Chapter 4
Hydrogen as Maritime Transportation Fuel: A Pathway for Decarbonization

Omer Berkehan Inal, Burak Zincir, and Caglar Dere

Abstract Shipping is the most energy-efficient way for the transportation of goods and it has a substantial role in the global economy. The vast majority of the ships are addicted to fossil fuels as an energy source due to economic advantages, strong bunkering nets, and well-experienced operations of marine diesel engines. However, environmental concerns drive the industry to take precautions on the ship-sourced greenhouse gas emissions, and the International Maritime Organization (IMO), the ruler of the maritime industry, is bringing strict rules to regulate the emissions under The International Convention for the Prevention of Pollution from Ships—Annex VI (MARPOL). On the way of decarbonization and emission-free shipping, marine alternative fuels may draw a framework for the future of the maritime industry. In this perspective, hydrogen is a promising alternative for maritime transportation with its carbon-free structure. Furthermore, green hydrogen is one of the electro-fuels for maritime transportation to solve the issue to achieve full decarbonization. The use of hydrogen for ships is still under investigation at the level of research projects. Therefore, elaboration of the feasibility from different points of view for the commercial fleet is necessary to enlighten the future of the industry. This chapter includes information about the status of maritime transportation, recent international maritime emission rules and regulations, and hydrogen compliance with the International Code of Safety for Ships Using Gas or Other Low-flashpoint Fuels (IGF Code). Furthermore, hydrogen production technologies, onboard hydrogen storage methods, hydrogen combustion concepts on marine diesel engines, and fuel cells are reviewed. Lastly, the conclusion section comprises the chapter discussion.

Keywords Hydrogen · Decarbonization · Maritime transportation · Zero-carbon

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O. B. Inal (✉) · B. Zincir · C. Dere
Marine Engineering Department, Maritime Faculty, Istanbul Technical University, Istanbul, Turkey
e-mail: inalo@itu.edu.tr

C. Dere
Marine Engineering Department, Faculty of Naval Architecture and Maritime, Izmir Katip Celebi University, Izmir, Turkey

A. K. Agarwal and H. Valera (eds.), *Greener and Scalable E-fuels for Decarbonization of Transport*, Energy, Environment, and Sustainability,
https://doi.org/10.1007/978-981-16-8344-2_4

4.1 Introduction

Global energy consumption has been continuously increasing year by year. It was 575 quadrillion BTU in 2015, and it is expected that the global energy consumption will be 663 quadrillion BTU in 2030 and 736 quadrillion BTU in 2040 (U. S. Energy Information Agency (EIA) 2017). Buildings, industry, and transportation are the end-users that consume energy worldwide. The transportation sector contains road, railway, aviation, and maritime, and it is an important energy-consuming share. According to the data of EIA, the transportation sector consumes 110 quadrillion BTU in 2015 and it is estimated that it will rise to 140 quadrillion BTU in 2040 (U. S. Energy Information Agency EIA (EIA) 2017).

Maritime transportation is the most important transportation type in the transportation sector. Ninety percent of global transportation (Deniz and Zincir 2016), 90% of outer freight, and 40% of inner freight of the European Union (EU) are done by maritime transportation (Fan et al. 2018). There are 98,140 commercial ships worldwide in 2020 which are 100 gross tons and above (United Nations Conference on Trade and Development (UNCTAD) 2020), and these ships consume approximately 300 million tons of fuel (International Maritime Organization (IMO) 2015). Furthermore, 72% of total fuel consumption was heavy fuel oil (HFO), while 26% is marine diesel oil (MDO), and 2% is liquefied natural gas (LNG) (International Maritime Organization (IMO) 2020). Some specifications of diesel fuel and marine low-grade fuels are shown in Table 4.1. The huge amount of fuel consumption results in a major amount of shipboard emissions. European Energy Agency (EEA) states that maritime transportation is responsible for 20.98% of the global NO_X emissions, 11.80% of the global SO_X emissions, 8.57 and 4.63% of the global PM2.5 and PM10 emissions, and 1.94% of the global CO emissions (European Energy Agency (EEA) 2019). Moreover, maritime transportation contributes to 3.1% of worldwide CO_2 emissions (International Maritime Organization (IMO) 2015).

International Maritime Organization (IMO) has been working on controlling and mitigating shipboard emissions from the past until now. IMO put emission limitations for NO_X and SO_X and PM emissions under MARPOL Annex VI Regulation 13 and 14, respectively. Table 4.2 shows NO_X emission limits and Table 4.3 shows SO_X and

Table 4.1 Specifications of diesel fuel and marinelow-grade fuels (Yi et al. 2021)

	Diesel	LSHFO180	LSHFO380	HSFO380
Ash (% m/m)	–	0.03	0.05	0.07
Carbon residue (% m/m)	–	3.2	6.5	16.6
Sulfur (% m/m)	< 0.035	0.475	0.477	3.05
Density (kg/m^3) at 20 °C	818	934.6	951.5	981.5
Kinematic viscosity (cSt) (°C)	3.35/20	180/50	380/50	380/50

LSHFO low sulfur heavy fuel oil
HSFO high sulfur fuel oil

Table 4.2 NO_X emission limits (International Maritime Organization (IMO) 2021a)

Tier	Ship construction date	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		$n < 130$	$n = 130–1999$	$n \geq 2000$
I	1 January 2000	17.0	$45n^{(-0.2)}$	9.8
II	1 January 2011	14.4	$44n^{(-0.23)}$	7.7
III	1 January 2016	3.4	$9n^{(-0.2)}$	2.0

Table 4.3 SO_X and PM limits (International Maritime Organization (IMO) 2021b)

SO_X and PM limits outside ECAs	SO_X and PM limits inside ECAs
4.50% m/m prior to 1 January 2012	1.50% m/m prior to 1 July 2010
3.50% m/m on and after 1 January 2012	1.00% m/m on and after 1 July 2010
0.50% m/m on and after 1 January 2020	0.10% m/m on and after 1 January 2015

PM limits in the fuel inside and outside of the Emission Control Areas (ECAs).

IMO also pay attention to CO_2 emissions by more strict rules and regulations. The Regulations on Energy Efficiency for Ships entered into force on 1 January 2013 (International Maritime Organization (IMO) 2011). The mandatory terms Energy Efficiency Design Index (EEDI) and the Ship Energy Efficiency Management Plan (SEEMP), and voluntary term the Energy Efficiency Operational Indicator (EEOI) were described. The EEDI determines the energy efficiency index for new building ships and encourages the use of more efficient materials and systems on ships. On the other hand, the SEEMP aims to increase the operational efficiency of ships. And voluntary EEOI is for calculating the voyage-based efficiency of ships. Later then, IMO Data Collection System entered into force on 1 March 2018 (IMO data collection system 2021c). It aims to record and control the annual voyage-based CO_2 emissions of ships larger than 5000 GRT worldwide.

The latest action of IMO is the Initial Greenhouse Gas (GHG) Strategy that is announced in 2018. The Strategy aims to achieve two targets. The first target is to reduce CO_2 emissions per transport work at least 40% by 2030 and 70% by 2050, compared to 2008, and the second target is to decrease GHG emissions to 50% by 2050, compared to 2008 (International Maritime Organization (IMO) 2018). By this strategy, the short-term (2018–2023), mid-term (2023–2030), and long-term (2030–…) candidate measures were defined (Table 4.4). One candidate measure or combination of two or more candidate measures can be used and it is left up to ship owners/operators. The strategy includes various operational and technical measures, but the use of alternative fuels is a prominent candidate measure. From short-term candidate measures to long-term candidate measures, a transition from low-carbon alternative fuels to zero-carbon alternative fuels is observed. Alternative

Table 4.4 Initial GHG strategy measures (International Maritime Organization (IMO) 2018)

Short-term measures (2018–2023)	Mid-term measures (2023–2030)	Long-term measures (2030+)
Improvement of the existing energy efficiency framework	Implementation programme for the effective uptake of alternative low-carbon and zero-carbon fuels	Pursue the development and provision of zero-carbon or fossil-free fuels
Development of technical and operational energy efficiency measures for both new and existing ships	Operational energy efficiency measures for both new and existing ships	Encourage and facilitate the general adoption of other possible new/innovative emission reduction mechanism(s)
Establishment of an Existing Fleet Improvement Programme	New/innovative emission reduction mechanism(s), market-based measures (MBMs)	
Speed optimization/speed reduction	Further continuation and enhancement of technical cooperation and capacity-building	
Measures for volatile organic compounds	Development of a feedback mechanism to enable lessons learned on implementation of measures	
Development and update of national action plans		
Continuing and enhancing technical cooperation and capacity-building		
Measures for port developments and activities		
Initiation of research and development activities on marine propulsion, alternative low-carbon and zero-carbon fuels, and innovative technologies		
Incentives for first movers of new technologies		
Development of a sufficient lifecycle GHG/carbon intensity guidelines for fuels		
Active promotion of the work of the IMO		
Undertake additional GHG emission studies		

fuels identified for maritime transportation are liquefied natural gas (LNG), liquefied petroleum gas (LPG), methanol, ethanol, ammonia, dimethyl ether (DME), ethane, biogas, biofuels, synthetic fuels, and hydrogen (Zincir and Deniz 2021). Among these alternative fuels, hydrogen is zero-carbon fuel that can meet the IMO Initial GHG Strategy reduction targets (American Bureau of Shipping (ABS) 2021). Moreover, if hydrogen is produced by water electrolysis which is powered by renewable energy, this type of hydrogen is named electrofuel. In general terms, electrofuels are hydrocarbon fuels that are produced from CO_2 and water while renewable electricity is the main source of production (Brynolf et al. 2018). The renewable electricity is converted to hydrogen by the electrolysis process and the later step is to combine hydrogen with carbon atoms to form hydrocarbon fuels, for instance, ammonia, methane, methanol, etc. (Rixhon et al. 2021). Therefore hydrogen is an important alternative fuel to achieve full decarbonization at maritime transportation.

This chapter explains that the use of hydrogen as an alternative fuel can be a pathway for decarbonized maritime transportation. The chapter contains hydrogen fuel properties, hydrogen production methods, hydrogen storage methods, application of hydrogen fuel on fuel cells and diesel engines. Lastly, the chapter conclusion will discuss the role of hydrogen in maritime transportation.

4.2 Hydrogen Fuel Properties

International Energy Agency (IEA) states that hydrogen is a promising fuel to meet future energy demands (Qyyum et al. 2021) and will have an important role in sustainable energy systems by 2050 (Staffell et al. 2019). Hydrogen is the most available element in various feedstocks, but it is unusual to find solely (Inal et al. 2021a). Hydrogen is a carbon-free and clean alternative fuel for maritime transportation. Therefore the combustion of hydrogen results in water only as a by-product.

The properties of hydrogen are shown in Table 4.5. The remarkable fuel properties of hydrogen are high laminar flame speed, wide flammability limits, high diffusivity, smaller quenching distance, and low minimum ignition energy (Deniz and Zincir 2016). Hydrogen is a high octane fuel and the high auto-ignition temperature of hydrogen is an issue to overcome, especially combustion at diesel engines. On the other hand, low minimum ignition energy of hydrogen brings quick combustion of hydrogen by external sources such as spark plugs. The wide flammability limits provide using variable fuel–air ratios for the optimum combustion conditions for lower fuel consumption and lower emissions. The high laminar flame speed of hydrogen improves the spread of the flame in the cylinder and contributes to more complete burning. Due to the high diffusivity, hydrogen forms a more homogenous fuel–air charge in the cylinder that also leads to higher combustion efficiency.

Despite its high LHV than conventional marine fuels, the energy density of hydrogen is low. For this reason, the volumetric energy capacity of gaseous hydrogen is 3000 times lower than diesel oil (Inal et al. 2021a). And for instance, compressed hydrogen needs six to seven times more storage area than the same energy content of

Table 4.5 Properties of hydrogen (Deniz and Zincir 2016; Inal et al. 2021a; Zincir and Deniz 2014, 2018)

Properties	Gaseous hydrogen	Liquid hydrogen
Auto-ignition temperature (°C)	571	571
Density (kg/m^3)	17.50–20.54	70.85–71.10
Energy density (MJ/m^3)	2101	8539
Diffusivity in air (cm^2/s)	0.63	0.63
Laminar Flame speed (m/s)	3.51	3.51
Flame temperature (°C at 1 bar)	2045	2045
Flammability limits (Vol.%)	4–75	4–75
Flashpoint (°C)	−150	−150
Lower heating value (MJ/kg)	120.1	120.1
Minimum ignition energy (mJ)	0.02	0.02
Octane number	>130	>130
Stoichiometric air–fuel ratio on mass basis	34.3	34.3
Storage type	*Compressed gas*	*Cryogenic liquid*
Storage temperature (°C)	25	−253
Storage pressure (bar)	300	1
Onboard storage cost (€/kWh)	1.29–1.71	
Fuel cost (€/kWh)	153	153
Exposure limit (mg/m^3—8 h)	336	336
Well to wheel life cycle emissions (g_{co2}/MJ)	Grid electricity: 139 Wind electricity: 2.59–20.74 Solar PV electricity: 6.67–66.67	

HFO (Chryssakis et al. 2014). The energy densities without taking into account the container and insulation of gaseous and liquid hydrogen are shown in Table 4.5. The low energy density is the main disadvantage of hydrogen for being a maritime transportation fuel. The main storage options of hydrogen are as a compressed gas at 25 °C and 300 bar or as a cryogenic liquid at −253 °C and 1 bar. Detailed hydrogen storage techniques are explained in Sect. 4.4. Hydrogen is neither corrosive nor toxic which lowers operational procedures and costs. But the storage cost of cryogenic hydrogen storage is higher than the compressed hydrogen storage. The reasons for these are special insulation material for the cryogenic storage, cooling and pumping units to recover gasified hydrogen from the tank and transfer it again to the tank cryogenically. Although hydrogen is not a toxic substance, exposure to hydrogen in a place that contains more than 336 mg/m^3—8 h results in asphyxiation.

Some main advantages of hydrogen are abundance, carbon-free structure, high energy conversion efficiency, variety of storage options, the possibility of long-distance transportation, higher LHV than the conventional marine fuels, and conversion options to other energy forms (Dincer and Acar 2015).

4.3 Hydrogen Production Methods

Hydrogen is an essential substance for various industries and 0.1 Gt of hydrogen is produced annually (Qyyum et al. 2021). Fifty-one percent of hydrogen production is for ammonia production, while 31% is for oil refining, 10% for methanol production, and 8% for other applications (Kannah et al. 2021). Hydrogen is produced from different feedstocks that 96% of them are fossil fuels (natural gas 48%, oil 30%, and coal 18%) and 4% from renewable resources (Taibi et al. 2018). The energy consumption of annual worldwide hydrogen production equals 2% of the global energy demand (American Bureau of Shipping (ABS) 2021).

Hydrogen production is determined in four different ways by their emitted GHG emissions during the process. These are brown hydrogen, grey hydrogen, blue hydrogen, and green hydrogen (American Bureau of Shipping (ABS) 2021). Brown hydrogen is the production way of using coal as feedstock, grey hydrogen is the production process of using other fossil fuels (natural gas, oil, etc.) as feedstock. Blue hydrogen is the process that uses fossil fuels as feedstock for hydrogen production, but the emitted carbon emissions are captured and stored by the carbon capture and storage (CCS) system. The emitted CO_2 emissions are approximately 90% lower than brown hydrogen and grey hydrogen. Lastly, green hydrogen is the production process that uses renewable energy sources (solar, wind) for electrolysis of water, or uses biomass or biological methods to produce hydrogen.

This section describes the hydrogen production methods based on feedstocks. The feedstocks are separated as hydrocarbon fuels, biomass, and water. The hydrogen production methods are also classified according to their production way color.

4.3.1 Hydrogen Production from Hydrocarbon Fuels

Hydrogen production methods from hydrocarbon fuels are hydrocarbon reforming and pyrolysis. These two hydrogen production methods are the most mature and used methods that meet almost the total global hydrogen demand (Nikolaidis and Poullikkas 2017). Hydrogen production from hydrocarbon fuels can be done at high efficiencies and low costs (Baykara 2018).

4.3.1.1 Hydrocarbon Reforming

Hydrocarbon reforming is the conversion process of hydrocarbon fuels to hydrogen by chemical techniques. The hydrocarbon reforming process is named steam reforming, partial oxidation, or auto-thermal reforming, according to the reactant substance. If the reactant substance is steam, the process is named steam reforming, if the reactant substance is oxygen, the process is known as partial oxidation, and if the hydrogen production process consists of these two reactions, the process is auto-thermal reforming (Chen et al. 2008).

Steam Reforming

Steam reforming is a hydrogen production method that uses natural gas, liquefied petroleum gas (LPG), methanol, jet fuel, naphtha, and diesel fuel as feedstocks (Kannah et al. 2021). But natural gas is the major feedstock for steam reforming that has high process thermal efficiencies up to 85% (El-Shafie et al. 2019) and the lowest CO_2 emissions compared to all hydrogen production from hydrocarbon fuels (Qyyum et al. 2021). During the steam reforming process, hydrocarbon fuel reacts with steam at a high temperature (700–1000 °C) environment. The product of this reaction is carbon monoxide (CO), hydrogen, and unreacted natural gas mixture which is called syngas. After the syngas generation, the later step of the steam reforming is the water–gas shift (WGS) reaction that converts CO to CO_2. The final step is methanation or gas purification to collect 99.99% purity of hydrogen from the process (Al-Qahtani et al. 2021). Equations (4.1)–(4.3) (Nikolaidis and Poullikkas 2017) and Fig. 4.1 show the main steps of steam reforming. If the hydrocarbon fuel contains sulfur compounds, the desulphurization process is done before the syngas generation step to prevent poisoning the reforming catalyst (Nikolaidis and Poullikkas 2017). Steam reforming is considered grey hydrogen production since the process uses fossil fuels. On the other hand, if the process contains CCS almost 90% of emitted CO_2 is captured. Thus the produced hydrogen is blue hydrogen.

Reforming step:

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2}m\right)H_2 \tag{4.1}$$

WGS step:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4.2}$$

Methanation step:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{4.3}$$

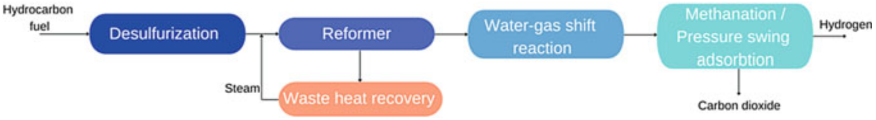

Fig. 4.1 Steam reforming steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

Partial Oxidation

Partial oxidation (POX) is the conversion process of hydrocarbon to hydrogen and carbon oxides by oxygen. The feedstocks for the POX are coal, heavy oil, methane, and naphtha (Nikolaidis and Poullikkas 2017). The POX with the feedstock of coal is also called gasification. After the desulphurization, the hydrocarbon feedstock is partially oxidized by oxygen to produce syngas. The further process is the same as steam reforming. Equations (4.4)–(4.7) and Fig. 4.2 show the main steps of the POX (Nikolaidis and Poullikkas 2017). POX is the most convenient hydrogen production method for using heavier hydrocarbon fuels, for instance, heavy fuel oil and coal (Chen et al. 2008). However, the hydrogen production by partial oxidation is more expensive due to the oxygen separation unit, and less energy efficient than the steam reforming (El-Shafie et al. 2019). Moreover, when the process uses heavier hydrocarbon fuels with lower carbon to hydrogen ratio, the POX results in higher CO_2 emissions (Al-Qahtani et al. 2021). The hydrogen production from the POX process is brown hydrogen when coal is used as feedstock; grey hydrogen when heavy fuel oil or methane is used as feedstock; and blue hydrogen when CCS is applied to capture CO_2 emissions during the hydrogen production process.

Reforming step:

$$C_nH_m + \frac{1}{2}nO_2 \rightarrow nCO + \frac{1}{2}mH_2 \text{ (catalytic process)} \tag{4.4}$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2}m\right)H_2 \text{ (non} - \text{catalyticprocess)} \tag{4.5}$$

WGS step:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4.6}$$

Methanation step:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{4.7}$$

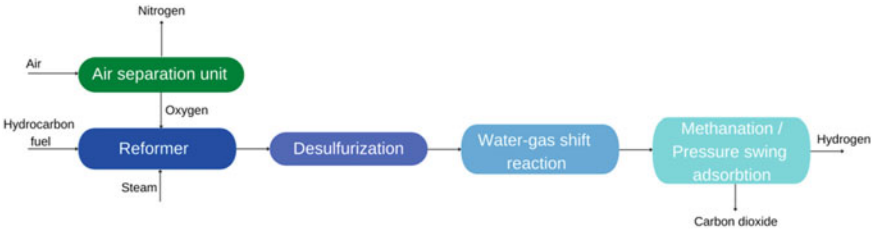

Fig. 4.2 Partial oxidation steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

Auto-thermal Reforming

Auto-thermal reforming (ATR) is the hydrogen production process by the combination of steam reforming and partial oxidation (Zincir and Deniz 2016). The ATR includes the exothermic POX and endothermic steam reforming processes. The heat from the POX is used during the steam reforming process to increase the hydrogen production rate (Nikolaidis and Poullikkas 2017). The remaining steps of the process are the same as steam reforming and POX. Equation (4.8) shows the main step of the ATR (Nikolaidis and Poullikkas 2017), and the process steps are similar to Fig. 4.2. The ATR also requires pure oxygen that raises the complexity and cost of the system (Dincer and Acar 2015). Hydrogen is produced by the ATR is grey hydrogen since the process uses methane and if CCS is applied to capture CO_2 emissions the produced hydrogen is blue hydrogen.

$$C_nH_m + \frac{1}{2}nH_2O + \frac{1}{4}nO_2 \rightarrow nCO + \left(\frac{1}{2}n + \frac{1}{2}m\right)H_2 \tag{4.8}$$

4.3.1.2 Pyrolysis

Pyrolysis is the decomposition of hydrocarbon fuels by heat. The decomposition reaction temperature is 350–400 °C for coal and 1400 °C and above for methane (El-Shafie et al. 2019). Products of the pyrolysis process are hydrogen-rich gas, gaseous hydrocarbon, and solid char (Kannah et al. 2021). Equation (4.9) (Nikolaidis and Poullikkas 2017) and Fig. 4.3 show the main chemical reaction of the pyrolysis process. Since there are no gaseous carbon emissions, the CCS is not needed. The pyrolysis process does not contain the WGS reaction and CO_2 capture process. Therefore, capital investments and hydrogen production costs are lower than steam reforming and partial oxidation (Muradov 1993). Despite its advantages, the pyrolysis process has a fouling issue due to the solid carbon product that reduces the effectiveness of the reactor (Guo et al. 2005). Although the pyrolysis process does not carbon oxide emissions, solid carbon is the product of the process and pollutes the environment. Hence, the produced hydrogen is either brown hydrogen or grey hydrogen when the feedstock is coal or other hydrocarbon fuels, respectively.

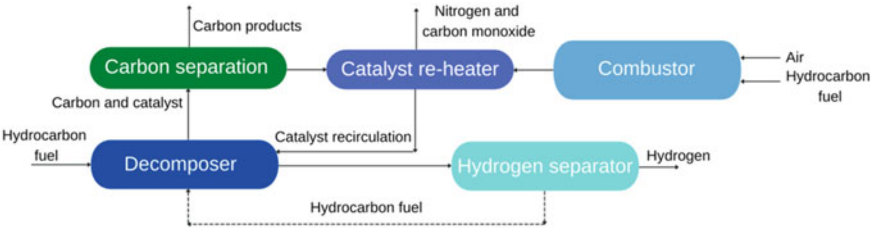

Fig. 4.3 Pyrolysis steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

$$C_nH_m \rightarrow nC + \frac{1}{2}mH_2 \tag{4.9}$$

4.3.2 *Hydrogen Production from Biomass*

Hydrogen from biomass is the renewable production way. There are two main categories for hydrogen production from biomass. One of them is the thermochemical process and the other one is the biological process. The subcategories of the thermochemical process are pyrolysis and gasification. The biological process contains biophotolysis, dark fermentation, and photo-fermentation. Although there are various ways of hydrogen production from biomass, most of the techniques are not mature enough, and the hydrogen production rate is not adequate to replace with fossil-based fuels (Qyyum et al. 2021).

4.3.2.1 Thermochemical Process

Thermochemical processes are pyrolysis and gasification, and biomass is converted to hydrogen and hydrogen-rich gases (Nikolaidis and Poullikkas 2017). These methods are the same as the processes with hydrocarbon fuels. Biomass pyrolysis commenced at 650–800 K, 0.1–0.5 MPa, (Demirbaş 2001) and an oxygen-free environment. The products of the process are gaseous compounds, liquid oils, and solid charcoal. The reforming and WGS reactions follow the pyrolysis process. The main steps of the process are shown in Eqs. (4.10–4.12) (Nikolaidis and Poullikkas 2017) and Fig. 4.4.

$$\begin{aligned}\text{Biomass pyrolysis} &\rightarrow H_2 + CO + CO_2 \\ &+ \text{hydrocarbon gases} + \text{tar} + \text{char}\end{aligned} \tag{4.10}$$

$$C_nH_m + nH_2O \rightarrow nCO + \left(n + \frac{1}{2}m\right)H_2 \tag{4.11}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{4.12}$$

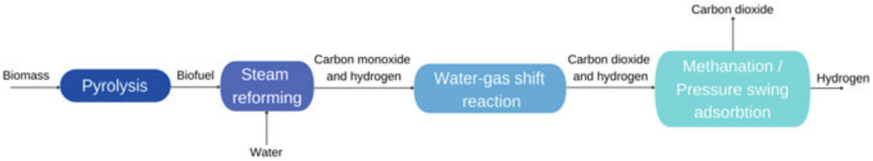

Fig. 4.4 Biomass pyrolysis steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

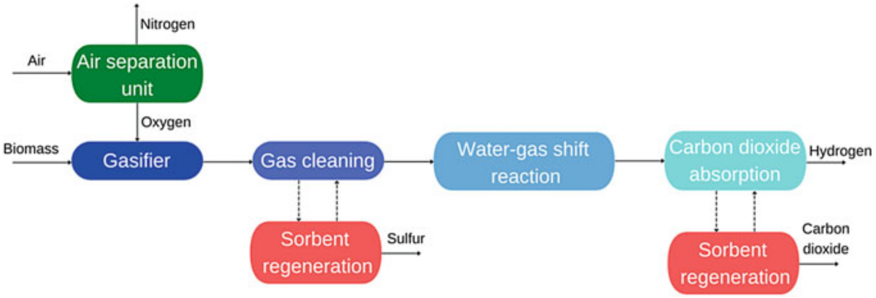

Fig. 4.5 Biomass gasification steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

Biomass gasification is the same process as coal gasification. It is the most well-known and promising hydrogen production method (Kannah et al. 2021). Biomass feedstock is partially oxidized by oxygen to form syngas. The operating conditions temperatures are between 500 and 1400 °C at 33 bar pressure (Iribarren et al. 2014). Equations (4.13) and (4.14) (Nikolaidis and Poullikkas 2017) and Fig. 4.5 show the main step of biomass gasification with air or steam respectively.

$$\begin{aligned}&\text{Biomass} + \text{air} \rightarrow H_2 + CO_2 + CO + N_2 + CH_4\\&\quad + \text{other} + \text{CHs} + \text{tar} + H_2O + \text{char}\end{aligned} \tag{4.13}$$

$$\begin{aligned}&\text{Biomass} + \text{steam} \rightarrow H_2 + CO_2 + CO + CH_4\\&\quad + \text{other} + \text{CHs} + \text{tar} + \text{char}\end{aligned} \tag{4.14}$$

Biomass pyrolysis and biomass gasification processes are renewable processes and the produced hydrogen is green hydrogen. Moreover, if the CCS is applied to these processes the negative carbon balance is achieved (Al-Qahtani et al. 2021).

4.3.2.2 Biological Process

The biological process uses biological technologies to produce hydrogen. The biological process commences at ambient temperature and pressure and the feedstocks are renewable and waste materials (Das and Veziroğlu 2001). The main methods of biological process are bio-photolysis, dark fermentation, and photo-fermentation. These hydrogen production methods are green production way of hydrogen.

Bio-photolysis

Bio-photolysis is some kind of replica of photosynthesis but the product is hydrogen gas. Water is given to green and blue algae as a feedstock. They can split the water molecules into hydrogen ions and oxygen. Hydrogenase or nitrogenase enzymes of

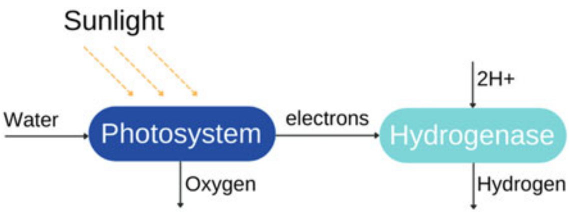

Fig. 4.6 Bio-photolysis steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

algae convert hydrogen ions to hydrogen gas (Kapdan and Kargi 2006). It is not a mature and commercial technology (Dincer and Acar 2015) and has drawbacks of low hydrogen production rate and large surface area requirement to get satisfactory light (Holladay et al. 2009). The general formula for the bio-photolysis is shown in Eq. (4.15) (Nikolaidis and Poullikkas 2017) and the basic steps are shown in Fig. 4.6.

$$2H_2O + \text{light} \rightarrow 2H_2 + O_2 \tag{4.15}$$

Dark Fermentation

Anaerobic bacteria digest carbohydrates in biomass feedstock to convert organic acids and then to hydrogen gas (Kapdan and Kargi 2006). This process is called dark fermentation. The process commences in oxygen-free and dark conditions. Dark fermentation is the most well-known and used method for hydrogen production from renewable biomass feedstock, for instance, lignocelluloses biomass, crop residues, organic waste, and algal biomass (Kannah et al. 2021). The hydrogen production rate depends on pH value (between 5 and 6) (Ni et al. 2006) and removal of produced hydrogen from the fermentation area since pressure rise decreases hydrogen production rate (Holladay et al. 2009). Despite dark fermentation has the advantage of continuous production of hydrogen day and night, the production capacity is low, the capital investment is high, and the process is on a laboratory scale (Dincer and Acar 2015; Kannah et al. 2021). The main chemical reaction of dark fermentation with acetate fermentation and butyrate fermentation is shown in Eqs. (4.16) and (4.17), respectively (Nikolaidis and Poullikkas 2017). Figure 4.7 shows the basic steps of the dark fermentation process.

Acetate fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 4H_2 + 2CO_2 \tag{4.16}$$

Fig. 4.7 Dark fermentation steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

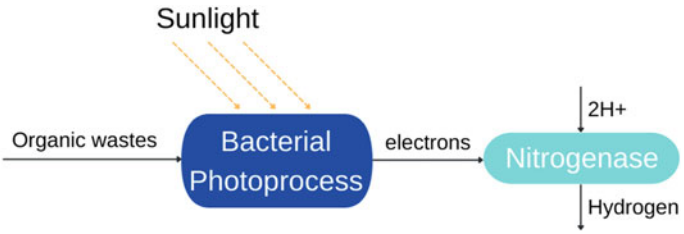

Fig. 4.8 Photo-fermentation steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

Butyrate fermentation:

$$C_6H_{12}O_6 + 2H_2O \rightarrow CH_3CH_2CH_2COOH + 2H_2 + 2CO_2 \tag{4.17}$$

Photo-fermentation

Photo-fermentation is a biological process that some photosynthetic bacteria that use solar power and organic acids to produce hydrogen and CO_2 (Das and Veziroglu 2008). This hydrogen production method is on a laboratory scale and has challenges such as large surface area requirement and low light utilization efficiency (Zincir and Deniz 2016). The main chemical reaction of the process is shown in Eq. (4.18) (Nikolaidis and Poullikkas 2017) and Fig. 4.8.

$$CH_3COOH + 2H_2O + \text{light} \rightarrow 4H_2 + 2CO_2 \tag{4.18}$$

4.3.3 Hydrogen Production from Water Splitting

Water splitting is another hydrogen production way and it can be done by three methods. These methods are electrolysis, thermolysis, and photo-electrolysis. Hydrogen from water splitting is the cleanest energy when the energy for water splitting is provided from renewable energy sources (Nikolaidis and Poullikkas 2017).

4.3.3.1 Electrolysis

Electrolysis is the most mature and well-known method for water splitting. The method is endothermic and requires high electric energy (Qyyum et al. 2021). The electrical current splits water at the anode and cathode of the electrolyzer unit.

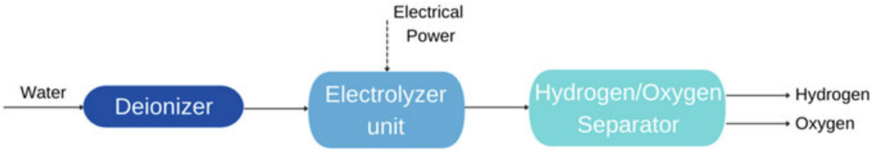

Fig. 4.9 Electrolysis steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

Hydrogen accumulates at the cathode and oxygen at the anode. The reaction for the water electrolysis is shown in Eq. (4.19) (Levene et al. 2007) and Fig. 4.9.

$$2H_2O \rightarrow 2H_2 + O_2 \tag{4.19}$$

There are three types of water electrolysis methods for hydrogen production. These are alkaline, proton exchange membrane (PEM), and solid oxide electrolysis (SOE). Alkaline electrolysis has the lowest system efficiency, the lowest capital cost, and higher hydrogen production. On the other hand, the PEM has higher system efficiency than the alkaline electrolysis, no corrosion and sealing related issues, but the capital electrolyzer cost is higher than the alkaline electrolysis. Lastly, nevertheless, the SOE is the most efficient electrolysis system, it is still under development and there are corrosion and sealing issues that have to be solved (El-Shafie et al. 2019).

Water electrolysis is an intensive electricity-consuming process. Therefore, when the electricity production is from fossil fuels, the process emits a high amount of CO_2 emissions and the produced hydrogen is brown hydrogen if the electricity is generated from coal energy and grey hydrogen if the electricity is generated from oil and natural gas. Fossil power plants can use CCS to capture CO_2 emissions. Therefore, the produced hydrogen by using generated electricity from these power plants results in blue hydrogen production. When the electricity is produced from renewable energy sources (wind or solar), the produced hydrogen is green hydrogen. The green hydrogen is also named electrofuel which has a carbon-free lifecycle from well-to-wheel or well-to-propeller at maritime transportation.

4.3.3.2 Thermolysis

Thermolysis is a water-splitting process that the water is decomposed to hydrogen and oxygen at a high temperature (Nikolaidis and Poullikkas 2017). The temperature has to be as high as more than 2500 °C to separate hydrogen (Funk 2001). The main chemical reaction of the process is shown in Eq. (4.20) (Steinfeld 2005) and Fig. 4.10.

$$2H_2O \rightarrow 2H_2 + O_2 T > 2500\,^{\circ}C \tag{4.20}$$

The thermolysis process is under development since the compatible material to high thermal stress issue and the development of an effective technique has to be solved (El-Shafie et al. 2019). The required heat can be provided from fossil fuels or

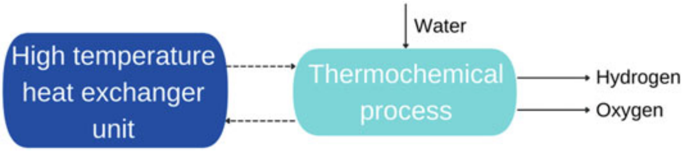

Fig. 4.10 Thermolysis steps (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

solar power, thus, the produced hydrogen will be brown or grey hydrogen and green hydrogen, respectively.

4.3.3.3 Photo-Electrolysis

Photo-electrolysis is a water-splitting method that transforms the photonic energy of sunlight into chemical energy (Dincer and Acar 2015). Water is decomposed to hydrogen and oxygen by the photonic energy that is similar to electrolysis. The photo-electrolysis method is a more efficient water splitting method than electrolysis (Qyyum et al. 2021). The photo-electrolysis systems use semiconductor materials which is the same as the photovoltaic systems (El-Shafie et al. 2019). Equations (4.21)–(4.23) show the main chemical reactions of the photo-electrolysis method (Nikolaidis and Poullikkas 2017).

Anode:

$$2p^{+} + H_2O \rightarrow 0.5O_2 + 2H^{+} \tag{4.21}$$

Cathode:

$$2e^{-} + 2H^{+} \rightarrow H_2 \tag{4.22}$$

Total reaction:

$$2e^{-} + 2H^{+} \rightarrow H_2 \tag{4.23}$$

Photo-electrolysis hydrogen production is expected to be a promising long-term solution for carbon-free hydrogen production, but before it will happen, a more durable and inexpensive photocatalyst has to be developed for commercial hydrogen production (Maeda and Domen 2010). The photo-electrolysis method produces green hydrogen (Fig. 4.11).

Table 4.6 compares hydrogen production methods with their advantages and disadvantages. Technology readiness levels (TRL) of hydrogen production methods are compared. Steam reforming and electrolysis are the most mature methods

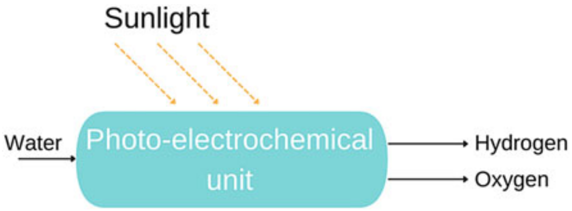

Fig. 4.11 Photo-electrolysis process (figure reproduced and adapted) (Nikolaidis and Poullikkas 2017)

and bio-photolysis, dark fermentation, photo-fermentation, thermolysis, and photo-electrolysis are the least mature methods. The efficiencies are indicated in the table, of the hydrogen production methods represent energy conversion efficiency from the external energy sources to hydrogen production. Since steam reforming is the most mature and used hydrogen production method, the most developed technologies with higher efficiency have been used. On the other hand, the hydrogen production methods such as photo-fermentation and photo-electrolysis are on a laboratory scale and under development and the efficiencies are the lowest. The sunlight energy conversion efficiency of these methods is also effective on the efficiency. Steam reforming, partial oxidation, and auto-thermal reforming emit CO_2 emissions and hydrocarbon pyrolysis forms solid carbon. As a consequence, these hydrogen production methods are not able to produce hydrogen in a green way. The remaining methods have green production ways and the variety of hydrogen production is promising for future renewable hydrogen production pathways. It is known that steam reforming is the most used hydrogen production method recently. Thus, steam reforming with CCS (blue hydrogen) is a good option during the transition from brown/grey hydrogen to green hydrogen pathways. And in the future, green hydrogen production pathways will be used for achieving zero well-to-wake emissions in maritime transportation.

Figure 4.12 shows the hydrogen production lifecycle costs by considering human health, ecosystem, and resources. The data of the figure is derived from the study of Al-Qahtani et al. that is done in 2021 (Al-Qahtani et al. 2021). They assessed the hydrogen production methods by taking into account the effects of hydrogen production methods on human health, the environment, and resources. According to the results of the study, steam reforming with CCS has the lowest hydrogen production cost recently. Pyrolysis and steam reforming without CCS followed it. The highest production cost is for coal gasification since it has the highest effect on human health and the environment. Nuclear and wind energies can cope with steam reforming, but solar energy is not an effective way to produce hydrogen for now.

Table 4.6 Comparison of hydrogen production methods (Qyyum et al. 2021; Dincer and Acar 2015; Kannah et al. 2021; Nikolaidis and Poullikkas 2017; Al-Qahtani et al. 2021)

Production methods	TRL Level	Efficiency	Advantages	Disadvantages	Produced hydrogen color
Steam reforming	9	74–85	Most mature and existing process	Emits CO_2, fossil fuel depended	Brown Grey Blue
Partial Oxidation	8	60–75	Proven and existing process	Emits CO_2, fossil fuel depended	Brown grey Blue
Auto-thermal reforming	8	60–75	Proven and existing process	Emits CO_2, fossil fuel depended	Brown Grey Blue
Hydrocarbon pyrolysis	3–5	–	Emission-free, low process steps	Solid carbon formation, fossil fuel depended	Brown Grey
Biomass pyrolysis	3–5	35–50	CO_2-neutral process, ample and cheap feedstock	Tar formation, unstable H_2 content	Green
Biomass gasification	5–6	40–50	CO_2-neutral process, ample and cheap feedstock	Tar formation, unstable H_2 content	Green
Bio-photolysis	1–3	10	CO_2-consuming process	Sunlight and large area requirement	Green
Dark fermentation	1–3	60–80	CO_2-neutral process, waste recycling, O_2-free process without light	Low H_2 production, low efficiency	Green
Photo-fermentation	1–3	0.1	CO_2-neutral process, waste recycling	Sunlight and large area requirement, low efficiency	Green
Electrolysis	9	40–60	Proven and existing process, ample feedstock, zero-emission with renewable energy	High capital cost, low efficiency	Brown Grey Blue Green
Thermolysis	1–3	20–45	Clean and reliable process, ample feedstock	Toxicity, corrosion issues, high capital cost	Brown Grey Green
Photo-electrolysis	1–3	0.06	Ample feedstock, zero-emission process	Sunlight requirement, low efficiency	Green

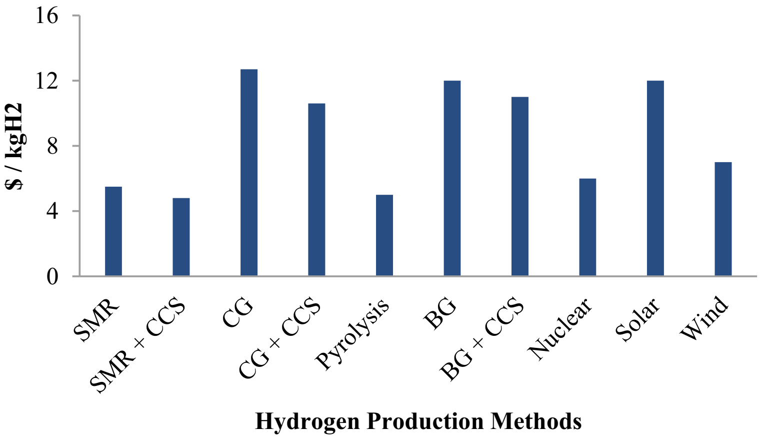

Fig. 4.12 Hydrogen production lifecycle assessment costs (data is derived and the graph is drawn) (Al-Qahtani et al. 2021)

4.4 Hydrogen Storage Techniques for Maritime

The main objective on the use of hydrogen for ships is to eliminate greenhouse gas emissions. In this motivation, alternative fuels are gaining importance, however, the ultimate zero emission goal can be reached by hydrogen thanks to its carbon-free structure. Hence, onboard storage of the hydrogen receives attention and many industrial techniques have been tried to apply for ships. The major obstacle seems as the onboard storage of the hydrogen before using it for powering the ship's propulsion systems. From a wider perspective, several milestones need to be achieved in order to switch the fuel system to a newer and less experienced one. In this manner, there are several levels such as bunkering stations, refueling infrastructures (connections, production, and distributions), storage, and their safety aspects (Andersson and Grönkvist 2019). However, this chapter only focuses on the available and applicable onboard storage techniques and other requirements for the hydrogen use is out of the scope.

Hydrogen fuel has some advantageous properties compared to conventional marine fuels. For instance, lower heating value of the hydrogen is approximately 3 times higher than diesel oil, 33 kWh/kg and 11 kWh/kg, respectively (Inal et al. 2021b). However, being in gaseous form under atmospheric conditions and having roughly 3000 times lesser volumetric energy compared to diesel requires increased space onboard ship for long voyages. Therefore, substantial technological improvements may be needed for spreading the hydrogen fuel in shipping industry. As a nature of the marine environment, the use of hydrogen shows different challenges compared to land-based facilities and other transportation sectors. This section provides a general overview to onboard hydrogen storage techniques that can be applicable for ships.

4.4.1 Onboard Hydrogen Storage

In this section hydrogen storage techniques for the onboard ship are reviewed. The four main storage technologies compressed, liquid, solid-state, and alternative carriers are elaborated, respectively, and shown in Fig. 4.13. Additionally, alternative carriers are separated into three subtitles as N_2 based, CO_2 based, and organic liquids.

4.4.1.1 Compressed Hydrogen Storage

The compressed hydrogen storage is the most developed and well-experienced method among different technologies. The hydrogen is kept under very high pressures around 350–700 bar which give a density of 23.3 kg/m^3 and 39.3 kg/m^3, respectively (Raucci et al. 2015). Table 4.7 shows the four different pressurized vessel types with the used material, typical pressure in bar, and approximate cost in USD per kg.

The most well-known tank types to store the hydrogen are type I and II, all-metal, and mostly metal development types because of their somewhat lower costs. Additionally, since the material of type II is a combination of metal and composite parts it has a lower weight contrasted with the all-metal, type I tank. Be that as it may, the composite material diminishes the solidness of the vessel and it can simply go up to 200 bars. The primary issue is the significant expense because of the utilization of cutting edge materials like carbon fiber, for the third and fourth kinds of capacity tanks (O'Malley et al. 2015). On the other hand, high-pressure hydrogen storage

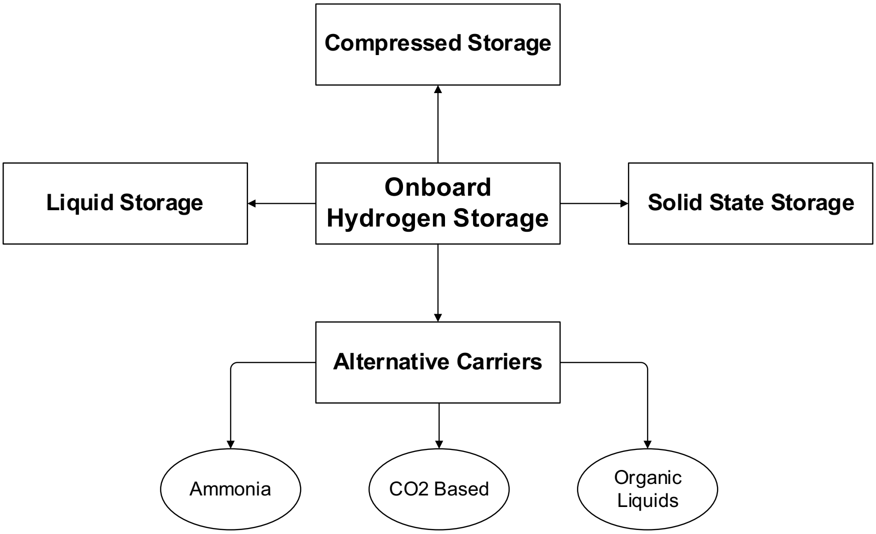

Fig. 4.13 Onboard hydrogen storage techniques (Inal et al. 2021b)

Table 4.7 Storage tank types (Rivard et al. 2019)

Type	Material	Typical pressure (bar)	Cost ($/kg)
I	All-metal construction	300	83
II	Mostly metal, composite overwrap in the hoop direction	200	86
III	Metal liner, full composite overwrap	700	700
IV	All-composite construction	700	633

tanks are in advantage with gravimetric density and well-proven by being used in fuel cell electric cars, Toyota Mirai, and Honda Clarity (Yamashita et al. 2015). This high gravimetric density serves to multiple times higher storage limit contrasted with low-pressure tanks (Rivard et al. 2019; Hoecke et al. 2021).

4.4.1.2 Liquid Hydrogen Storage

The subsequent method to store hydrogen is by liquification. The central of putting away hydrogen in fluid structure is to lessen temperature to −253 °C which is its bubbling temperature. The benefit of liquefaction is the capacity to arrive at high hydrogen densities at environmental pressing factors, which is 70 kg/m3 and multiple times higher than the vaporous structure (Hoecke et al. 2021). The heat transfer should be limited to keep the temperature at the ideal level to store a cryogenic fluid. In the interim, cryogenic capacity is certifiably not a far idea for the maritime industry because of liquefied natural gas (LNG) transportation and boil-off gas use in marine diesel motors. Incidentally, LNG seems like another solid option through green shipping with its lesser carbon content contrasted with substantial fuel oil and marine diesel oil, additionally, with its free sulfur content.

The main piece of liquid hydrogen storage is to limit evaporation. Evaporation of hydrogen has two incidental effects; the first is the pressing factor increment within the tank and the second is the deficiency of the burned through effort during the liquefaction of the hydrogen. The decrease of heat transfer through the tank is the critical answer for stopping the evaporation. To fulfill this, the volume to surface proportion ought to be maximized, and this is reachable with circular tank shapes that have the biggest volume to surface proportion. In conclusion, the boil-off rates are below 0.1% per day with strongly insulated spherical tanks (Amos 1998).

4.4.1.3 Solid-State Hydrogen Storage

There are various methods to store hydrogen in solid materials but the promising ones; metal hydride and boron-based storage have been reviewed. Firstly, metal hydrides were elaborated with magnesium hydrides. Secondly, the two most common boron-based storage materials $NaBH_4$ and NH_3BH_3 were summarized. There is a vast number of researches are ongoing on putting hydrogen into a solid carrier, however, this scope is limited with the promising types for the marine environment.

The metal hydrides store hydrogen by synthetically holding the hydrogen to the metal as can be seen by the name. Hydrides have interesting properties for adsorbing and delivering hydrogen at various temperatures and pressing factors, in this way, each metal hydrides have various attributes. There two different ways of delivering hydrogen from metal hydrides; thermolysis and hydrolysis. Albeit the point is something very similar for both ways, they are genuinely unique. While thermolysis is a reversible endothermic cycle, hydrolysis is exothermic and irreversible. As a rule, metal hydride storage is primarily centered around the thermolysis-based activity. Notwithstanding there are different metal hydrides storage strategies, for instance, elemental, intermetallic, or complex, this paper mainly centered around elemental metal hydrides and boron-based (borohydrides) from complex metal hydrides.

The major solid-state elemental metal hydride is magnesium hydride since magnesium is widely available, magnesium hydrides are affordable and attractive hydrogen storage methods with a density of 1.45 g/cm^3 and high hydrogen storage capacity of 7.6% (wt) (Yartys et al. 2019). Notwithstanding these benefits, the hydrogenation response energy of magnesium is moderate as a result of the framed MgH_2 layer in the capacity vessel. This layer decreases the diffusion speed of hydrogen into further steps of metal along these lines the hydrogenation getting slower and slower (Webb 2015). To overcome this issue, the operation temperature transcends 300 °C for adequate magnesium hydride formations.

On the other hand, boron-based solid-state hydrogen storage is an alternative to metal hydrides. Boron is classified as a metalloid and involves both metallic and non-metallic properties. There are mainly two boron-based storage can be found in the literature; $NaBH_4$ and NH_3BH_3. Both have bigger than 10% (wt) hydrogen capacity thanks to light boron with high storage capacity. Firstly, $NaBH_4$ with a hydrogen storage capacity of 10.8% (wt) can be released from hydrogen at 530 °C (Hoecke et al. 2021). The advantage of $NaBH_4$ is the ability to give four moles hydrogen via reaction with water. Since the ships can produce pure water from the seawater thanks to evaporators, this reaction is beneficial. However, hydrogenate is not as simple as the dehydrogenation process, so the reverse reaction is hard. On the other hand, NH_3BH_3 is another boron-based storage material for hydrogen. The gravimetric hydrogen capacity of this compound is higher than $NaBH_4$ and it offers 19.4% (wt). One of the methods to release hydrogen from the compound is to apply heat, and above 500 °C the process would be completed. The second is the hydrolysis reaction in an acidic solution at room temperature.

4.4.1.4 Alternative Hydrogen Carriers

Ammonia

Ammonia is the key chemical in fertilizer production that forms 80% of the global consumption by combining hydrogen with nitrogen from the air (Hansson et al.

2020). Ammonia has a high gravimetric hydrogen storage capacity of 17.7% (wt) at a 10 bar liquid state (Zincir 2020). Ammonia-based storage of hydrogen is a good option for ships with its easy-to-handle properties, and its ability to be produced without carbon dioxide by the Haber–Bosch process (Foster et al. 2018). This process is an exothermic reaction that can be occurred at high temperature and high pressure, it can be expressed as the following Eq. (4.24):

$$\mathrm{N}_2 + 3H_2 \leftrightarrow 2NH_3 \quad \Delta H^\circ = -91.8\frac{\mathrm{kJ}}{\mathrm{mol}} \tag{4.24}$$

The most common way to produce hydrogen from ammonia is thermolysis which needs very high temperatures typically above 650 °C (Mukherjee et al. 2018). At this point, catalyst gain importance but the need for temperature would have arisen if the catalyst getting cheaper.

CO_2 based

Methanol and formic acid are seen in this section as alternative hydrogen carriers for the shipping industry. Since both are viewed as elective hydrogen carriers, they differ from ammonia by their chemical properties.

Initially, formic acid has a gravimetric hydrogen storage limit of 4.4% (wt) and it is relatively low compared with different strategies. The main benefit of formic acid is the simple dehydrogenation measure at moderately lower temperatures compared to ammonia or methanol. However, it actually has a comparable issue as far as costly noble metal catalysts (Pérez-Fortes et al. 2016). Creation of formic acid from the hydrogenation of CO_2 is an uptrend as of late yet the high-pressure factor during the CO_2 separation is as yet an issue. Secondly, methanol is the simplest alcohol and it has a gravimetric hydrogen storage capacity of 12.5% (wt). Most commonly examined way of the renewable methanol is by hydrogenation of CO_2. Dehydrogenation of methanol is realized mainly by steam reforming, oxidation, or thermolysis. The typical process occurs around 230 °C and up to 5 MPa. As an advantage, the relatively cheaper catalyst can be used during the synthesis of methanol.

Organic Liquids

Liquid organic hydrogen carriers (LOHCs) are based on the hydrogenation and dehydrogenation of the compounds to store hydrogen (Hu et al. 2015). The advantage of this method is easy handling compared to compression and appears like a promising method for ships.

The hydrogenations and dehydrogenation of LOHCs are exothermic and endothermic processes, respectively. Since the hydrogenation is an exothermic reaction, the generated heat should be removed to ensure the equilibrium. However, during dehydrogenation, heat energy should be supply for extraction of the hydrogen from the carrier. Therefore, using organic liquid for ships as a hydrogen carrier requires sustainable heat production and also a suitable heat management system to provide continuity and the efficiency of the hydrogen storage. Furthermore, LOHCs contain noble metal catalysts and this increases the cost. Although there are several types of research on the use of non-noble metals, the lifetime of the catalyst is still a challenge to address (He et al. 2018). For instance, dodecahedron-N-ethyl carbazole is one the most investigated hydrogen carrier, and it needs costly materials like platinum or palladium as a catalyst.

Hydrogen has an extremely low ignition point and high combustibility, consequently, storage and use ought to be at the highest point of safety in a high-risk region like ships. Here the primary issue happens because of the poisonous properties of ammonia and explosion risk of high-pressure hydrogen tanks. Furthermore, bunkering framework and the worldwide spread of hydrogen bunkering stations are an outright requirement for the shipping industry in the meaning of applicability. However, it is likewise a typical issue for a wide range of storage techniques because of the usage frequency of hydrogen in the maritime industry. In this viewpoint, storage limit per weight and volume acquire significance for the ease of use onboard ships. The conspicuous techniques are compressed hydrogen in regards to its technological maturity and ammonia with relatively simpler storage conditions. Liquid hydrogen may be another solution in the next years if the onboard tank isolation and refrigeration system can be solved efficiently. The others are somewhat frail alternatives because of weighty ocean conditions and worldwide bunkering availabilities.

The efficiency is directly evaluated from the point of view of the energy need for hydrogen storage requirements. Van Hoecke et al. analyzed the total energy required to produce and store 1 kg hydrogen and the compressed hydrogen requirements seem like the optimum one among different methods (Hoecke et al. 2021).

Lastly, from the reliability perspective, ease of bunkering and onboard operational requirements are reviewed to evaluate the storage methods. The previous experiences in shipping industry are the key element to evaluate the reliability for bunkering and fuel operations. In this manner, liquid storage such as methanol, ammonia, liquid hydrogen, and also solid-state storage are the strong options. However, liquid hydrogen supply port still requires new and safe infrastructures and spread all over the world. Hence, methanol and ammonia are one step ahead of liquid hydrogen but formic acid has not been tested onboard ship yet and it reduces the advantage of methanol for CO_2 based storage in reliability.

4.5 Hydrogen Fuel Cells in Shipping

Fuel cells are electrochemical devices that can use hydrogen directly to generate electric power without any combustion process (Inal and Deniz 2018; Sharaf and Orhan 2014). There are many different application areas such as; fuel cell electric vehicles in the transportation sector, backup power sources for portable applications or energy, and heat generators for high power demands in stationary applications (Bassam 2017a; Ellamla et al. 2015; Hasani and Rahbar 2015; Inal and Deniz 2021; Ma et al. 2021; Sorlei et al. 2021; Abkenar et al. 2017; Wu and Bucknall 2020). Fuel cells play an important role during the transition to sustainable energy production with their fewer GHG emissions compared to fossil fuel using technologies like internal combustion engines (Bicer and Dincer 2018). In this perspective, hydrogen fuel cells offer a great advantage for ships when the new emission regulations which are aiming to reduce GHG emissions of maritime transportation are considered (Bicer and Dincer 2018).

Fuel cells are formed from an electrolyte that is placed between a fuel electrode (anode) and an oxidant electrode (cathode). The hydrogen fed into the anode side releases its electrons to pass from an external circuit where the load is connected. Then, hydrogen atoms pass through the electrolyte to the cathode side and in presence of oxygen, they reunite with its electrons which are released at the anode side of the cell by producing water at the cathode side. The basic working equations can be seen in Eqs. (4.25) and (4.26).

Anode:

$$H_2O \rightarrow 2e^- + 2H^+ \tag{4.25}$$

Cathode:

$$O_2 + 2e^- + 2H^+ \rightarrow H_2O \tag{4.26}$$

4.5.1 Fuel Cell Types

Fuel cells can be categorized according to their electrolyte types (Tronstad et al. 2017). There are mainly five types of commercial fuel cells; alkaline, proton exchange membrane, molten carbonate, solid oxide, and phosphoric acid. Alkaline fuel cell (AFC) is the first fuel cell type developed in 1939 (De-Troya et al. 2016). It works below 100 °C and uses relatively affordable alkaline electrolytes and this made it popular for a long time. AFCs are mostly used in NASA space shuttles to generate power during space missions. However, limited power capacity and requirements of pure hydrogen cause to lose its popularity compared to new fuel cell types. Proton exchange membrane fuel cells (PEMFC) are the most common and developed technology among different fuel cell types. It works at low temperatures and uses hydrogen in high purity as a fuel (Barbir 2005). In case of the need to use hydrocarbons as fuel, several methods of hydrogen extraction should be performed. PEMFC has two different working characteristics according to operating temperature; low and high. Low-temperature types (LT-PEMFC) are the most traditional ones compared to high-temperature working fuel cells (HT-PEMFC). As can be noticed from the classification, low-temperature types work below 100 °C, besides, high-temperature types work above 120 °C up to 200 °C (Rosli et al. 2017). The working temperature difference comes from the membrane material and its characteristics meanwhile the development of novel membranes and catalysts allows to work at higher temperatures. The higher temperatures offer an ability for reaching higher efficiency and it reduces the sensitivity to impurities in the fuel, for example, HT-PEMFC is 3–5% less sensitive to CO compared to LT-PEMFC (Boaventura et al. 2011). The same approaches are valid for the three other high-temperature working fuel cells; solid oxide fuel cell (SOFC), phosphoric acid fuel cell (PAFC), and molten carbonate fuel cell (MCFC). Both can use hydrocarbons like natural gas as fuel thanks to high working temperature and internal reforming ability to produce hydrogen (Tronstad et al. 2017). However, it should be noted that, in the case of using hydrocarbons, the formation of CO_2 will be happened during the internal reforming to produce hydrogen. Therefore, not only power generation technology but also fuel type is also important in the aim of reaching zero-emission. While MCFC works around 600–800 °C, PAFC operates around 150–200 °C, and SOFC can reach to 1000 °C (Inal 2018; Marefati and Mehrpooya 2019). MCFC and SOFC have relatively higher energy output capacity (MW levels) and higher efficiency compared to low-temperature fuel cell types. They can be used with heat recovery systems, for instance, high-temperature fuel cells can be combined with steam and gas turbine systems by using flue gases to increase the total efficiency. In this case, the total efficiency can reach 85% (Tronstad et al. 2017). On the other hand, high-temperature fuel cells have slower start-up times, lower power density, and material corrosion disadvantages (Han et al. 2012). Due to the slow response time of fuel cells, an additional power source is required to supply peak power needs and store the excess energy for specific mission profiles (Garcia et al. 2009). Furthermore, since the researches on the extension of the fuel cell lifetime mostly focus on the PEMFC, the periodic change of electrolyte and components increase the operational cost for other types, especially for high-temperature types (Table 4.8).

Ship propulsion systems have high power requirements especially when they are compared with fuel cell cars. Therefore, it limits the range of fuel cell types as the main power unit. In this manner, MCFC and SOFC are the prominent types but PEMFC is also rapidly increasing the power capacity. Moreover, fuel cells are modular and it increases the flexibility of shipbuilding opportunities. So, fuel cells can be also an effective solution for electric production instead of the propulsion unit. But it should be noted that most of the ship-sourced emissions are coming from the main diesel engine which is used for powering the propeller.

Table 4.8 Fuel cell types according to operation temperatures and efficiencies (Inal and Deniz 2020; Tronstad et al. 2017; Biert et al. 2016)

Type	Operation temperature (°C)	Efficiency (%)
AFC	50–90	50–60
LT-PEMFC	60–100	40–60
HT-PEMFC	120–200	40–80
PAFC	150–250	40–50
SOFC	800–1000	50–85
MCFC	600–700	40–85

4.5.2 *Maritime Fuel Cell Projects*

Several fuel cell ship projects have been carried out for years and the most significant ones are briefly explained in this section.

4.5.2.1 FellowSHIP

The FellowSHIP is one the most important fuel cell ship projects with the aim of demonstrating MCFC system onboard ship. The substantial side of the project is the use of a hydrocarbon fuel (LNG) instead of the pure hydrogen for a fuel cell system on an offshore supply vessel named "Viking Lady". After an operation period of 18,500 h any NO_x, SO_x, and PM emissions are observed (Ovrum and Dimopoulos 2012).

4.5.2.2 METHAPU

The METHAPU project was aiming to develop and validate the successful application of methanol using SOFC system onboard ship. The tests were applied on a car carrier ship where the 20 kW SOFC is used which is developed by Wartsila (Bassam 2017b). The project has demonstrated the feasibility of methanol with fuel cell and assessed the environmental impact of this new fuel.

4.5.2.3 Nemo H2

Nemo H2 program was a good demonstration of onboard hydrogen storage and PEMFC usage for powering a passenger ferry which operates in Amsterdam. Hybridization of 60 kW fuel cell system with lead acid battery packages shows a good performance, however, lack of hydrogen bunkering infrastructure causes not to enter into service (McConnell 2010).

4.5.2.4 ZEMSHIP

The project is designed as an inland passenger ship equipped with PEMFC to serve in Hamburg, Germany. The ultimate goal was to demonstrate a zero-emission shipping using hydrogen fuel. In this perspective, installation of hybrid battery and fuel cell system successfully operated between 2006 and 2010.

4.5.2.5 SchIBZ

This project is designed for the 500 kW diesel using SOFC system but only 27 kW is demonstrated on a multipurpose ship. Moreover, 50% electrical efficiency is reached for more than 1000 h by using low sulphur diesel oil by emitting lower pollutant emission compared to diesel engines at the 10 kW tests stands (Ma et al. 2021; Biert et al. 2016).

4.5.2.6 Pa-X-ell

The Pa-X-ell is the second project under SchIBZ program by focusing on the safety aspects of methanol fed HT-PEMFC powered ships. Rather than efficiency, emission or technical perspective, the project aims to find a suitable placement and management system for onboard alternative fuel and fuel cell applications (Table 4.9; Figs. 4.14 and 4.15).

Table 4.9 Examples of several fuel cell ship projects

Project	Time	FC type	Fuel type	Partners
FellowSHIP	2003–2013	MCFC	LNG	DNV&GL and Wartsila
METHAPU	2006–2009	SOFC	Methanol	Wartsila
Nemo H2	2008–2011	PEMFC	Hydrogen	Alewijnse
ZEMSHIP	2006–2010	PEMFC	Hydrogen	Proton motor
SchIBZ	2009–2016	SOFC	Diesel	Thyssen krupp
Pa-X-ell	2009–2016	HT-PEMFC	Methanol	Meyer werft

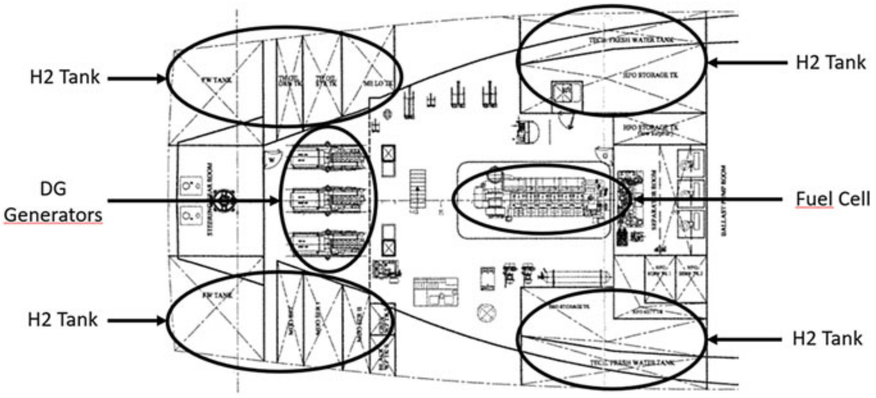

Fig. 4.14 Possible placement of hydrogen tanks and fuel cell systems on the engine room plan of a chemical tanker ship (figure reproduced and adapted) (Inal 2018)

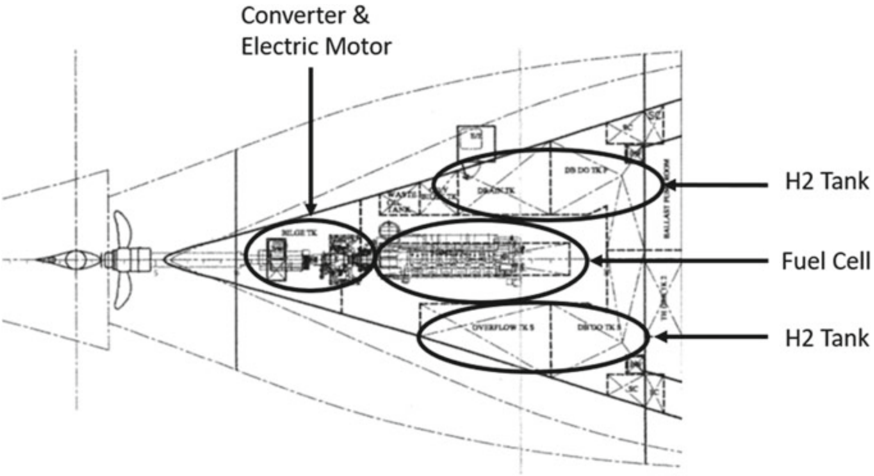

Fig. 4.15 Possible placement of converter, electric motor, and hydrogen tanks on the engine room plan of a chemical tanker ship (figure reproduced and adapted) (Inal 2018)

4.6 Hydrogen Combustion in Marine Engines

Hydrogen is considered the most up-and-coming energy source because of its high heating value for unit mass, wide range of combustion limits, carbon–neutral content, and obtainability from renewable energy sources. This makes hydrogen as an attractive alternative fuel in the future. In this section, the potential usage of hydrogen in marine diesel engines will be examined.

4.6.1 Combustion of Hydrogen in Internal Combustion Engines

Carbon-free fuels are becoming significant topic in internal combustion engines. In order to decrease the harmful emissions of carbon-contained fuels, hydrogen is a prominent way for the transition of fuels into the environmentally friendly perspective.

There are significant breakthroughs at usage of hydrogen in the internal combustion engines. As a fuel, with zero-carbon content, H_2 results in neither carbon emission nor soot, the water is produced as a combustion product. However, the pure H_2 has technical drawbacks in combustion as well as in storage and transportation.

Hydrogen has higher heat value than other conventional fuels together with rapid burning and high reactivity specifications. Although intrinsic limitations of combustion of pure hydrogen in internal combustion engines owing to low ignition energy, there are many applications on both spark ignited and compression ignition engines.

The self-ignition of hydrogen and limited compression ratios in operation become more critical in high equivalence ratios. Therefore, applicable hydrogen combustion is generally limited to lean-combustion processes. The lean-combustion limitation enables low load operation with reduced peak power, can be eliminated by increased boost inlet pressures. Additionally, H_2 can be advantageous to use with fuels that have relatively lower burning velocity and flammability. For instance, while the maximum burning velocity is 280 cm/s for hydrogen (Kwon and Faeth 2001), it is 6–8 cm/s and 40 cm/s for ammonia (Ronney 1988) and methane (Fells and Rutherford 1969), respectively. In the hydrogen-doped hydrocarbon fuels, the flame temperatures and flammability characteristics are increased. Therefore, the NO_x emissions increases together with increased H_2 fraction in the mixture because of the elevated combustion temperatures (Li et al. 2014). On the other hand the H_2 content in the fuel brings favourable effects on CO_2 and soot emissions. The combustion concepts of hydrogen and subsequently marine engine applications are examined in the following parts.

4.6.1.1 Hydrogen as a Main Fuel for Internal Combustion Engines

Hydrogen fuel can be used in reciprocating engines with different cycles. The hydrogen combustion in the engines, as a main fuel, has been studied for premixed combustion applications for instance spark ignited engines and homogenous charge compression ignition engines generally. There are also some studies for compression ignition engines. Hydrogen has some intrinsic advantages and disadvantages for combustion in reciprocating engines where depends on characteristics of the engine and cycles.

Thanks to lean combustion capability of the hydrogen, the in-cylinder temperatures are not sufficient that to generate NO_x emissions at low load condition. That is a combustion characteristic of hydrogen, which allows low load operation. The capability of lean combustion characteristic enables NO_x emission reduction as an effective emission control strategy. The Fig. 4.16 represents the NO_x variation as a function of equivalence ration for hydrogen combustion (Tang et al. 2002). The compression ratios, in dataset, are between 12.5 and 15.3. It seems the limit for NO_x generation around 0.5 equivalence ration where a significant increment occurs above this value.

However in spite of high flammability temperature, low ignition energy of hydrogen causes unintended combustion timing near stoichiometric conditions, leads higher emissions levels (White et al. 2006). While auto ignition temperature is high for hydrogen, the activation energy quite low, comparing with the gasoline or methane (Lewis and Elbe 1962). Although the hydrogen has a wide operable equivalence ratio range, the limits, derived from increased NO_x levels and uncontrolled ignition, create a critical trade-off mechanism for combustion of hydrogen between power output and emissions. Hydrogen can be burned with spark plug in SI engines. Timing of ignition and injection has crucial role on combustion control (Hamada et al. 2013). Nevertheless, there are some issues to be solved in the engine design or operation basis

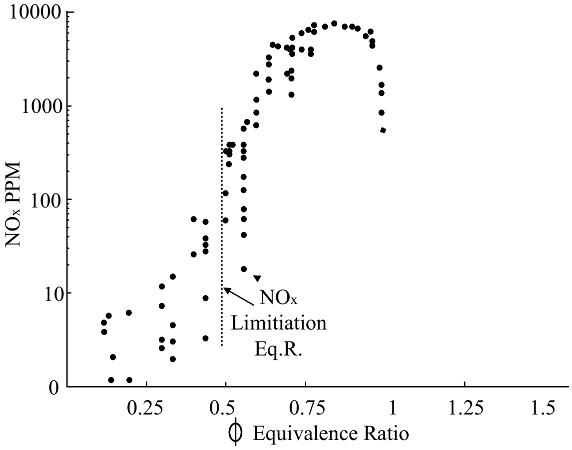

Fig. 4.16 NO_x generation as a function of equivalence ratio for H_2 combustion (figure reproduced and adapted) (Tang et al. 2002)

within the operation of the engine with hydrogen to inhibit knocking and nitrogen oxide emissions. NO_x emission is derived from higher in-cylinder gas temperatures.

4.6.1.2 Hydrogen-Natural Gas Combustion

Natural gas has less carbon fraction than fuel oil by mass, thereby, the natural gas utilization is considered alternative fuel for carbon emission reduction. Particularly, lean-burn combustion of natural has is highly attractive because of reduced NO_x emissions and allowing high compression ratios. However, relatively low combustion speed and high ignition temperature gives disadvantage on natural gas combustion. In order to improve the combustion characteristics researchers show that, hydrogen addition can improve the flame speed (Ma and Wang 2008; Sapra et al. 2018). The schematic representation of H2-NG operation in a marine engine is demonstrated in Fig. 4.17.

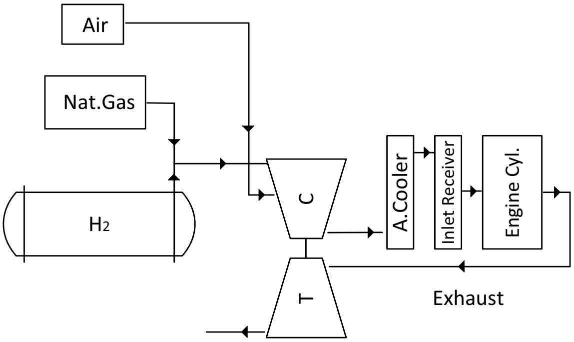

Fig. 4.17 The H_2 and Natural gas utilization in a marine SI engine

While the hydrogen addition can be carried out before TC together with natural gas, the NG can be injected to compressed air-H_2 mixture before cylinder inlet. The operation, performed in lean combustion with natural gas, the in-cylinder processes and the temperatures hence the NO_x values can be diminished while the H_2 addition has contrary effect on all. However, by controlling the intake air amount, the temperatures and the NO_x emissions could be achieved as the same amount which are under limitations.

Together with NO_x accomplishment thehydrogen provides more clean combustion with less carbon monoxide and complete combustion without hydrocarbon.

4.6.1.3 Hydrogen-Diesel Combustion

Combustion of hydrogen with diesel is carried out with diesel pilot fuel for the initiation of the combustion for the reason of high-self ignition temperature of hydrogen (Chintala and Subramanian 2016). Diesel combustion suffers from CO_2 and PM emissions because of the carbon mass fraction of the fuel. Altering the some part of diesel with the hydrogen by considering combustion energy equivalent of the diesel gives favourable effect on both carbon emissions and PM. Hydrogen addition can be conducted by two ways as intake port injection and injection at the beginning of compression stroke. A marine diesel scheme is demonstrated for the operation of the hydrogen in a two stroke marine diesel engine (Serrano et al. 2021) in Fig. 4.18.

The figure represents the engine that has uni-flow scavenging model. Hydrogen can be injected during induction via ports which are seen at the bottom of the liner or be injected after intake port and exhaust valve closes during compression. After the

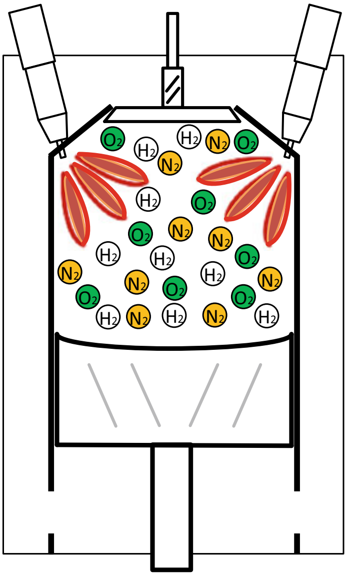

Fig. 4.18 Hydrogen mixture in a 2-stroke marine diesel engine (figure reproduced and adapted) (Serrano et al. 2021)

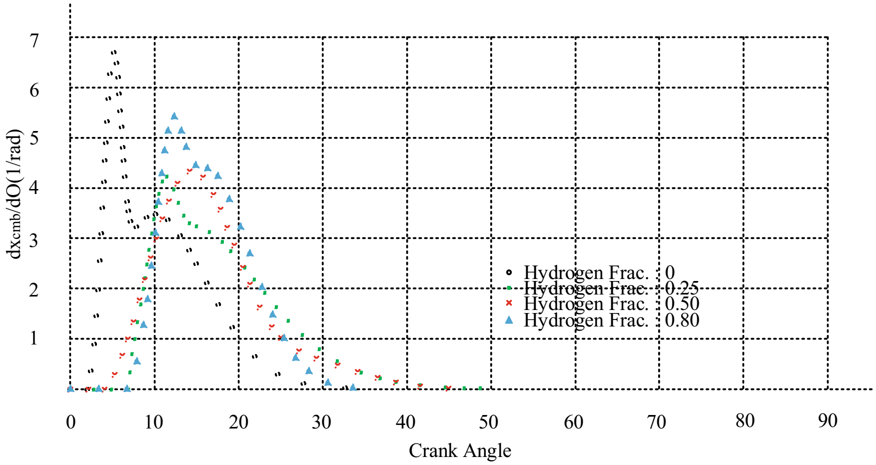

Fig. 4.19 Parameterized heat release rate of fuel mixture for different H_2 fractions (figure reproduced and adapted) (Serrano et al. 2021)

compression, the combustion is triggered by diesel injection around TDC. Hydrogen has an advantage to accelerate burning speed which causes different heat release rate during combustion process. The parametric heat release rate variation of fuel mixture (HFO-H_2) for different hydrogen fractions is given in Fig. 4.19 (Serrano et al. 2021).

It can be observed that two phase combustion (premixed and diffusive) becomes interpenetrated combustion phases with the addition of hydrogen. Also the study considers the water injection (WI) which causes ignition delay in H_2 doped mixtures, however, WI has no significant effect on heat release rate shape.

The rapid combustion of hydrogen could result in higher NO_x emission. As well as during diesel operation, the exhaust gas recirculation method (Wang et al. 2018) or water addition in the intake charge can be utilized to solve a high amount of NO_x generation in hydrogen-diesel combustion. The injection of the water in the air provide controlled combustion without self-ignition of hydrogen or knocking (Serrano et al. 2019). Addition of hydrogen in to the diesel combustion also increases the diesel combustion specific efficiency (Varde and Frame 1983).

4.6.1.4 Hydrogen-Ammonia Combustion

Ammonia is considered as a clean energy carrier, compared with carbon contained fossil fuels with its carbon-free structure and obtainability from renewable energy sources as solar energy, wind energy or biomass. Both thanks to its energy density and easy storage capability, it can be used as a fuel in internal combustion engines, including marine engines (Zincir 2020). Ammonia is a significant hydrogen carrier with a capability of storage. It can be stored as liquefied phase in the room temperature which also allows an easy transportation. Howbeit there are favourable reasons to use,

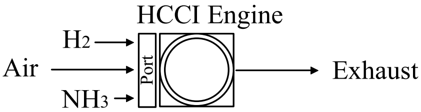

Fig. 4.20 H_2 and ammonia injection into the intake port for HCCI engine

the combustion properties as burning limitations (speed) and generation of nitrogen oxide emissions limit the operation of ammonia (Zhu et al. 2021). Therefore, it is a prevalent way that the ammonia is used with fuels, which have high reactivity. Diesel fuel, gasoline or natural gas improves the combustion performance of the ammonia as well as hydrogen (Feng et al. 2020; Yapicioglu and Dincer 2018). However, the high reactive fuels used with the ammonia, except hydrogen, contain carbon atoms, which prevent to achieve carbon dioxide neutral combustion. Hydrogen has an accelerant role on combustion, both increasing the reactivity and decreasing the time for ignition of the fuel. In order to increase the performance and practicality of ammonia, the hydrogen addition is a prominent way, which enables ammonia to use in internal combustion engines (Li et al. 2014; Lee et al. 2010) by injecting the ammonia and hydrogen in to the intake port. The representative scheme is shown in the Fig. 4.20 for the HCCI engine.

The combination of ammonia and hydrogen is regarded as ideal environmentally friendly fuel in the zero-carbon manner and has been studied by many researchers (Choi et al. 2015; Tang et al. 2021).The study (Wang et al. 2021) shows that even the addition of just 5% hydrogen improves combustion performance. By the addition of hydrogen the flame temperature increased 2080 K to ~2160 K and the laminar flame speed increased 13 m/s to 38 m/s around 1.1 equivalence ratio for 0% H_2 to 40% H_2 fraction, respectively in ammonia combustion. The doped hydrogen leads an increased propagation of combustion and also results in high NO_x emissions (Rocha et al. 2019). Additionally, hydrogen addition helps to enhance the reactivity and the combustion rate of ammonia (Lee et al. 2010). On the other hand unburned ammonia can be used to decrease NO_x emissions together with the high power output availability for the combustion (Valera-Medina et al. 2019).

4.6.1.5 Hydrogen Usage for Heat Production

Boilers are used for heating purposes in the vessels. Oil tankers require heat and boiler operation during their voyages particularly (International Maritime Organization (IMO) 2020). The boilers also use conventional fuels which have carbon content. In the perspective of carbon–neutral operation, there are also some applications of hydrogen not in ships yet but industry exists. Catalytic combustion of hydrogen can be used for heat production purposes. Marine boilers, capable of producing steam for on-board usage, are convenient for the replacement of gas boilers for cleaner production. The mixture of methane and hydrogen can be used without major modification in burners, operated by natural gas (Ilbaş and Yilmaz 2012). The utilization of hydrogen together with ammonia and the hydrogen burners achieve zero carbon emission mission (Hussein et al. 2019; Meraner et al. 2020). The studies mainly investigated the NO_x performance of the systems and a slight increase has been observed in hydrogen rich combustion (Pashchenko 2020).

4.6.2 Marine Engine Applications

To the best of author's knowledge, pure hydrogen combustion is not applicable yet, in marine engines. Due to the high power rates of marine engines and high temperatures through the components as exhaust valves, bring limitations for hydrogen combustion, while hydrogen requires high temperature for auto-ignition.

On the other hand, the injection of hydrogen in to the cylinder is another issue for marine engines which have two-stroke cycle and uniflow scavenging which allows bypass of hydrogen to the exhaust manifold without intervening the combustion process. Injection of H_2 at the beginning of compression stroke is a solution which requires additional equipment, providing high pressure hydrogen in to the cylinder.

There are various studies about application of hydrogen combustion concept in marine engines.

An ammonia-hydrogen combustion is investigated for a marine engine theoretically in the research (Wang et al. 2021). The study carried for medium speed marine diesel engine (800 rpm) with homogenous charge combustion concept, for the ignition of the mixture for varying hydrogen fraction, intake temperature and pressure and for different fuel/air ratios. The study reveals that the flame propagation of ammonia enhanced with the addition of hydrogen. The equivalence ratio has an important effect on in-cylinder pressure, temperature and flame propagation. As the hydrogen concentration increases the strictness of initial condition of intake charge decreases. It is also stated that, in order to mitigate the NO_x emissions, additional treatment for reduce peak combustion temperature, as exhaust gas recirculation or after treatment are required.

In another study, the emission contribution of a ship to the environment during its lifetime was examined (Bicer and Dincer 2018). The study focussed on ocean going tanker and cargo vessel. The ships' environmental effects are revealed by comparing heavy fuel oil and other environmental friendly fuels as ammonia and hydrogen. Needless to say that production of hydrogen or ammonia costs CO_2 equivalent that the most environmentally friendly sources used for the production are renewable energy sources. In the study, it was found that the CO_2 equivalent of the heavy fuel oil is five times more than the hydrogen fuelled engines by considering hydrogen production with geothermal energy sources.

The combination of hydrogen and heavy fuel oil Combustion (HFO) in a marine diesel engine had been investigated in another research. In order to meet the emission requirements water injection was proposed as a NO_x emission reduction technology. The study comprises a modelling methodology for the prediction of combustion. The modelling study and the validation had been completed with the dataset of HFO combustion for two stroke low speed (125 rpm) marine diesel engine with 16 MW power rate (Serrano et al. 2021). The study includes different hydrogen fractions in intake air for different engine loads to observe the effect on engine efficiency and the mean effective pressure. It is indicated that hydrogen can be supplied with two methods; (1) through port injection and (2) the injection after intake port closes. Since the two-stroke marine diesel engines have uniflow scavenging, some part of intake air passes the cylinder without any combustion process. In the port injection of hydrogen, significant amount of hydrogen bypasses the combustion zone which affects the efficiency of the engine. As a solution of problem, variable exhaust valve timing is applied to the engine operation in different loads. The exhaust valve timing advanced and the reduction of hydrogen bypass was achieved. The (2) second strategy is claimed as more effective than the (1) prior injection strategy without any excess leakage of hydrogen. However, additional modification is needed for injection after port closes. To sum up, hydrogen addition had increased the total efficiency by around 3.0% for max power of the marine diesel engine, and it has been indicated the high efficiency levels could be achieved with injection after the intake port closes. Another intake port injection study has been carried out for small sized two stroke marine diesel engines with 500 kW power (Pan et al. 2014). The hydrogen effect on the greenhouse gases for different fractions of hydrogen has been investigated. Noteworthy, reduction could be achieved in only idle speed of the engine, because of the limited flow amount of hydrogen into the intake air. It is obvious that the amount of hydrogen ratio highly affect the engine emissions. For the idle speed 20 to 37% of reduction of CO_2 emissions could be achieved. Study shows as the hydrogen contributes to the total energy input for the engine the emissions reduction can be achieved.

Natural gas combustion modelling with hydrogen has been investigated in marine spark ignited engine. The natural gas engine measurement were used to develop the engine combustion characteristics via modelling tool (Sapra et al. 2020). The cases are different mixtures' ratio of hydrogen and natural gas, different equivalence ratios with the engine load variation. The study shows Seiliger modelling has satisfied higher accuracy than Double-Wiebe function in the prediction of combustion process. In another experimental study, the hydrogen is used in 500 kW marine gas engine that performed with different engine loads and 2 different hydrogen fraction as 10–20% by volume (Sapra et al. 2018). The study shows that, the combustion duration has been reduced as a consequence of increased combustion speed by hydrogen. Additionally, the combustion could be controlled at lower equivalence ratios which also help to increase efficiency as providing complete combustion of carbon atoms. It seems 4% higher engine efficiency when compared to natural gas combustion. The few studies applied for marine engine purposes are given in this part. The application of hydrogen combustion will increase in the future of maritime sector.

4.7 Conclusion

Reducing the impact of shipping emissions on global warming is provided through carbon-free fuels. As a carbon-free fuel hydrogen is a promising alternative together with ammonia for the future of maritime transportation. Production of hydrogen need an energy source that can be provided by hydrocarbons, biomass, water-splitting, produce carbon emissions except using energy from renewable energy sources. While examining the favourable environmental impact of hydrogen, the emission costs in production process, must be taken into account. After production process, hydrogen storage is an important issue because of being gas phase in atmospheric conditions. While the volume required to store hydrogen at onshore facilities is not an issue, onboard storage is crucial due to the ship's limited gross tonnage. There are different ways to store hydrogen onboard as; liquid storage, compressed storage, solid-state storage, and alternative hydrogen carriers which have relative ease of storage capability. It is exceptionally evident that in not so distant future and with the present innovation, hydrogen can't be a solid option for ships yet, so the inventory network, bunkering, and capacity ought to be improved.

The hydrogen production lifecycle costs were examined in the study. According to the comparison of lifecycle costs of hydrogen production methods, steam reforming with CCS has the lowest hydrogen production cost recently. Pyrolysis and steam reforming without CCS followed it. The highest production cost is for coal gasification since it has the highest effect on human health and the environment. Nuclear and wind energies can cope with steam reforming, but solar energy is not an effective way to produce hydrogen for now.

The usage of hydrogen, to generate power in ships, performed by two main ways as fuel cells and internal combustion engines. Fuel cells are still expensive than conventional internal combustion engines. However, endeavours on emission mitigation drive the industry to alternative fuels and alternative energy producers. From this perspective, hydrogen fuel and fuel cells are promising technology with only water emissions. In the case of using hydrocarbons as fuel, fuel cells have still substantial advantages compared to marine diesel engines such as higher efficiency, lesser maintenance expenditures, lesser noise, and vibration onboard ships. Nevertheless, the first capital cost of fuel cells, limited lifetime, and difficulties onboard hydrogen storage of hydrogen are the major cost drivers and safety issues. For the maritime industry, hydrogen and fuel cells are still in early stages and immature technologies. As given before there are several problems to address. Whether these problems are resolved, it will be more realistic to expand fuel cell ships in commercial use.

The other way is combustion of hydrogen. Adding hydrogen to the intake air for the internal combustion engines both increasing the combustion efficiency and the engine total efficiency. The application reduces the emissions with the help of enhanced reaction capability and carbon-free content. While hydrogen can be burned in small spark-ignited engines directly, the knocking and self-ignition characteristics of hydrogen allow lean combustion and hinder usage in high power rated engines as marine engines. However, the addition of hydrogen into marine fuels as natural gas, heavy fuel oil, or ammonia fuel gives significant advantages on emissions. Additionally, the dual-fuel conceptsignificantly reduces the deficiencies of each individual fuel in combustion as low combustion speed, high soot emissions. The hydrogen utilization on ships initiated recently and it is expected to grow up in the near future of the shipping. To facilitate hydrogen usage at maritime transportation, bunkering infrastructures have to be spread worldwide, engine and fuel cell manufacturers have to speed up their development process, and safety procedures onboardhave to be identified completely for hydrogen. Additional attention is needed for the adaptation of hydrogen based operation, during stricter emission regulations in maritime sector.

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