogen oxides, sulphur oxides, and particulate matter [62,63]. It is one of the most-used types of gaseous fuels, with an estimated annual consumption of 285 million tonnes of oil equivalent [64]. Despite the lower carbon emissions per unit of energy compared to conventional marine fuel, LNG-fueled ships do not necessarily have lower GHG emissions when considering the entire life cycle. Studies on the advantages of LNG over marine gas oil have shown that during the assumed 100-year life cycle, GHG emissions can be reduced by 15% at best, which can only be achieved in systems using high-pressure injection dual-fuel engines combined with the continuous precise control of upstream methane emissions [65].

Hydrogen is a promising alternative to LNG because it extends the environmental benefits and decarbonization potential not only to the marine industry but also to other transportation sectors where the electrification of the energy supply is not an exclusive solution. The total demand for hydrogen in Europe was estimated at 8.6 Mt in 2020 [66]. The

largest consumers of produced hydrogen are oil refineries with an estimated consumption of 50% of the total hydrogen production. Ammonia production plants are the second-largest hydrogen consumer at 29% while other, smaller consumers are comprised of other chemical industries. The transportation sector, an emerging hydrogen consumer, currently accounts for only 0.02% of the total hydrogen consumption [66]. The use of hydrogen as a marine fuel comes with some drawbacks that present challenges that need to be overcome. The main challenges relate to safety, as hydrogen is extremely flammable compared to conventional marine fuels and much lower concentrations are required to cause an explosion, so strict safety measures must be taken during transportation and storage. Another issue is the price and method of hydrogen production. Indeed, for hydrogen to be environmentally acceptable as a fuel, it must be produced with the lowest possible carbon emissions, and such production methods make hydrogen more expensive compared to conventional fuels. Finally, it has a lower energy density than conventional marine gas oils, which means that a larger storage volume is required, which makes storage under high pressure necessary [67]. Although hydrogen combustion does not cause carbon emissions, the current industrial hydrogen production method of steam methane reforming (SMR) contributes significantly to greenhouse gas emissions [68–70]. Renewable hydrogen processes can significantly reduce carbon emissions associated with hydrogen production and consumption by eliminating the energy conversion losses and GHG emissions associated with conventional steam reforming [71–75]. Recent studies have shown that the indirect global warming potential of hydrogen over a 100-year horizon can be 11 ± 5 [76], which is more than 100% higher than previously estimated values of 5 ± 1 [77,78]. This indicates a 4–16 times greater impact on global warming than the mass-equivalent CO_2 yield would produce over the following 100 years and can potentially become an additional obstacle in large-scale hydrogen use.

As ammonia production uses hydrogen as a reactant for the Haber–Bosch production process and both ammonia and hydrogen are potential alternative marine fuels, they are compared from the aspect of their global warming potential indicators (GWP) for a 100-year period in Table 2.

Table 2. Global Warming Potential indicators for the 100-year horizon [65,76–82].

Gas Type	Chemical Designation	GWP$_{100}$
Carbon dioxide	CO_2	1
Methane	CH_4	21–36
Nitrous oxide	N_2O	310–365
High-GWP gases	CFCs, HFCs, HCFCs, PFCs, SF6	2–23,900
Ammonia	NH_3	0 [1]; (1.12–140) [2]
Hydrogen	H_2	4–16

[1] Only combustion. [2] Including production and long-term emissions.

Although ammonia itself is considered a zero GWP100 carbon-free compound, there are issues with using ammonia as a decarbonization fuel in the maritime industry, such as lack of appropriate ammonia-fueled power generators, safety assessment procedures, and hazard mitigation measures [10,83]. MAN Energy Solutions work on commercially viable internal combustion engines fueled with ammonia has provided several insights into the use of ammonia as a fuel. It has been found that some of the materials used in internal combustion engines are intolerant of ammonia and that the combustion properties of ammonia are lacking with significant NOx with potential N_2O and ammonia emissions [84].

1.3. Hydrogen Projects

The generation and storage of energy in the form of hydrogen and the application of fuel cells as an energy source are being studied and researched for both terrestrial [85–87] and marine systems [88–90]. A comparative analysis of 106 projects currently underway

focused on transitioning to full pollutant reduction in the maritime sector found that the number of projects related to the use of alternative fuels is increasing significantly for pre-2020 projects, while the number of projects related to biofuels, batteries, and the use of wind energy is decreasing at the same time. There is a strong preference for projects focused on the production of hydrogen and hydrogen-based fuels for the maritime industry [91]. To approach the EU carbon neutrality strategy and reduce carbon emissions by 2050 [92], the REFHYNE green hydrogen project was planned with the intention of building a 10 MW hydrogen proton exchange membrane electrolyzer plant by the end of 2022 [93]. Siemens has commissioned a carbon-neutral 8.75 MW proton exchange membrane (PEM) electrolysis plant in Germany, the capacity of which can be increased to 17.5 MW in the future [94]. In the USA, there are plans to build an alkaline electrolysis plant with an estimated production of 10 tonnes of hydrogen per day [95]. In China, a 20 MW hydrogen electrolyzer plant has already been built and is planned to be expanded to 60 MW by 2024 [96]. The project cost for alkaline electrolyzers in China has been estimated at 354 EUR/kW. This is about 75% lower than the estimated project cost for electrolyzers in Western countries of 1238.44 EUR/kW. However, this price reduction is not primarily caused by inherent differences or advantages of the technology used, but to lower labor costs and up-stream domestic market supply [97]. A secondary reduction in price is achieved with the use of thicker electrolyzer stack separators and older type porous nickel electrode materials, which lowers current density and hydrogen production efficiency. This affects electrolyzer reliability, shortens the expected operating time, and increases the overall levelized cost of energy [98]. Although the construction of green hydrogen production plants has started worldwide, there is still a lack of efficient and safe hydrogen storage and distribution infrastructure, which is a critical problem for hydrogen as a fuel [99].

1.4. Hydrogen Maritime Regulatory Framework

Even though the marine transport hydrogen market potential is clearly significant, procedures and standards for hydrogen generation, storage, and distribution, as well as for fuel cell systems on ships, are not yet fully defined. Since hydrogen is considered a low-flashpoint fuel, the International Code of Safety for Ship Using Gases or Other Low-flashpoint Fuels (IGF Code) applies, even though this standard primarily relates to liquefied natural gas [100]. The safety aspects of using and transporting liquefied hydrogen on ships are also defined in [101]. In addition, reference is made to regulations and instructions from ship classification societies that specify classification requirements for fuel cell systems from the perspective of safety, fire protection, management, regulations, and monitoring [102–104]. Due to the insufficiently clear legal framework, classification societies require the assessment of marine vessels in all stages of development, construction, and installation [105]. The remaining undefined legal aspects and potential ambiguities are determined and identified by a risk assessment [106–108]. Other standards that have been applied or developed to meet the needs of terrestrial systems that may impact the use of hydrogen in marine applications are discussed in [109–112].

2. Hydrogen Production

Hydrogen is flammable, odorless, colorless, and tasteless gas. It is considered to be one of the most promising alternative energy sources with potential to replace the current reliance on fossil fuels. Although hydrogen is one of the more common elements in the known universe, naturally occurring gaseous or elemental hydrogen is rare and is usually commonly bound in water and hydrocarbon compounds [68,113,114]. For that reason, hydrogen must be artificially produced and stored prior to its use. The physical properties of hydrogen under standard conditions are presented in Table 3.

Table 3. Physical properties of hydrogen [113–119].

Property	Symbol	Value
Gas density	$\rho_{H_2,g}$	0.0807 kg/m^3
Liquid density	$\rho_{H_2,l}$	70.8 kg/m^3
Specific heat capacity	C_p	14.199 MJ/kgK
Lower explosion limit in air	LEL	4%
Upper explosion limit in air	UEL	77%
Lower detonation limit in air	LDL	18.3%
Upper detonation limit in air	UDL	59%
Autoignition temperature	AIT	559.85–585 °C
Minimum ignition energy	MIE	0.19 MJ

Hydrogen produced on-site can be used in the production facility itself, or it can be sold to an external hydrogen merchant company. A cluster of industrial consumers or a single large hydrogen consumer can be served by a dedicated large industrial installation, while small retail consumption usually does not require a separate production facility. In these situations, hydrogen can be delivered and distributed by established transportation methods [66]. It can be used as an industrial process feedstock as well as a fuel cell or internal combustion engine energy source. Considering its low GWP$_{100}$, it has a potential to serve as an energy carrier in energy storage systems powered by intermittent renewable electrical power sources. The annual global production of hydrogen is estimated at 120 metric tons. Approximately 62.5% of this production is comprised of pure hydrogen gas, while the rest is a mixture of hydrogen and other gases [120]. Depending on the method of production and interpretation of technical standards, the carbon footprint of produced hydrogen can vary substantially [121]. Artificially generated elemental hydrogen can be classified with respect to the energy source used to produce it, required technology, production process, and application. Color-based classification is one of the primary methods utilized to describe hydrogen types [122,123] based on currently available production methods and technologies, as presented on Figure 1.
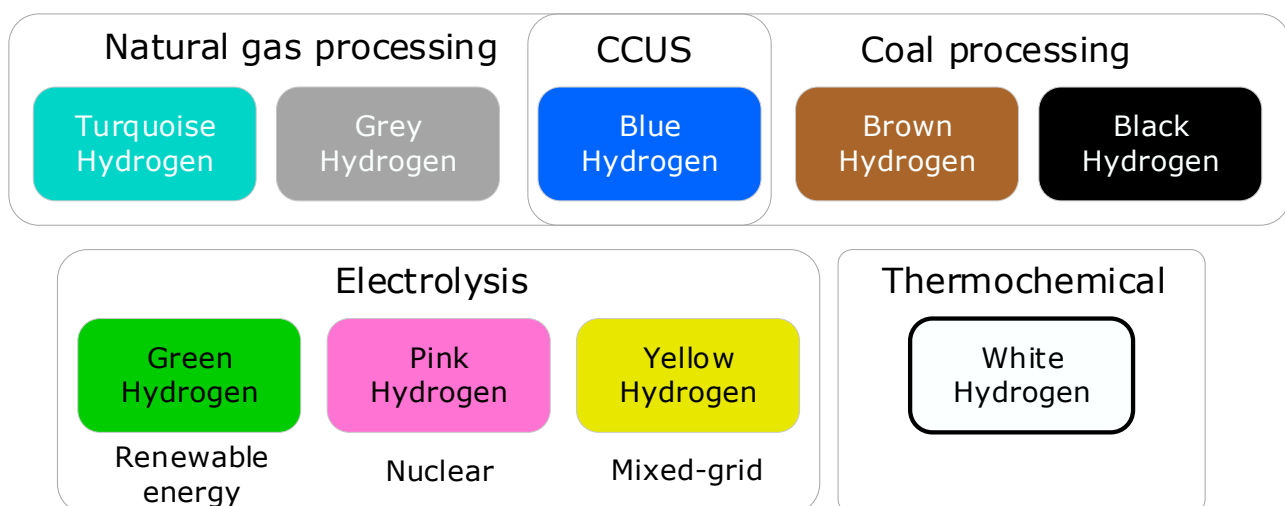
Figure 1. Hydrogen color-based classification methodology.

2.1. Gray Hydrogen

Initially, hydrogen was differentiated into hydrogen derived from fossil fuel feedstock by hydrocarbon reaction processes such steam reforming, also called gray hydrogen, while green hydrogen referred to hydrogen produced by the process of water electrolysis. This distinction is inadequate as new potential technologies and production methods are being researched and implemented [73,122,124,125]. Gray hydrogen now refers to the hydrogen

produced by the most common and widely used industrial method of natural gas steam reforming without any application of carbon capture, utilization, and storage (CCUS) methods or technologies. In the process of steam reforming, high-temperature steam is used to chemically react hydrocarbon fuel forming syngas, a mixture of hydrogen and carbon monoxide. Although a variety of hydrocarbon-based gases can be used [126,127], a commonly used fuel for hydrogen production is methane [127].

Process of steam reforming begins by partially reacting hydrocarbon fuel (methane) with steam at 900 °C temperature and pressures between 1.5 and 3.5 MPa. This endothermic or heat-absorbing reaction produces syngas with a ratio between hydrogen and carbon monoxide on the order of 3:1, according to Equation (1) [128–130]:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{1}$$

In order to further increase the quantity of produced hydrogen, the process continues with a water–gas shift reaction. The addition of steam or condensate is used to reduce effluent gases temperature to around 370 °C, after which carbon monoxide reacts with the steam in a shift converter in the presence of iron-oxide. This exothermic or heat-releasing reaction forms additional hydrogen and carbon dioxide according to Equation (2) [128–130]:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{2}$$

This gives the net chemical process for steam methane reforming according to Equation (3) [128–130]:

$$CH_4 + 2H_2O \rightarrow CO_2 + 4H_2 \tag{3}$$
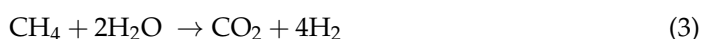
In order to finalize the process, a hydrogen purification and separation step is carried out by pressure swing adsorption process where pure hydrogen is separated from added carbon dioxide and other impurities [131,132]. During this process, four moles of hydrogen can be produced from a single molecule of a methane and water molecule pair. Although it is evident that for every four moles of hydrogen, only one mole of byproduct carbon dioxide is produced, the chemical reaction is endothermic. This means that in order to sustain a chemical reaction, it is necessary to provide additional heat to the system. In cases where the necessary heat is provided by the combustion of natural gas or fossil fuels, CO_2 emissions can significantly increase, with reported values of up to 41% of total CO_2 emissions [99,133]. Even if the heating energy could be provided in some other way, a single mole of CO_2 represents a carbon footprint equal to that of the direct combustion of natural gas or methane [128]. This is the primary reason why the production of clean hydrogen by steam reforming is not environmentally suitable if the process presumes the release of coproduced CO and CO_2 into the atmosphere. The second major issue is the efficiency of the steam reforming process. Due to conversion losses, a portion of the original hydrocarbon fuel's energy is lost without a positive environmental benefit. The typical hydrogen yield in steam reforming process is 70% with CO_2 concentrations as high as 20%, which can limit its potential uses [68,134]. The steam reforming of natural gas typically generates 8 or 9 $kgCO_{2eq}/kgH_2$ [99,135,136]. Different studies suggest an even higher environmental impact between 10.9 and 13.8 $kgCO_{2eq}/kgH_2$ [137,138]. This correlates with 2030 and 2050 estimates of 11 $kgCO_{2eq}/kgH_2$ for gray hydrogen produced from Russian natural gas transported over 5000 km [139]. In cases where steam reforming CO_2-emission mitigation is being researched, however, resulting CO_2 emissions are still comparably high with reports of 6.3–7.25 $kgCO_2/kgH_2$ [140,141].

2.2. Black and Brown Hydrogen

Black or brown hydrogen is derived from the coal gasification of bituminous (black) and lignite (brown) coal, respectively. Hydrogen produced by the gasification of biomass feedstock other than coal is not usually designated as black/brown hydrogen [122]. Nevertheless, the core of the waste-to-energy (WtE) or waste-to-hydrogen (WtH) processes

is similar to that of black/brown hydrogen [142]. Suitable waste includes but is not limited to the following: wood waste, municipal solid waste, discarded packaging, plastics, biodegradable waste, recyclable waste, and inert waste [143]. Biomass gasification converts carbon-based feedstock through partial oxidation into a gaseous mixture that can contain hydrogen, methane, hydrocarbons, carbon monoxide, carbon dioxide, and nitrogen [144]. Coal is a widely used feedstock for the biomass gasification process. It commonly contains carbon, hydrogen, oxygen, nitrogen, sulphur, and chlorine with other trace elements [145]. Coal is ordinarily gasified at temperatures greater than 900 °C, under pressures ranging between 1 and 10 MPa in gasification processes such as fixed-bed gasification, moving-bed gasification, fluid-bed gasification, or entrained-flow gasification [146,147]. Gasification can include pyrolytic, reforming, and water–gas shift reaction, partial oxidation and methanation processes described by Equations (4)–(8) [69,145,148,149]. During the fast pyrolysis stage, coal is thermally degraded in the absence of air as per Equation (4):

$$C_nH_mO_y \rightarrow tar + H_2 + CO_2 + CH_4 + C_2H_4 + \cdots \qquad (4)$$
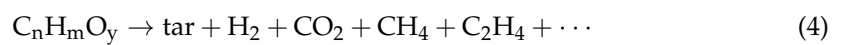
This removes water content and releases volatile products. The quality and dryness of the coal can therefore impact gasification thermal efficiency. Water vaporization and devolatilization can have a significant effect on thermal efficiency and the resulting calorific value of the produced syngas in cases where coal used as feedstock has high moisture content, or in cases where the feedstock is a coal–water slurry [150]. After drying and devolatilization, crushed and pulverized coal reacts with steam and/or oxygen under high temperature and pressure and produces a gaseous mixture of carbon dioxide, carbon monoxide, hydrogen, and other trace elements. This is similar to the steam reforming stage in the gray hydrogen steam methane reforming process and can be described with Equation (5):

$$tar + xH_2O \rightarrow xCO + yH_2 \qquad (5)$$

Carbon dioxide is reformed according to Equation (6):

$$tar + CO_2 \rightarrow xCO + yH_2 \qquad (6)$$

Processed hydrocarbons undergo partial oxidation and produce carbon monoxide and hydrogen as per Equation (7):

$$C_nH_m + \frac{n}{2}O_2 \rightarrow nCO + \frac{m}{2}H_2 \qquad (7)$$
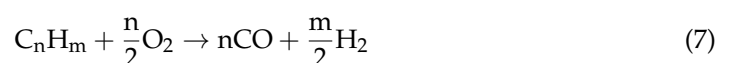
The increase in hydrogen concentration is calculated according to the water–gas shift reaction described in Equation (2). The further purification of hydrogen involves methanation as per Equation (8).

$$CO + 3H_2 \rightarrow CH_4 + 2H_2O \qquad (8)$$

Methanation removes trace amounts of carbon monoxide from the produced gas and allows the use of purified hydrogen in ammonia synthesis. One of the reported coal gasification advantages is the conversion of high moisture and ash content feedstock into a useful product and high cold gas efficiency syngas production [151,152]. Coal gasification process efficiency differs according to the type of coal feedstock and gasifier technology. For various gasifier technologies, the calorific efficiency of the produced gas (cold gas efficiency) is reported to be between 78 and 80% [146]. A joint Japan–Australia brown hydrogen Hydrogen Energy Supply Chain (HESC) project for the production and distribution of liquified hydrogen launched in 2018 with the aim to produce 22,500 tons of hydrogen per year [153]. It was promoted as an important step in establishing a low-emission commercial hydrogen production technology, a hydrogen export industry, and the development of purpose-built ships for overseas liquid hydrogen transport [154,155]. Prior to project implementation, a comparative hydrogen pathway study was performed. It was found that

the brown coal pathway with CCS financially outperforms renewable solar- and/or wind-powered hydrogen production by 0.01159–0.03026 EUR/MJ, but suffers from CCS scaling restrictions and a limited brown coal supply [156]. Emissions from coal-based hydrogen production systems are found to be significant even with CCS implementation. Fossil-based hydrogen production with CCS is estimated to be competitive to gray hydrogen only with carbon prices between 22.59 and 47.23 EUR/tCO$_{2eq}$ [157]. A proposed HESC project [158] approach to brown coal hydrogen production would release 40 gCO$_2$/MJ [159]. Black/brown hydrogen pathway costs in China are still relatively low. The coal-based hydrogen cost is estimated to be approximately 50% that of renewable hydrogen, which makes it competitive on the market [160,161]. In 2020, China produced 471,882 Mt of coke fuel with a predicted future rise in production [162]. A new coal-to-hydrogen project with hydrogen production capacity of 350,000 tons per year was put into operation in Yulin, China. The carbon dioxide reduction is estimated to be 220,000 tons per year based on an annual operating time of 8000 h [163]. The gasification of feedstock other than coal usually has lower thermal and conversion efficiency due to lower volumetric energy density and higher moisture content. The mixed feedstock gasification of waste can produce output gas with a hydrogen concentration of up to 82% [143]. This level of hydrogen purity is not high enough for direct use in various industrial processes, fuel cells, and hydrogen-powered vessels, so the hydrogen still needs to be concentrated.

2.3. Blue Hydrogen

Due to the fact that black, brown, and gray hydrogen production processes inherently produce GHG emissions, the reduction in generated CO$_2$ cannot be mitigated at the level of the process itself. For this reason, carbon capture, utilization, and storage (CCUS) methods or technologies are being applied to fossil fuel hydrogen production. This combination of conventional hydrogen production and new innovations in carbon removal and sequestering are referred to as blue hydrogen. CCUS encompasses a variety of methods that capture CO$_2$ from large production sources or directly from the atmosphere [164]. Industrial processes and power generation plants can implement carbon capture and storage (CCS) systems in order to avoid CO$_2$ emissions. Captured CO$_2$ can be compressed and carried in the pipeline or transported by road, railway, or sea for use in various applications. Alternatively, captured CO$_2$ can be sequestered and trapped underground as a permanent storage solution. The Bio Energy with CCS (BECSS) goal is CO$_2$ removal from the atmosphere with a focus on waste biomass/biofuel energy applications. Direct air capture (DAC) as a standalone application aims to remove atmospheric CO$_2$, while the exclusive carbon capture and utilization (CCU) purpose is typically oriented towards replacing fossil with captured carbon. The potential cost of CCUS-enabled blue hydrogen production is approximately 50% of the equivalent green hydrogen production, which makes blue hydrogen competitive in areas where the price of fossil fuels is relatively low. A secondary benefit can be found in the fact that CCUS technologies have the potential to mitigate emissions in existing brown, black, and gray hydrogen production facilities that are associated with over 800 metric tons of CO$_2$ per year [165]. In the effort to reduce carbon emissions, blue hydrogen capture methods are primarily focused on the removal and sequestration of CO$_2$ produced as a byproduct of the gray hydrogen production process and carbon extraction from flue gases created by natural gas combustion that is used to provide heat for the steam methane reforming process. Less obvious GHG emission pathways in the blue hydrogen process comprise secondary emissions of CO$_2$ and methane caused by the energy consumption of carbon capture equipment [59]. The carbon capture efficiencies of CCUS technologies have significant variation. Efficiency estimates for a steam methane reforming based hydrogen plant with CCS technologies focused on capturing shifted syngas, flue gas, and pressure swing adsorption tail gas were reported to be in the range between 50% and 90% [59,166–168]. In the case of autothermal reforming and natural gas decomposition, efficiency was presumed to be between 53% and 85% [167]. In the steam reforming process there is intentional and routine atmospheric venting or flaring of unburned methane [169].

This additional emission coupled with potential leaks in the system must be taken into account when considering blue hydrogen GHG emission values and CCUS efficiency [59,170]. It was shown that the CO_2-induced costs higher than 483 EUR per ton of emitted CO_2 could make green hydrogen cheaper than gray hydrogen, but that the difference is considerably higher when blue hydrogen is taken into account [171]. Even though the long-term advantages of blue hydrogen are still unclear, blue hydrogen is considered a hydrogen production pathway that can enable the global transition from conventional hydrogen production processes towards green and renewable hydrogen [122]. A regulatory framework that separates gray, blue, and green hydrogen is provided by [172–174]. Clarification and distinction are made between low-carbon hydrogen and renewable hydrogen according to emission reduction and the energy content generation pathway. Renewable hydrogen is defined as hydrogen that derives its energy content from renewable sources other than biomass while at the same time achieving a 70% GHG emission reduction when compared to fossil fuels. In comparison, low-carbon hydrogen refers to hydrogen where the energy content is derived from non-renewable sources that meets the GHG emission reduction threshold of 70% compared to fossil-fuel-based hydrogen. Although this addresses uncertainties that can impact future research in CCUS technologies, one major issue remains, and that is a lack of an exact regulatory framework methodology for the calculation and determination of green and blue hydrogen [175]. CertifHy Steering Group, however, has proposed recommendations and guidelines for renewable and non-renewable hydrogen carbon footprint calculation [176]. Some countries provide subsidies for the implementation of CCUS in blue hydrogen production that attempt to address the health and environmental costs that arise from pollution underpricing [177]. USA announced a regulatory framework for a tax credit allowance for ultra-low-carbon hydrogen production with subsidies of up to 3 USD/kg [178–180]. In 2020, the Netherlands granted a SDE++ 5 billion EUR subsidy to the CCUS industry over a period of up to 15 years [181] and 2.4 billion EUR in 2021 [181,182]. The Port of Amsterdam is part of a Hydroports Hydrogen Hub project and expects the development of a blue hydrogen production facility that can facilitate the international maritime transition to hydrogen [183–185]. Although it is claimed that the introduction of subsidies can be easier than the taxation of polluting technologies, subsidies often fail to achieve stated goals, overburden the public budget, negatively impact the market, and prove to be difficult to remove after the subsidized industry becomes codependent [177]. The European Union has subsidized CCUS projects with 587 million EUR without clear long-term results [186]. Germany has declined granting subsidies to blue hydrogen in favor of green hydrogen production due to uncertainties regarding oil and gas market volatility coupled with the unclear GHG emission production value of blue hydrogen production facilities [187].

2.4. Turquoise Hydrogen

The turquoise hydrogen production process is based on methane pyrolysis where the primary process outputs are hydrogen and solid carbon as per Equation (9) [188]:

$$CH_4 \rightarrow 2H_2 + C \tag{9}$$

An advantage of the thermal decomposition of methane is the absence of oxygen, which prevents the formation of carbon oxides in the reaction stage. Instead of carbon oxides, the process produces solid carbon that can be stored in the form of filamentous carbon, carbon nanofibers, or carbon nanotubes [189,190]. Unreacted methane in the produced gaseous mixture can be removed by absorption or membrane separation, which can increase the hydrogen concentration to 99% by gas volume [189]. In comparison to the steam methane reforming process, the pyrolysis of methane produces approximately 50% less hydrogen per mole of methane, with 45.26% lower energy consumption [191]. As a consequence of strong carbon–hydrogen bonds, the conventional thermal decomposition of methane requires high temperatures, above 1000 °C [188,192,193], which can be lowered through the use of metal catalysts such as cobalt, iron, nickel, or carbon-based catalysts

such activated carbons or carbon black [194]. It has been discussed that, in contrast to pure methane decomposition, natural gas contains other chemical compounds, such as CO_2, water, higher hydrocarbons, and sulphur compounds that can chemically react during pyrolysis and have an impact on the composition of the process output as well as the process selectivity and conversion rate [195]. The carbon intensity of turquoise hydrogen can be up to 90.8% lower than that of gray hydrogen with potential to achieve a negative carbon intensity of up to -10.40 $kgCO_2/kgH_2$, if renewable natural gas is used as feedstock [196]. A techno-economic study showed that the thermocatalytic decomposition of methane from biogas is financially viable only on large scales, where the process plant is diversified with respect to multiple product streams [197]. Despite it being a known technology, the turquoise hydrogen process is not yet widely implemented. Nevertheless, there are companies and projects that attempt to establish turquoise hydrogen as a possible global pathway to decarbonization [198–203].

2.5. Green and Yellow Hydrogen

Research, reports, and studies intermix nomenclature for gray, blue, yellow, and green hydrogen [121,122]. Renewable hydrogen refers to hydrogen that derives its energy content from renewable sources other than biomass while at the same time achieving a 70% GHG emission reduction when compared to fossil fuels [172–174]. At first, green hydrogen referred to any hydrogen produced from renewable resources [204,205]. This ordinarily suggests hydrogen produced through the process of water electrolysis powered by renewable sources of energy, such as photovoltaics or wind turbines [206,207]. With the expansion of new technologies, green hydrogen terminology was adapted to consider potential GHG emission impact, energy concerns, or other climate effects generated by the production methodology [208–211]. Electrical energy that powers the process of water electrolysis does not have to be produced exclusively by renewable power sources but can also be provided from a power grid. Hydrogen produced by the process of electrolysis where energy is supplied by a power grid electricity mix is designated as yellow hydrogen [122,123]. Even though the electrolysis process produces no CO_2 emissions by itself, the electrical energy that powers the production process can attribute significant GHG emissions to the overall process of hydrogen production. In Europe, the value of emissions related to the power grid electricity mix in Europe varies significantly between countries [212,213]. A high GHG intensity for some EU member states in 2020 was the result of solid fossil fuel consumption, relatively low renewable power plant capacity, and limited nuclear power in the national electricity mix. Greenhouse gas intensity was lowest in Sweden at 8 gCO_{2e}/kWh while Poland had the highest GHG intensity with 710 gCO_{2e}/kWh [212,213]. In order to mitigate uncertainties with respect to the blue and gray hydrogen, gradient assessment has been proposed where the primary metric is the Hydrogen Cleanness Index (HCI), which takes into an account the following: direct, indirect, third-party, and hydrogen-purification-related CO_2 emissions [61]. Recent EU regulations have been put in place to clarify differences in hydrogen types [172–174] that make a clear distinction between low-carbon and renewable hydrogen that focuses on a 70% reduction in GHG emissions when compared to fossil fuels [172–174].

Three primary technologies for green hydrogen water electrolysis are the following: alkaline water electrolysis (AEL), proton exchange membrane electrolysis (PEMEL), and solid oxide electrolysis (SOEL) [99,214,215].

Alkaline water electrolysis is considered to be a mature state-of-the-art technology [99]. Alkaline electrolyzers consist of electrodes submerged in the electrolyte solution, separated by a permeable diaphragm. The electrolyte solution is typically a high-conductivity solution such as aqueous potassium hydroxide [216,217]. There is an electrical current that passes between the electrodes and through the electrolyte. Water is reduced to hydrogen and

hydroxide ions at the cathode, while, at the anode, negatively charged hydroxide ions are oxidized according to Equations (10)–(12):

$$H_2O + 4e^- \rightarrow 2H_2 + 4OH^- \tag{10}$$

$$4OH^- \rightarrow O_2 + 2H_2O + 4e^- \tag{11}$$

$$2H_2O \rightarrow O_2 + 2H_2 \tag{12}$$

The gas and electrolyte mixture is transported from the electrodes towards the phase separation tank, which removes produced gases from the electrolyte, which is then returned to the electrolysis cell. The principal advantage of alkaline electrolyzers is a high production capacity of up to 750 Nm^3/h, which makes them suitable for large industrial applications. The cost of electrodes is relatively low as they are ordinarily made from iron or nickel [217]. The highest efficiency of a conventional alkaline electrolyzer is in a range between 68% and 77% at working temperatures between 60 °C and 90 °C. The typical current density is reported to be 0.3 A/cm^2, although higher current densities of up to 2 A/cm^2 have been reported [215,218]. The disadvantages of alkaline electrolyzers are a relatively low efficiency and rate of hydrogen production, the corrosive nature of the electrolyte solution, and the current density constraint due to ohmic resistance [217]. Hydrogen purity is proportional to electrolyzer current density and alkaline electrolyzer underloading is expected to produce a hydrogen mixture with more impurities that can potentially become explosive. For that reason, the minimal acceptable load of alkaline electrolyzers is in a range between 10% and 25% of the nominal load [214]. Research on the use of alkaline electrolyzers for hydrogen production in harsh marine environments for off-shore applications has showed that alkaline electrolyzers do not show any significant morphological or compositional change in the presence of salt spray [219].

In PEMEL electrolysis, the liquid electrolyte is replaced with a proton exchange membrane (PEM) configured in zero-gap configuration in which electrodes directly contact the surface of the proton membrane. Electrochemical reactions in a PEMEL electrolyzer can be expressed with Equations (13) and (14) [99,220]:

$$H_2O \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^- \tag{13}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{14}$$

Firstly, oxygen and protons are formed at the anode. Newly formed protons are able to pass through the proton exchange membrane towards the cathode where they are reduced to molecular hydrogen. The efficiency of a PEMEL electrolyzer is determined primarily by the electrode and membrane material. The cathode is ordinarily made from platinum-coated carbon, while a common membrane material is Nafion® polimer [221]. The advantages of a PEMEL electrolyzer arise from the zero-gap design, which makes the dimensions and size of the electrodes and membrane more flexible and compact. The distance between the electrodes is constrained by the thickness of the proton exchange membrane and is typically between 100 and 200 μm. The working temperature of PEMEL is ordinarily less than 100 °C with reported efficiency of 70% at current densities of 1 A/cm^2. Higher current densities of up to 15 A/cm^2 are possible, however with significantly lower efficiency [222]. Project NEPTUNE, however, demonstrated that an Aquivion® membrane electrolyzer with a Pt-Co catalyst can operate with a relatively high current density of 4–8 A/cm^2 at the operation temperature of 90 °C [223]. As PEMEL do not use corrosive or toxic electrolytes, they are considerably safer than alkaline electrolyzers. They do not suffer from the same partial-loading issues as alkaline electrolyzers and therefore can be directly powered by electrical power sources with variable or unstable voltages or currents [224]. The production rate is relatively low, at approximately 50 Nm^3/h. The disadvantages of PEMEL electrolyzers are the high electrode and membrane material cost, relatively short life cycle, and required use of highly distilled or deionized water [225].

Solid oxide electrolysis is based on the electrolytic splitting of water vapor at high temperatures [226]. Solid oxide electrolyzers operate on considerably higher temperatures than alkaline or proton exchange membrane electrolyzers. The typical operating temperature range for solid oxide electrolyzers is between 700 °C and 1000 °C. This high operating temperature improves electrolysis efficiency up to 90%, but it also accelerates system component degradation [218]. The electrolyte is ordinarily made from thin ceramics that allow the conduction of oxide ions. The ceramic electrolyte is typically zirconium dioxide ceramic stabilized with yttrium or scandium oxides with thicknesses between 30 μm and 150 μm [130]. The cathode is typically made from oxides based on perovskite and must be highly porous in order to ensure oxygen diffusion towards the electrolyte. Anode is usually made from platinum, although other materials such as nickel are being researched in order to reduce the material cost [227]. The electrochemical reactions of cathode and anode can be expressed with Equations (15) and (16):

$$H_2O + 2e^- \rightarrow H_2 + O_2^- \tag{15}$$

$$O^{2-} \rightarrow \frac{1}{2}O_2 + 2e^- \tag{16}$$

Water supplied to the cathode reduces to hydrogen and oxide ions. Negative oxide ions permeate the ceramic electrolyte and cross to the anode where they oxidize to form oxygen. The current density of a solid oxide electrolyzer is higher than in alkaline electrolyzers but still lower than in proton exchange membrane electrolyzers with a typical range between 0.3 and 0.8 A/cm^2 [228]. Higher working temperatures reduce the energy needed for a water-splitting reaction and increase power-to-hydrogen efficiency. This is particularly interesting in cases where thermal energy required for steam generation is supplied externally and is otherwise treated as a process byproduct or waste heat. Combining hydrogen production with other chemical reactors can be used to produce several output fluids such as ammonia, methanol, or formic acid [229]. Although they have high efficiency, their production capacity is relatively small, at approximately 40 Nm^3/h [230]. Solid oxide electrolyzers have shown promise in seawater splitting with an energy conversion efficiency up to 72.47% and maintained hydrogen production of 183 mL/min [231]. Solid oxide electrolyzers have been supported globally through projects such as RelHy [232], NewSOC [233], eGhost [234], and Liquid fuels R&D Project [235] with an aim to improve the performance, durability, and cost-competitiveness of solid oxide systems.

The membraneless electrolyzer does not use a membrane or diaphragm to separate cathode and anode. The overall separation and transportation of hydrogen and oxygen products is based on the Segre–Silberg effect [99]. The primary effects are advection caused by forced flow of the fast moving fluid as well as buoyancy forces exerted on hydrogen and oxygen products created at the electrodes [236]. The chemical reactions on the anode and cathode are expressed by the Equations (17) and (18):

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{17}$$

$$H_2O \rightarrow 2e^- + 2H^+ + \frac{1}{2}O_2 \tag{18}$$
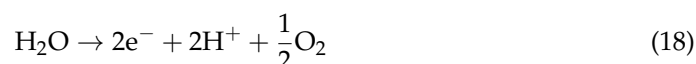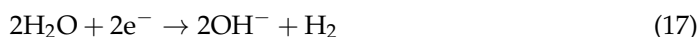
Hydrogen and oxygen bubbles that are formed near the electrodes stay there and do not migrate through the electrolyte due to the high electrolyte flow gradient [99,236]. The liquid electrolyte flows parallel to the electrodes and carries hydrogen and oxygen towards the separate output channels. The advantage of a membraneless electrolyzer is the removal of the electrode-separating membrane, which simplifies the electrolysis system and reduced the overall costs. They can operate at any pH level with a simple configuration and low component count [237]. Membraneless electrolyzers can be scaled up without added complexity and negatively impact the production process only by increasing the size of the electrodes [238]. Due to the lack of a membrane, impurities or particulate matter in the liquid electrolyte can increase the ionic conductivity of the electrolyte and negatively impact

the electrolyzer efficiency [239]. A disadvantages of membraneless electrolyzers is the lower efficiency caused by the relatively high distance between the electrodes that increases system ohmic resistance. The efficiency of the membraneless electrolyzer is ordinarily in a range between 60% and 68% at current densities of 0.2–0.6 A/cm^2 [240] although there are reported higher current density systems with 0.75 A/cm^2 [241]. At higher current densities, product separation becomes a challenge. At a current density of 0.3 A/cm^2, hydrogen crossover can become significant and the hydrogen–oxygen mixture can potentially be within the flammability limit [242]. Membraneless electrolyzers are due to their robustness and flexibility investigated as a potential seawater hydrogen production system [243].

2.6. Purple/Pink Hydrogen

Nuclear power enables different hydrogen production pathways depending on if the nuclear power is used as a thermal or electrical energy source. These comprise thermochemical water splitting, low- and high-temperature water electrolysis, or steam methane reforming pathways [244]. Purple or pink hydrogen refers to hydrogen production from nuclear power [123]; however, the primary energy pathway is nuclear electrical energy [122]. Depending on the reactor type, thermal energy capacity can be between 1400 and 2500 MW$_{thermal}$ with an electrical energy capacity in the range of 560–1000 MW$_{electrical}$. This corresponds to an average outlet temperature between 300 and 950 °C [244]. A nuclear reactor can operate at base load, but it can also follow the power grid demand that varies over the course of the day. Nuclear power plants are not ordinarily operated in load-following mode but instead provide base load electricity supply to the power grid [245]. The base load can be adjusted to incorporate hydrogen production facilities so the excess energy can be stored as hydrogen [246]. This is conducive to both low- and high-temperature hydrogen electrolysis production technologies. Current globally measured uranium resources are sufficient to last approximately 90 years [247]. The limited supply of uranium-235 and technical obstacles hinder large-scale expansions of nuclear power, which can inhibit long-term nuclear-based hydrogen production [248].
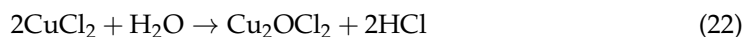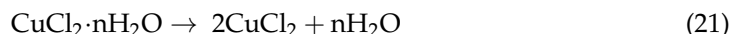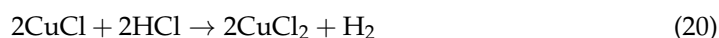
2.7. White/Red Hydrogen

White hydrogen is an ambiguous name. It is used to refer to naturally occurring or geological hydrogen that is stored in natural deposits [249–251]. A new proposal for color coding the white hydrogen connects the color-coding scheme with previously unconnected hydrogen production processes of thermal and thermochemical water splitting [252]. These processes are sometimes referred to as red hydrogen [253].

Water thermolysis is a direct thermal decomposition of a water molecule into constituent hydrogen and oxygen according to Equation (19) [254]:

$$H_2O \rightarrow H_2 + \frac{1}{2}O_2 \tag{19}$$

Water thermolysis is energy intensive and requires high temperatures. The degree of dissociation depends on the process temperature with reported 4% at 2500 K and 64% at 3000 K [254] at 0.1 MPa atmospheric pressure. A major issue with this production method is the prevention of H2O recombination prior to hydrogen and oxygen separation. The second issue is the relatively high equipment cost associated with the high temperatures that occur during the process itself. In order to lower the temperature required for thermal splitting, it is possible to utilize redox materials. This thermochemical water splitting can reduce the process temperature down to 1000 °C [255]. In thermochemical cycles, used chemicals are internally recycled without environmental waste emission, which makes them ecologically preferable hydrogen production processes based on fossil fuels. There are over 300 different water-splitting cycles, some of which can be carbon-free while others entail GHG emissions [256–259]. One of the promising thermochemical water-splitting cycles is the Cu-Cl cycle. There are several types of Cu-Cl cycles (one-step,

three-step, four-step, or five-step). The four-step Cu-Cl cycle is described by the following Equations (20)–(23) [260,261]:

$$2CuCl + 2HCl \rightarrow 2CuCl_2 + H_2 \tag{20}$$

$$CuCl_2 \cdot nH_2O \rightarrow 2CuCl_2 + nH_2O \tag{21}$$

$$2CuCl_2 + H_2O \rightarrow Cu_2OCl_2 + 2HCl \tag{22}$$

$$Cu_2OCl_2 \rightarrow 2CuCl + \frac{1}{2}O_2 \tag{23}$$

The copper-chloride cycle begins with electrolysis where copper-chloride is oxidized in the presence of hydrochloric acid. This reaction generates hydrogen. Aqueous copper-chloride exits from the electrolysis cell and is crystalized to produce solid $CuCl_2$. Water-free solid $CuCl_2$ is hydrolyzed to produce copper oxychloride and hydrochloric acid. The hydrolysis reaction typically occurs at temperatures between 350 and 400 °C [262]. The last step is the decomposition reaction in which copper oxychloride is decomposed into oxygen and molten CuCl, typically at 530 °C. The copper-chlorine cycle is a promising thermochemical process due to its relatively low thermal requirements. This lower operating temperature means that the Cu-Cl cycle could potentially utilize process or waste heat from nuclear reactors in order to produce hydrogen. Drawbacks of the Cu-Cl cycle are hydrolysis issues with respect to the $CuCl_2$ decomposition temperature and excess steam that is not consumed during the reaction [260–263]. Recent improvements regarding excess steam consider the recirculation of unused steam and show an up to 50% potential reduction in hydrolysis thermal energy, which makes the Cu-Cl cycle a more viable solution [263]. It was shown that thermochemical cycles could have a lower impact on the environment than nuclear-powered low- and high-temperature electrolyzers [264]. Estimated costs for indirect thermochemical cycles powered by nuclear thermal energy are approximately 2.22–2.70 EUR/kg$_{H2}$ [265]. Concentrated solar thermal hydrogen production projects have been funded by the EU as an effort towards the uptake and commercial viability of thermal and thermochemical hydrogen production solutions [266].

2.8. Summary of Color-Coded Hydrogen Solutions

Hydrogen production solutions based on color coding describe various production methods that have different advantages and issues. Major advantages, disadvantages, problems, and obstacles of hydrogen production methods according to the color coding are summarized and presented in Table 4.

Table 4. Color-coded hydrogen: advantages, disadvantages, problems, and obstacles.

Color Coding	Production Method	Advantages	Disadvantages	Problems/Obstacles
Gray	SMR	- Mature technology - Cost effective	- High GHG emissions - Efficiency losses in SMR process	- GHG emissions released into the atmosphere - Fossil fuel dependent
Black/Brown	Gasification	- Mature technology - Can be utilized with various feedstock types	- High GHG emissions - Lower hydrogen purity	- GHG emissions released into the atmosphere - Fossil fuel dependent
Blue	SMR/Gasification with CCUS	- Used in conjunction with mature production processes - lower carbon footprint	- Residual GHG emissions - cost effectiveness varies on original production pathway	- Fossil fuel dependent - Requires subsidies - Lack of regulatory framework - Unclear long-term advantages
Turquoise	Pyrolysis	- Low carbon intensity due to solid carbon byproduct	- Lower hydrogen production - Low process selectivity and conversion rate	- Not widely implemented - Viable on larger scales where the production process is diversified

Table 4. *Cont.*

Color Coding	Production Method	Advantages	Disadvantages	Problems/Obstacles
Green	Renewable electrolysis	- Zero-carbon-emission pathway	- Relatively high production cost	- Lack of renewable power source infrastructure
Yellow	Grid-powered electrolysis	- Low-carbon-emission pathway	- Additional load on the existing power grid	- Highly dependent on the grid electricity price and grid-mix carbon intensity
Purple/Pink	Nuclear-powered processes	- Low-carbon-emission pathway	- Load-following requirements on nuclear power plants - Limited global supply of nuclear fuel	- Public opinion on nuclear power - Unfeasible large-scale nuclear power plant expansions
White/Red	Thermal/thermochemical water splitting	- Low-carbon-emission pathway - Internal recycling of used chemicals	- Energy intensive - Hydrolysis issues regarding decomposition temperature and excess steam	- High energy requirements - H_2O recombination - Use in conjunction with waste nuclear heat is limited by issues regarding large-scale nuclear power expansion

3. Hydrogen Storage—Principles and Safety Aspects

Even though the global majority of hydrogen production is based on the environmentally unfavorable method of steam methane reforming, hydrogen as an energy source is limited not by production capacity, i.e., the amount of hydrogen produced, but by problems associated with short- and long-term storage [267–269]. There are many different methods of hydrogen storage, which can be generally classified as the storage of elemental hydrogen and storage of chemically bonded hydrogen [55,270,271]. In the production processes of steam methane reforming and electrolysis, hydrogen is produced in the elemental state. The specific energy of hydrogen is relatively high and is equal to 120 MJ/kg or 33.33 kWh/kg [272]. The density of elemental hydrogen at a temperature of 25 °C can be determined according to Equation (24) [117]:

$$\rho_{H_2,25C} = 0.807 \cdot p_{H_2,25C} \tag{24}$$

where $\rho_{H_2,25C}$ is the density of hydrogen in the gaseous state at a temperature of 25 °C and $p_{H_2,25C}$ is the pressure under which hydrogen is stored, in MPa.

3.1. Compressed Hydrogen

At a temperature of 25 °C and a pressure of 0.1 MPa, the density of hydrogen is relatively low and is 0.0807 kg/m^3. Diesel fuel can have a density over 104 times higher than hydrogen under atmospheric conditions [273]. The density of hydrogen can be increased by compressing the gaseous hydrogen or by lowering the temperature at which the hydrogen is stored. When hydrogen is stored under pressure, the elemental hydrogen remains in a gaseous state, whereas when the temperature is lowered, the hydrogen is liquefied and stored in a liquid state. The pressure at which hydrogen is stored depends on safety requirements and the needs of the end consumers. Typically, hydrogen is stored at a pressure between 20 MPa and 100 MPa [274]. Hydrogen-powered hybrid trains and buses use hydrogen at a nominal pressure of 35 MPa. In the automotive industry, a higher pressure of 70 MPa is used due to the spatial limitations of hydrogen storage [275]. On hybrid and electric ships, which sail on relatively short distances, the hydrogen storage pressures explored and implemented are lower than in the automotive industry due to the complexity and hazards associated with higher hydrogen storage pressure. Hybrid ship power topologies with hydrogen storage pressures from 20 MPa to 350 MPa are being researched and implemented [107,273,276–279]. Hydrogen under a pressure of up to 25 MPa has a satisfactory energy density and acceptable spatial storage limitation only for extremely short distances with sailing times less than 5 min [88]. Increasing the pressure under which hydrogen is stored increases the energy density but also increases

the safety risks. At a temperature of 25 °C and a pressure of 70 MPa, the density of hydrogen increases from 0.0807 kg/m^3 to 56.49 kg/m^3. The energy density increases from 2.69 kWh/m^3 to 1882.8 kWh/m^3. The disadvantage of this method of hydrogen storage on ships is the increased complexity of the hydrogen filling, transfer, and storage system for high-pressure operation, the risk of fire and explosion, the loss of energy during pressurization, and the space limitations regarding the location of the ship's hydrogen tanks. In determining the stored hydrogen energy, it is important to consider the losses that occur during the compression process with respect to the energy contained in the compressed hydrogen. Compression losses of hydrogen can be in the range of 10–20% of the stored energy [280,281]. A further increase in pressure can have a significant impact on safety. In the event of damage to the tank, piping, or valves, the compressed hydrogen can suddenly escape from the tank and cause further damage to equipment or personal injury. When combined with air or oxygen, an explosive atmosphere is created that requires little energy to ignite or explode. The range of explosion limits for a mixture of hydrogen and air is between 4% and 77% and for a mixture of hydrogen and oxygen between 4% and 95.2% [280,281]. On ships, hydrogen tanks stored at pressures greater than 1 MPa must be located on the open deck [282,283]. For land-based systems, the storage area where the hydrogen tanks are located must be adequately ventilated, and the tanks must not be exposed to temperatures above 500 °C [284]. Storage must take into account the particular marine conditions that can have a corrosive effect on the tank, piping, and valves. When pressurizing or refilling hydrogen in marine tanks, the temperature rise caused by the adiabatic compression process must be taken into account. A temperature rise can lead to thermal stresses and damage to tanks, valves, and pipelines [275,285]. Pipeline losses depend on the volumetric flow, which makes the calorific value of hydrogen an important factor in evaluating pipeline transportation efficiency. When considering low molecular weight of hydrogen, the compression of gaseous hydrogen requires more work, which means either a higher compression speed or an increase in the number of compression stages [286]. Depending on the initial pressure and temperature of stored hydrogen, unrestricted expansion can either increase or decrease the hydrogen temperature according to the Joule–Thomson coefficient. At room temperatures, the Joule–Thomson coefficient of hydrogen is negative, so the expanding gas temperature increases. This potential for autoignition is a significant safety consideration during stages of the compression, transport, and distribution of compressed hydrogen [286,287].

3.2. Liquid Hydrogen

The liquefaction of hydrogen is another method of storing hydrogen in its elemental state. Hydrogen liquefies at a temperature of −253 °C and has a density of 70.85 kg/m^3 at atmospheric pressure, which corresponds to an energy density of 2361.43 kWh/m^3 [288]. Liquefied hydrogen is typically stored at a pressure of 0.6 MPa [289]. Liquefaction increases the energy density of hydrogen, but also creates energy loss that occurs during the liquefaction process, which can be up to 35% of the total energy of liquefied hydrogen [271,281]. The liquefaction of hydrogen requires a process of compression, precooling, and isentropic expansion. At temperatures above −73 °C, hydrogen cannot be cooled by adiabatic or isentropic expansion. To reach this temperature, hydrogen must be cooled by other means, such as the vaporization of nitrogen [290]. Although there are several hydrogen liquefaction technologies, each process is relatively complex and requires expensive and complex equipment that can account for up to 50% of the total cost of the liquefaction process [290]. Only high-purity hydrogen is liquefied, which adds additional costs to the hydrogen production process. Compared to the liquefaction process, the distribution of liquefied hydrogen is fast and requires relatively little energy. The increase in hydrogen energy density achieved by the liquefaction process is not negligible, which is why liquefied hydrogen is being researched and used as an energy and power source for hybrid and all-electric marine energy systems [291–293]. All parts of the liquid hydrogen storage system that are in direct contact with liquefied hydrogen must withstand extremely low temperatures. Special

attention must be paid to the formation of ice, which can potentially cause the rupture of piping, valves, and tanks. The stored liquid hydrogen must be vaporized before it is fed to the fuel cells. Controlled vaporization is used to deliver the hydrogen to the fuel cells at an appropriate pressure and temperature [291]. As the stored liquid hydrogen vaporizes, the pressure in the tank increases. If the amount of evaporated hydrogen is greater than the total hydrogen consumption, the excess hydrogen must be released into the atmosphere, which can lead to increased energy losses.

3.3. Chemically Bonded Hydrogen

Chemically bonded hydrogen storage includes the processes of storing hydrogen in the solid state by absorption in solids or by adsorption on solid surfaces [294]. Although there are many different chemical processes, hydrogen storage in metal hydrides is the most commonly considered process in marine systems [295–298]. In metal hydride storage processes, molecular hydrogen splits into atoms near the metal. The individual hydrogen atoms are relatively small in size and can be stored in the crystal lattice of the metal. The advantage of this storage method is an increase in hydrogen density of up to 200% compared to liquefied hydrogen [289]. The disadvantage is poor gravimetric storage efficiency, which ranges from 1% to 8% [275,299]. At a gravimetric storage efficiency of 8%, 12.5 kg of metal hydride is needed to store one kilogram of hydrogen. The advantage of storing hydrogen in metal hydrides is increased safety. The release of hydrogen from metal hydrides is an endothermic reaction, so the tank containing the metal hydrides must be heated to release the hydrogen. In the event of a metal hydride tank rupture, hydrogen is released under relatively low pressure, and further release of hydrogen can be prevented by removing the heat source. The thermal energy required to release hydrogen from metal hydrides can be as much as 25% of the energy of the stored hydrogen [275]. Hydrogen storage in metal hydrides is more important in systems with limited oxygen availability, such as fuel-cell-powered submarines [300].

3.4. Summary of Hydrogen Storage Solutions

Different hydrogen storage solutions in marine sector differ in applicability, issues, and concerns. The advantages and disadvantages of hydrogen storage solutions are summarized and presented in Table 5.

Table 5. Comparison of hydrogen storage solutions.

Storage Type	Advantages	Disadvantages
Compressed	- Mature technology	- Limited energy density and storage - Pressurization and explosion safety issues
Liquid	- Increased energy density - Fast distribution with low energy requirement	- Low temperature - Liquefaction energy losses - Safety issues - Vaporization must be controlled
Chemically bonded	- Increased energy density - High safety	- Poor gravimetric storage efficiency

4. Hydrogen in Marine Systems

Both liquid and compressed hydrogen can be used as fuel to power ships, either with fuel cells or alternatively by internal combustion engines. Fuel cell technology has been around for a long time and is one of the cleanest sources of energy. The propulsion energy for ships is obtained by feeding hydrogen into the fuel cell, where its energy is converted into electrical energy and heat, producing pure water as the output product. The electrical energy is used to power propulsion motors and other electrical loads, the waste heat can be used for space heating and hot water, and the water can be captured and reused. Fuel cells can be easily connected to the existing power grid and can be used in combination with

battery energy storage systems and diesel engines to implement hybrid propulsion systems and are also suitable for retrofitting existing ships. In favor of their use on ships is the fact that they have no moving parts and are simply connected in parallel, making them scalable and easily adaptable to the specifics of the ship in terms of the use of valuable ship space. These characteristics make the technology particularly suitable for ferries, RoPax vessels, and similar smaller vessels in coastal regions, especially where battery-based propulsion solutions cannot fully meet the vessel's operational requirements (i.e., lack of supporting battery charging infrastructure).

4.1. Marine Hydrogen Projects

The research and development of hybrid and all-electric ship topologies with fuel cells usually implies the use of proton exchange membrane (PEMFC) fuel cells in combination with battery energy storage systems. Marine projects that are considered or have the potential for the use of hydrogen-based power generation are presented in Table 6.

Table 6. Comparison of perspective energy carriers in marine transportation sector.

Ship	Vessel Type	Hydrogen Storage Type	On-Board Power System	References
SF Breeze	High-speed Pax ferry	Liquid H_2	Diesel engine PEM fuel cell Battery	[291]
MF Hydra	Ro-Pax Ferry	Liquid H_2	Diesel engine PEM fuel cell Battery	[301,302]
Havila Kystruten	Passenger vessel	Liquid H_2	Diesel engine PEM fuel cell Battery	[303,304]
Topeka	Ro-Ro vessel	Liquid H_2	Diesel engine PEM fuel cell Battery	[305]
Sea Change	Catamaran ferry	Compressed H_2	PEM fuel cell Battery	[306–308]
Gold Green Hygen	Tourist boat	Compressed H_2	PEM fuel cell Battery	[309]
Suiso Frontier	Tanker	Liquid H_2	Diesel-electric	[310]
JAMILA	Tanker	Liquid H_2	Combined-cycle gas turbine power plant	[311]

The SF Breeze project established that compressed and chemically bonded hydrogen storage solutions are not applicable for high-speed ferry use due to the weight and space constraints of the metal or composite hydrogen tanks. Instead, a liquid hydrogen storage solution was proposed [291]. Due to higher energy density as well as the ease of distribution and storage, liquid hydrogen is used on the *MF Hydra* ferry, and is planned for the *Havila Kystruten* and *Topeka* vessels. Compressed hydrogen solutions are nevertheless considered for *Sea Change* and *Gold Green Hygen* vessels with expected shorter sailing time and more frequent refueling.

Unlike fuel cells, the technology to use hydrogen in internal combustion engines is not yet ready for widespread use on ships. Leading marine engine manufacturers are investing significant resources into developing engines that can burn hydrogen either in pure form or blended with other fuels, and this situation is expected to change in the near future. The combustion of hydrogen produces nitrogen oxide emissions as with any other fuel, but greenhouse gas emissions are significantly reduced compared to fossil fuels. Internal combustion engines are also less efficient than fuel cells, which makes them a less favorable solution for use on-board ships [312]. However, the use of hydrogen in internal

combustion engines may be justified if there is a possibility to convert existing engines to run on hydrogen or a mixture of hydrogen and other fuels. Hydrogen-powered vessels can have a 4% lower cost than an equivalent diesel-powered vessel for hydrogen prices lower than 3 EUR/kg. This is of a particular interest if the hydrogen fuel is classified as green hydrogen [313]. The *Suiso Frontier* liquid hydrogen carrier built by Kawasaki Heavy Industries as a part of a HESC project does not use hydrogen as a fuel but is instead driven by a conventional diesel-electric propulsion system, which further increases the proposed HESC project carbon footprint [310,314]. A combined-cycle gas turbine power plant for liquid hydrogen tanker *JAMILA* is proposed in [311]. It is shown that proposed system can deliver a 31 MW zero-emission power output with an estimated ship speed of 16 knots, even in adverse weather conditions and a sailing degradation scenario.

4.2. Hydrogen Production On-Board

The current capacity of hydrogen fuel production, storage, and distribution does not provide sufficient conditions for the full global deployment of hybrid vehicles and ships with hybrid topologies based on hydrogen cells [268,315]. To ensure the profitability of production and refueling of ships with hydrogen fuel, it is necessary to secure the size of the market and increase the consumption and sale of hydrogen [107]. According to [275], electrolysis is the most promising solution for the production of hydrogen for marine use, since renewable energy sources can be used to power the electrolysis process. Hydrogen can in principle be produced on board by the electrolysis of seawater, and the electrolyzers can be powered by the ship's electrical grid. Impurities in the water used for electrolysis can negatively affect the electrochemical reaction and reduce the efficiency of the process. Dissolved chemical elements and impurities can deposit on the electrodes or membrane, which is why deionized water is usually used for the electrolysis process [316,317]. The on-board production of deionized water from seawater first requires fresh water to be obtained through filtration and desalination processes. The fresh water must then be additionally filtered and deionized by the reverse osmosis process [318]. Only after deionization can the electrolysis process begin. The production of hydrogen by the electrolysis process requires up to seven times more energy than the steam reforming process, and, if not powered by renewable energy sources, it can produce up to three times more CO_2 [99,319]. The operation of the electrolyzer with diesel generators is not suitable due to greenhouse gas emissions and energy losses during production and storage. It is possible to use renewable energy sources such as photovoltaic cells, but with significant limitations in terms of the available power, surface area, volume, and mass of installed cells [320]. Since the production of hydrogen is an energy-intensive process, the use of marine electrolyzers and hydrogen fuel cells for ships with relatively short routes is not preferred and is considered environmentally sound only if the electrolyzers are powered by renewable energy sources while the fuel cells serve as an auxiliary energy source [321].

5. Conclusions

In order to introduce hydrogen as an energy source for ship propulsion in a way that is justified from a techno-economic point of view and environmentally sustainable to meet the requirements of existing and future regulations in line with the transition to zero emissions, it is necessary to know not only the technological implementation options but also the accompanying economic and logistical aspects directly related to the specific requirements of the maritime sector. In this paper, the use of hydrogen in the international maritime industry is objectively and critically considered from the aspects of applicability, storage, and production according to a color-coded classification. Factors in favor of the use of hydrogen as a fuel for marine propulsion are presented. The advantages, disadvantages, problems, and obstacles of hydrogen production methods according to color coding are summarized and presented. The principles and safety aspects of hydrogen storage on ships are discussed. Finally, the use of hydrogen in maritime systems and ongoing hydrogen projects at sea are discussed. Recent EU regulations clarifying and standardizing the

difference between renewable and low-carbon hydrogen are presented. This removes some uncertainties in the long-term European hydrogen strategy and provides the shipping sector with further insight into new potential energy pathways for green, environmentally friendly, and sustainable maritime transport. The aspects presented in this review can serve as a guide for comparing hydrogen with other alternative energy sources in terms of cost efficiency and long-term environmental impact with respect to the specifics of a given shipping route.

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