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Review article

A review of low and zero carbon fuel technologies: Achieving ship carbon reduction targets

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ABSTRACT

The shipping industry has paid unprecedented attention to reducing emissions and pollution in recent years. In particular, the International Maritime Organization has enacted many regulations on ship emissions, and the industry has increasingly focused on the development and application of low-carbon marine fuels. The use of low carbon alternative fuels can effectively solve the current environmental and energy problems. At present, the alternative fuels available for ships include liquefied natural gas, liquefied petroleum gas, methanol, biodiesel, hydrogen and ammonia, etc. In the short term, liquefied natural gas, liquefied petroleum gas, methanol technology is more mature, which can be applied to ships. In the long term, biodiesel, hydrogen fuel and ammonia fuel will inevitably become the mainstream of alternative fuels for ships. However, there are some challenges in the use of alternative fuels, such as leakage of liquefied natural gas and liquefied petroleum gas, low calorific value of methanol and biodiesel, and difficult storage of hydrogen and ammonia. This work will summarize and analyze the utilization potentiality of low carbon alternative fuel, low carbon combustion technologies for ships, and some of the new clean power technologies, which has important guiding significance for the development of low carbon fuel for ships in the future.

Introduction

With the improvement of technology, the consumption of fossil fuel is increasing, various countries pay more attention to improve energy utilization and decrease pollutant emission. Among the attention of emission problem, the greenhouse effect caused by the greenhouse gas is an urgent environmental pollution problem. Greenhouse effect refers to the effect that solar short-wave penetrates the atmosphere into the ground, with the ground absorbing heat and the temperature rising [1]. The greenhouse gases in the atmosphere act like a thick glass, turning the earth into a closed greenhouse, and more than half of global greenhouse gas is from the combustion of fossil fuels [2]. Table 1 illustrates the influences of various gases on the greenhouse effect. Among them, CO_2 (carbon dioxide), which accounts for about 75 % of greenhouse gases, is the main cause of the greenhouse effect, and the global emissions of CO_2 since 1900 are given in Fig. 1 [4]. It is worth noting that the ocean accounts for about 71 % of the global area, the marine transport accounts for more than 80 % of the global transport, and the annual CO_2 emissions from ships account for about 6 % of the global emissions. At present, more than 100 gross tons of ships have reached 100,000, and the total capacity has risen to 2.1 billion tons. Fig. 2 shows the number and capacity of global merchant ships. Besides, due to the lower emission standards of ships than vehicles, the emissions of nitrogen oxides and sulfur oxides from ships account for more than 20 % of the global emissions [6]. Therefore, reducing the use of fossil fuels and the CO_2 emission for marine engines are the most effective ways to improve the environment.

In April 2018, the Maritime Environment Protection Committee (MEPC) developed a preliminary strategy for reducing greenhouse gas emissions from shipping. By 2030, reducing CO_2 emissions from shipping by 40 %; By 2050, reducing CO_2 emissions from shipping by 70 %; By the end of the century, achieving the vision of greenhouse gas free shipping. The control of ship exhaust emissions can not only improve the greenhouse effect, but also reduce the pollution of the sea. In June 2021, International Maritime Organization (IMO) also regulated Energy Efficiency Existing Ship Index (EEXI) and Annual Operational Carbon Intensity Indicator (CII) at the 76th session of the Marine Environment Protection Committee (MEPC) for reducing greenhouse gas emissions. At present, compression combustion engines, which run on diesel or Marine fuel oil with a high sulfur content, are used in most ships. Various

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countries and regions have carried out regulations for other marine engine emissions, which are shown in Table 2. It can be seen that the emission of PM (Particulate matter), NO_X (nitrogen oxides), HC (hydrocarbons) and CO (carbon monoxide) has been regulated in different degrees in the marine engine regulations. And by comparing these emission standards, it can be found that China has relatively loose restrictions on the marine emissions, but more detailed restrictions on different displacements. Additionally, SO_X emission is also a major emission for ships. It is mainly related to the sulfur (S) content of fuel, that is, almost all the sulfur in fuel is oxidized into SO_X after engine combustion. Hence, using fuels with lower sulfur content is the most effective way to reduce SO_X emissions, as specified by MARPOL Annex VI, which is shown in Table 3. For the fuels with higher sulfur content, alternative measures, such as EGCS (exhaust gas cleaning systems), are also allowed (in the SO_X ECAs and globally) to reduce sulfur emissions.

The ship's power system is mainly composed of main power plant, auxiliary power plant, other auxiliary engines and equipment. And the diesel engine is one of the most commonly used main power plants in ships. For the marine diesel engines, carbon emissions are mainly determined by the amount of diesel, so improving engine thermal efficiency can reduce fuel consumption and carbon emissions [12–14]. On the other hand, alternative fuels can reduce CO_2 emissions from the source, which are divided into the following categories: Low-carbon fuels, namely liquefied natural gas (LNG), liquefied petroleum gas (LPG), etc.; Alcohol fuel, namely methanol (CH3OH), ethanol (C2H5OH), etc.; Biofuel, namely bio-methanol, biodiesel, etc.; Decarbonization fuel, namely ammonia (NH3), hydrogen (H2), etc. [15]. In addition to alternative fuels, fuel cells, sail power and other new technologies can also be used to reduce emissions of ships. However, what is the mainstream alternative fuel for ships in the future remains controversial. Elgohary et al. [16] predicted that LNG would become a substitute for marine fuels in the future by comparing several parameters of different alternative fuels, such as availability, reproducibility, safety, cost, performance, economy and emission regulations. And the short sea shipping results proved to be specially remarkable against deep sea transport [17–20]. Noor et al. [21] investigated the background, engine performance, research progress and existing problems of biodiesel, and believed that biodiesel and its hybrid fuel had a bright future in the application of ships. Xing et al. [22] reviewed the technical progress of marine fuel cell system in detail, and analyzed the future development direction and challenges of fuel cell. Furthermore, the World Bank attracted more attention that issued a series of shipping industry decarbonization reports [23–25]. The report refers to the development potential of zero-carbon marine fuels in developing countries and indicates that ammonia and hydrogen are the most promising zero-carbon marine fuels in ship transport. The report also points out that LNG fuel may play a ' limited role ' in shipping decarbonization due to excessive methane emissions. In summary, LNG will gradually fade out of the market in the next few decades; biodiesel and methanol will not be widely used due to fuel consumption and price constraints; and green ammonia and green hydrogen will become the main fuel for zero carbon emissions of ships in the future. Moreover, for some small transport ships or cruise ships, green power such as fuel cells or sails can be used for auxiliary navigation, so as to minimize greenhouse gas emissions.

The work summarized and analyzed the clean fuels as well as

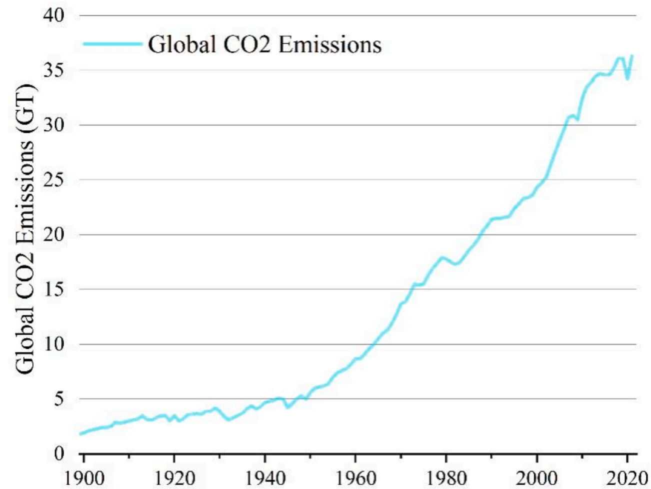

Fig. 1. Global CO2 emissions [3].

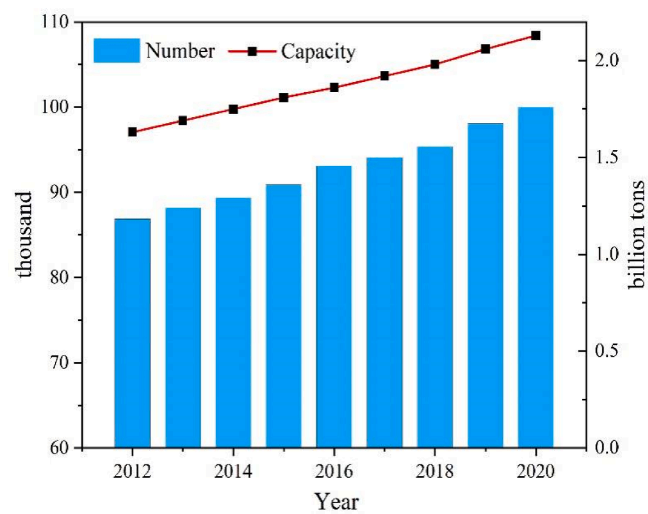

Fig. 2. The number and capacity of global merchant ships [5].

emerging clean technologies for ships in recent years. According to the characteristics of the alternative fuels, they were divided into low-carbon fuels, carbon neutral fuels and carbon-free fuels. The fuel characteristics, technology development status and existing problems of each alternative fuels were summarized. Moreover, the new power systems, such as fuel cell and sail power, were also analyzed. Finally, the future development trend of ship clean power was forecasted. The work has important guiding significance for the development of low-carbon fuels for ships in the future.

Low-carbon technologies for marine diesel engine

Fossil fuels are commonly used in conventional ships, but the CO_2

Table 1
The influence of different gases on greenhouse effect [3].

Gas	Solar radiation	Rayleigh scattering	Thermal radiation	Continuity	Temperature lapse rate	Heat capacity
N_2	–	+	–	–	–	+
H_2O	+	–	+	+	+	–
O_2	–	+	–	–	–	+
Ar	–	–	–	–	–	+
CO_2	+	+	+	+	–	+
CO	–	–	+	–	–	+

Table 2
Marine engine regulations.

Emission regulations	Ship Types		CO (g/kWh)	HC (g/kWh)	NO_X (g/kWh)	PM (g/kWh)	Date
EPA Tier 4 standards for marine diesel category 1/2 engines [7]	$P \geq 3700$		–	0.19	1.8	0.12	2014
			–	0.19	1.8	0.06	2016
	$2000 \leq P < 3700$		–	0.19	1.8	0.04	2014
	$1400 \leq P < 2000$		–	0.19	1.8	0.04	2016
	$600 \leq P < 1400$		–	0.19	1.8	0.04	2017
EU stage V emission standards for inland waterway vessels [8]	$19 \leq P < 75$		5	4.7	4.7	0.3	2019
	$75 \leq P < 130$		5	5.4	5.4	0.14	2019
	$130 \leq P < 300$		3.5	1	2.1	0.1	2019
	$P \geq 300$		3.5	0.19	1.8	0.015	2020
China II marine engine emission standards [9]	$5 \leq SV < 15$	$P < 2000$	5	6.2	6.2	0.14	2021
		$2000 \leq P < 3700$	5	7.8	7.8	0.14	
		$P \geq 3700$	5	7.8	7.8	0.27	
	$15 \leq SV < 20$	$P < 2000$	5	7	7	0.34	
		$2000 \leq P < 3700$	5	8.7	8.7	0.5	
		$P \geq 3700$	5	9.8	9.8	0.5	
	$20 \leq SV < 25$	$P < 2000$	5	9.8	9.8	0.27	
		$P \geq 2000$	5	9.8	9.8	0.5	
	$25 \leq SV < 30$	$P < 2000$	5	11	11	0.27	
		$P \geq 2000$	5	11	11	0.5	
Brazilian Emission Standards for Nonroad Engines [10]	$130 \leq P \leq 560$		3.5	4	4	4	2017
	$75 \leq P < 130$		5	4	4	4	2017
	$37 \leq P < 75$		5	4.7	4.7	4.7	2019
	$19 \leq P < 37$		5	7.5	7.5	7.5	2019
IMO MARPOL Annex VI NO_X emission limits [11]	P greater than 130	$n < 130$	–	–	3.4	–	2016
		$130 \leq n < 2000$	–	–	$9 \cdot n^{-0.2}$	–	
		$n \geq 2000$	–	–	1.96	–	

Power (P) unit: kW; Displacement (SV) unit: L/cylinder; Speed (n) unit: rpm.

Table 3
MARPOL Annex VI fuel sulfur limits [11].

Date	Sulfur Limit in Fuel (% m/m)	
	SO_X ECA	Global
2000	1.50	4.5
2010.07	1	
2012		3.5
2015	0.10	
2020		0.5

SO_X ECA: SO_X Emission Control Areas

emission is often high in the combustion exhaust gas. At present, there are many ways to reduce CO2 emissions from Marine engines. Firstly, the carbon capture and storage (CCS) technology can collect the CO2 from ships and store it in various ways to avoid its emission into the atmosphere, which is an effective measure for ships to achieve carbon emission reduction [26–28]. Secondly, the use of low-carbon fuels instead of fossil fuels can fundamentally solve the problem of carbon emissions. Furthermore, carbon emissions can also be reduced by improving fuel efficiency to reduce the use of fossil fuels. And in the section, the marine technologies and methods of improving the fuel efficiency are summarized.

Combustion efficiency improvement for marine engines

At present, most international trade ocean transport ships use low-speed engines as propulsion power due to their relatively large size [29]. Low-speed engines are usually called ‘low-speed diesel engines’ because they usually run on ‘Diesel cycle’, which injecting diesel or other fuel near the compressed top dead center (TDC). Diesel engine has the characteristics of high thermal efficiency and good fuel compatibility, but the use of diesel (fossil fuel) determines the serious combustion pollution. Therefore, how to improve the energy efficiency and reduce the greenhouse gas emission is the key of marine diesel engine research. There are many researches on improving fuel consumption and exhaust emissions for diesel engines, and they are summarized in Table 4. It can be found that the fuel consumption can be effectively improved by changing the initial boundary conditions in the cylinder. And compression ratio has a significant impact on thermal efficiency, so ships generally use engines with large compression ratio. However, the improved diesel engine is at a higher combustion temperature, there is more heat exchange between the in-cylinder wall and the environment during combustion, and there is also heat loss in the combustion exhaust gas. Therefore, in order to improve the heat loss of diesel engines, it is necessary to reduce the combustion temperature. In recent years, low-temperature combustion (LTC) technologies, such as Homogeneous Charge Compression Ignition (HCCI), Premixed Charge Compression Ignition (PCCI) and Reactivity Controlled Compression Ignition (RCCI), have been proposed. LTC technology can not only reduce the in-cylinder combustion temperature and improve the engine heat loss by controlling the combustion mixing characteristics, but also reduce the emission of NO_X and SOOT and achieve the dual optimization of fuel consumption and exhaust gas [40–44]. In addition to improving diesel combustion and consumption characteristics, marine engine combustion emissions can be improved by using exhaust gas post-treatment technology. Table 5 illustrates the marine exhaust gas treatment technology [29]. It is worth noting that black carbon from ships is one of the main causes of greenhouse effect and polar melting glaciers. How to display and reduce the emissions of black carbon from ships is also the focus of future marine low-carbon technology research.

Marine engines powered by fossil fuel combustion face increasing emission limits such as carbon oxides, nitrogen oxides and sulfur, which require a variety of technologies to meet the requirements. It will increase the complexity of the marine power system, and the application of various technologies has limited ability to improve carbon emissions and cannot achieve a significant reduction in emissions. Therefore, the new clean alternative fuels, which comprehensively solve the emission problems, have become a research focus for ships.

Waste heat recovery technologies for ships

The engine converts chemical energy into mechanical energy through fuel combustion, and there is energy loss during the conversion process. Marine engines consume a lot of fuel in actual operation, but only about half of the energy is converted into ship power, and the rest is emitted to the environment as waste heat [45,46]. Fig. 3 shows the energy conversion diagram of a two-stroke marine engine, it can be seen that exhaust gas and cooling water are the main carriers of waste heat. Recycling and utilizing part of waste heat can improve the overall thermal efficiency of marine engine and reduce the use of fossil fuels. At present, there are various technologies to recycle waste heat from ships, such as waste-heat-recovery boiler technology, power cycle technology, etc. Waste-heat-recovery boiler technology is to make water absorb the

Table 4
Marine diesel engine combustion technologies.

Author	Method	Engine type	Content	Outcomes
Zhang [30]	Experiment	Heavy diesel engine	Effect of different intake pressure on combustion and soot emission of diesel engine	The increase of the intake pressure will promote the mixing of oil and gas, improve the starting point of diffusion combustion, and reduce the soot emission
Yuan [31]	Simulation	TBD620 diesel engine	Effect of intake conditions on combustion of EGR diesel engine	Appropriately reducing the intake temperature and increasing the pressure can reduce NO_X and soot emissions and avoid fuel consumption loss
Jayashankara [32]	Simulation	DI diesel engine	Effect of injection timing and intake pressure on diesel engine performance	Increasing intake pressure can improve combustion thermal efficiency and reduce soot emission
Wang [33]	Experiment	Heavy diesel engine	Effect of injection strategy on particulate matter of diesel engine	Under the post injection strategy, increasing the injection pressure will reduce soot emission
Liu [34]	Simulation	DI diesel engine	Effect of compression ratio on thermal efficiency of diesel engine at different peak pressures	The thermal efficiency can be significantly improved by increasing the peak pressure, compression ratio and excess air coefficient
Funayama [35]	Simulation and Experiment	Heavy diesel engine	Effect of compression ratio and specific heat ratio on theoretical thermal efficiency	Increasing the compression ratio and specific heat ratio will significantly improve the theoretical thermal efficiency
Enya [36]	Simulation	Heavy diesel engine	A new ideal combustion cycle	The increase of compression ratio is beneficial to improve engine indicating thermal efficiency
Miyairi [37]	Experiment	DI diesel engine	Effect of surface insulation of different parts on engine performance	Insulating the bottom of the head and the top of the liner can reduce fuel consumption
Assanis [38]	Experiment	Diesel engine	Effects of metal pistons with 0.5 mm and 1 mm ceramic coatings on engine performance	Compared with metal pistons, 0.5 mm coating can improve the thermal efficiency by 10 %, but 1 mm coating can reduce the thermal efficiency by 6 %
Cao [39]	Simulation	A two-stroke low-speed marine diesel engine (HUDONG D200A)	An advanced heat insulation coat, named Smart Thermal Coating (Smart TIC)	The thinner Smart TIC can significantly increase the volumetric efficiency and thermal efficiency of the engine

Table 5
Marine engine exhaust gas treatment technology.

Technical name	Technical classification	Technology principle
Selective Catalytic Reduction (SCR)	High-pressure SCR: Install the SCR in front of the turbine; Low-pressure SCR: Install the SCR behind the turbine	Spraying the urea into the combustion products to get ammonia, and ammonia reduces the NO_X in the exhaust.
Exhaust Gas Recirculation (EGR)	High-pressure EGR: Turbine front exhaust; Low-pressure EGR: Turbine rear exhaust	Adding the mixture of exhaust and air into the cylinder to reduce the combustion temperature and the NO_X emission.
Wet Combustion	Intake humidification, cylinder water, fuel emulsification and other forms	Humidifying the fuel to reduce the combustion temperature and the NO_X emissions
Exhaust Gas Cleaning System (EGCS)	Open, closed and mixed	Using seawater or alkaline material to clean the exhaust gas
Black Carbon	–	Light fuel oil technology, particle capture technology and their combination

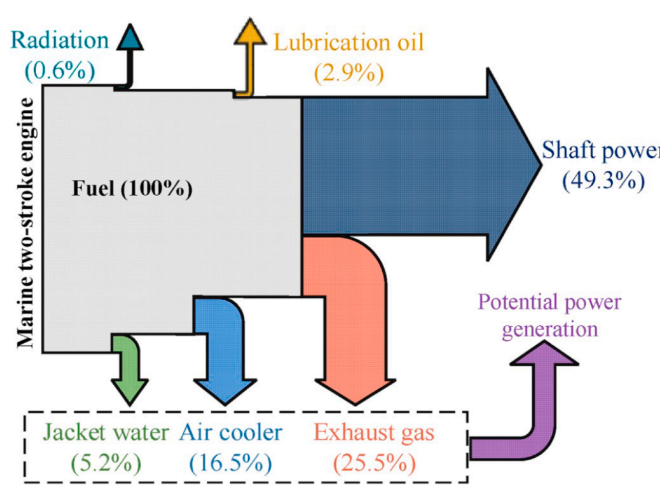

Fig. 3. Heat balance diagram of a marine two-stroke engine [47] (with permission).

waste heat of engine exhaust with phase change, and generate steam with strong power to drive turbine work. Relevant literature [48] explains that the technology can recover the waste heat generated by the engine and improve the overall thermal efficiency by 5.3 %. Power cycle technology takes working medium as the carrier, converts waste heat energy into kinetic energy, and drives equipment to work. Power cycle technology is one of the main means of marine engine waste heat recovery, it is mainly divided into organic Rankine cycle (ORC), steam Rankine cycle (RC), Brayton cycle (BC), Karina cycle (KC) and so on [47]. Among them, Rankine cycle has attracted wide attention due to its simple structure, low price and high efficiency, and there are many researches on ORC [49–54]. In addition, due to people have demands for comfort of life during sailing, the waste heat from engine can also be used for heating, refrigeration and seawater desalination to improve fuel utilization efficiency [55–58].

Various waste heat recovery technologies have been commercialized in large ships, but the reduction of emissions and the satisfaction of daily needs are still in the initial stage, which cannot meet the target of 70 % carbon reduction by 2050 and zero carbon emissions by the end of the century. Hence, it is necessary to replace fossil fuels with low-carbon fuels to reduce carbon emissions.

Alternative fuels for marine engine

In order to achieve lower carbon emission intensity, marine alternative fuels require a lower C/H ratio, and there are no pollution components such as sulfur and nitrogen in the fuel. According to the fuel composition classification, marine alternative fuels can be roughly divided into low-carbon fuels, alcohol fuels and zero-carbon fuels, as shown in Fig. 4. It is worth noting that most marine engines are low-medium speed engines, and the current research on alternative fuels for high-speed vehicles cannot be properly applied to ships [59]. Therefore, this section summarizes the research on alternative fuels for ships.

Low-carbon fuel

Liquefied natural gas

Natural gas (NG) refers to the combustible gas contained in the ground, and now, natural gas is commonly used in ships [60]. In the composition of natural gas, low-molecular alkane compounds account for more than 95 % of the composition and the unit combustion heat value is high. Moreover, due to the low proportion of carbon element and sulfur element in the composition, there is almost no SO2 in the combustion products, and the emission of CO2 is reduced by about 60 % compared with that of diesel combustion products, which can effectively improve the formation of acid rain and greenhouse effect [61,62]. But gaseous natural gas is not easy to store, and there is a risk of leakage, so natural gas is stored in liquid form in ships. Liquefied natural gas (LNG) refers to the liquid natural gas obtained by cooling to 111 K under normal pressure. Due to the dehydration and desulfurization treatment in the liquefaction process, LNG has higher methane content and less combustion pollutants [63]. Fig. 5 shows the fuel supply system of an LNG ship. The LNG is from the storage tank into the carburetor for vaporization treatment, then into the heater for temperature control, and finally into the buffer tank to continuously combust in the engine [64]. And now, the LNG marine engines are mostly dual-fuel engines, that is, a large proportion of natural gas is used instead of diesel for combustion. The dual-fuel engine is directly refitted by diesel engines, which makes the advantages of clean exhaust emissions from natural gas combustion and achieves significant emission reduction effect [65]. At present, the development of LNG technology has been mature, and the application ships have reached hundreds. Table 6 summarizes the main LNG engines in the world. At present, marine LNG engines are mainly divided into two types: modified engines and newly built engines. The modified engines can only mix diesel and natural gas, while the newly built engines can achieve pure natural gas combustion. In addition, the newly built engine can comprehensively optimize the engine structures and working parameters according to the fuel characteristics, and its emissions are better than that of the dual-fuel modified engines [67]. Table 7..

Natural gas engines have a variety of classification, according to the different way of NG delivery and mixing strategy, they can be divided into port injection engines and in-cylinder direct injection engines. Among them, in-cylinder intake engines are also divided into high-pressure direct injection engines and low-pressure premixed injection engines. And now, due to the strong power performance and good emission, the high-pressure direct injection engines are widely used in ships [68]. Marine LNG engines mostly adopt dual-fuel combustion

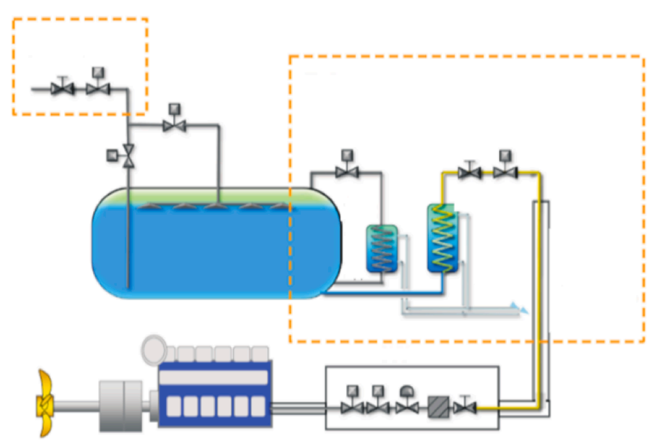

Fig. 5. Fuel supply system of an LNG ship [64].

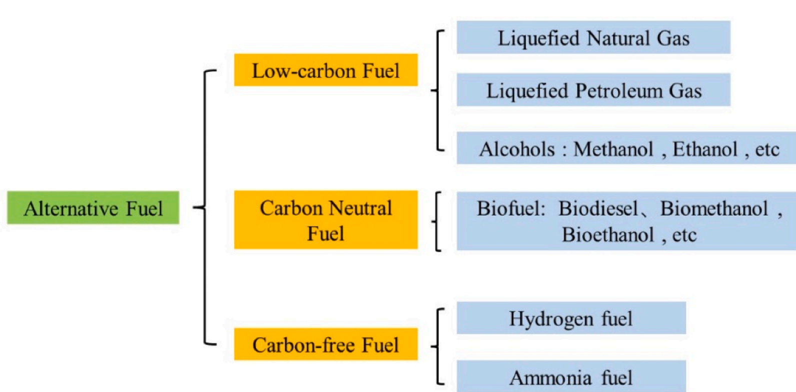

Fig. 4. Alternative fuels for ships.

Table 6
Summary of main marine LNG engines [66].

Compangy	Nation	Engine Type	Power (kW)	Speed (r·min-1)	Emissions
Daihatsu	Japan	6DE28DF	1730	720	Tier III
Yanmar	Japan	EY26DF/EY26L	1530	720	
MTU	Germany	MTU4000	1000–2000	600–800	Tier III
Mitsubishi Heavy Industries	Japan	KU30GSI	3650–5750	720	NO_X < 300 × 10–6
Caterpillar	UAS	G20CM34	10,000	720	TA-Luft2
MAN	Germany	35–44/51–60 medium speed dual fuel engine	500–21600	720	Tier III
WinGD	Switzerland	X62DF/X72DF	193,500	89	Tier III
Caterpillar	UAS	M46DF	965/cycle	500	
Kawasaki Heavy Industries	Japan	L30KG	3670–4005	750	Tier III
Mitsui group	Japan	MD36G	3000–7000	600	
Wartsila	Finland	W20DF-B	160 /cycle	1000	
Wartsila	Finland	W34DF	480/cycle	720	
Wartsila	Finland	W46DF	1145/cycle	600	
Wartsila	Finland	W31DF	530/cycle	720	Tier III
Hyundai Heavy Industries	Korea	HIMSEN	480/cycle	720	Tier III
Hyundai Heavy Industries	Korea	H54DF	8820–26460	600	Tier III

Table 7
Researches of LNG engines control strategy.

Author	Strategy	Pressure	Thermal efficiency	NO_X	HC	CO
Song [69]	Holes under high load, single hole under low load	–	↑	–	–	–
Yang [70]	Change the side angle of the injector	–	↑	↑	↓	↑
Mousavi [71]	Increase the number of injector holes	↑	–	↑	↓	↑
Yousefi [72]	Advance diesel injection timing under low loadlow speed and medium load-high speed conditions	–	↓	–	↓	–
Mousavi [71]	Advance the baseline injection timing of the diesel fuel from − 17 to − 70 CAD ATDC	↑	–	↑↑	↓	↓
Yousefi [73]	The strategy of split diesel injection that two-pulse injection	–	↑	↓	–	–
Zhu [74]	Gradually increase the EGR ratio	↓	–	↓	–	–
Kimihiko [75]	Gradually increase the EGR ratio	–	–	↓	–	–
Niu [76]	25 % EGR coupled with smaller Miller cycle (5° late valve closing Angle)	–	–	↓	–	–

mode, there are many control technologies on them, as shown in Fig. 6, and Table 7 illustrates some techniques used to improve the LNG engine. It is worth noting that the performance of natural gas substitution rate is different under different loads. Under low load conditions, the thermal efficiency decreases with the increase of substitution rate, and the NO_X emission increases first and then decreases; under medium–high load conditions, with the increase of substitution rate, thermal efficiency gradually increases, CO emission keeps decreasing, while NO_X emission keeps increasing [77,78]. Natural gas has a high ignition point (763 K) and generally requires other fuels for ignition and combustion, diesel is usually the ignition fuel. Due to the large size of marine engines, large aperture injectors are needed for fuel injection, and there are many experimental studies on spray characteristics of large diameter diesel injectors [79–83]. Furthermore, a large number of studies have been conducted on the injection strategy of LNG dual fuel engines. It is found that the engine performance can be improved effectively by changing the fuel injection timing, multiple injection, post injection and early injection. Moreover, Exhaust Gas Recirculation (EGR) is the technology that remixing the exhaust gas from the engine with the air and feeding it into the cylinder [84]. EGR technology can not only recycle the thermal energy in the exhaust gas, but also reduce the content of NO_X in the exhaust gas, and effectively improve the combustion and emission problems of the engine.

LNG as an alternative fuel for ships, the technology is relatively mature, but the emissions are also the current problems. As the fossil fuel product, LNG has limited ability to reduce CO_2 emissions, and the incomplete combustion of LNG will be accompanied with unburned methane emissions, resulting in a much higher impact on greenhouse effect than CO_2. In addition, when the LNG ship is operating at sea, it is in direct sunlight, and the temperature on the top of LNG fuel tank is relatively high. Although there is a thermal insulation layer on the outside of the tank, the high temperature environment in offshore operation increases the gas rate of LNG in the tank, resulting in fuel loss. Moreover, H_2S exists in natural gas, which is highly corrosive to the fuel tank and will cause damage to the tank. Therefore, the heat insulation coating with low thermal conductivity, such as acrylic polyurethane, can be considered to reduce the unnecessary loss caused by the temperature difference between inside and outside the tank. Although LNG still has some problems, such as incomplete exhaust gas emission and imperfect ship structure, in general, LNG is a good alternative fuel for ships and has a good prospect for development.

Liquefied petroleum gas

Liquefied petroleum gas (LPG), along with LNG, is now a common alternative fuel used in ships. LPG ships mainly carry petroleum compounds, which are propane and butane, and mixtures of the two. Depending on the mode of cargo transport, LPG ships are divided into three types: full-pressure, semi-cooled and semi-pressurized (cold-pressed), and full-cooled. The ships can be directly used as the supply site of LPG fuel ships, which is very convenient compared with the shore site of LNG. The fuel supply system of LPG fuel ships is mainly composed of gas tank, high pressure pipe, pressure reducer, closed loop actuator, mixer and control unit. When working, LPG is heated and vaporized by the heat exchanger, flowed through the inlet pipe into the pressure reducer to reduce the pressure required by the engine, then mixed with air or other fuels in the mixer, and finally flowed into the engine for combustion. The fuel supply can be adjusted through the engine speed, inlet pipe pressure and other parameters to achieve the best power performance, economy and emissions. MAN company launched the ME-LGI series LPG engines, which have achieved real ship applications and mainly used in LPG carriers. And as an alternative fuel for ships, LPG has the following advantages:

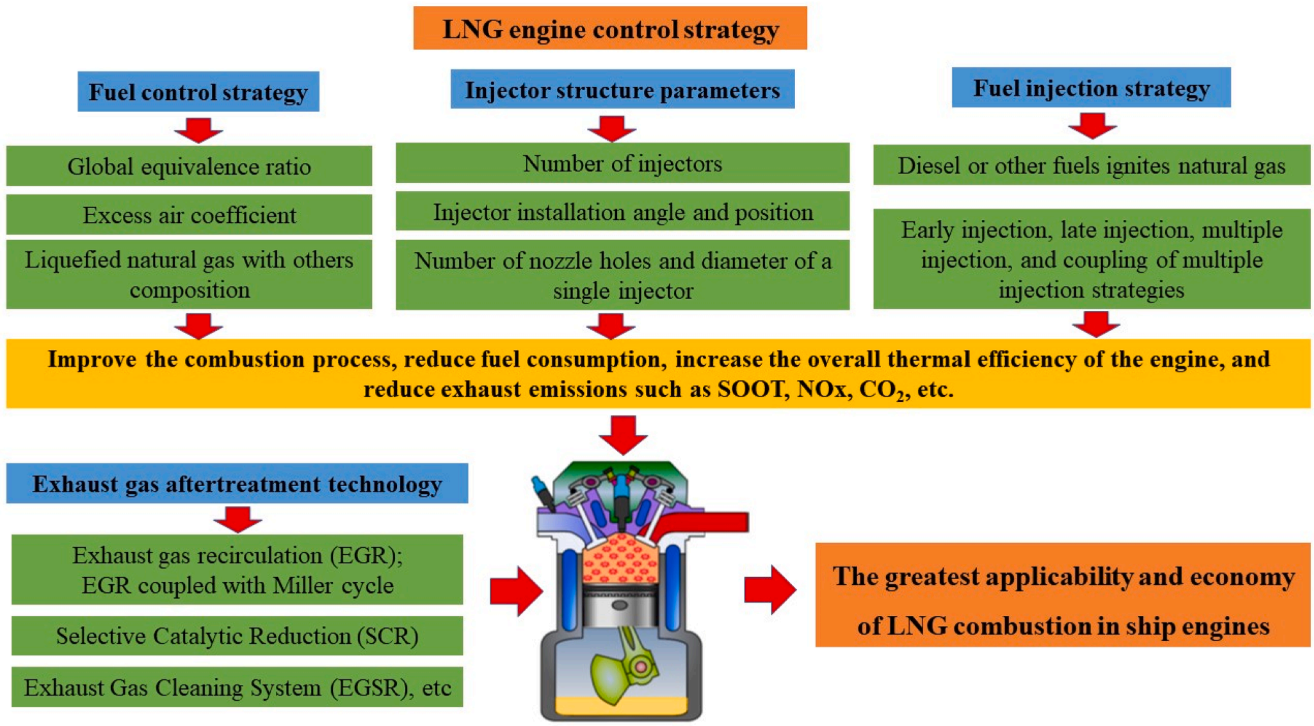

Fig. 6. Marine LNG engines control strategies.

(1) LPG is gaseous before injection, so it can form a uniform mixture with more complete combustion and lower unburned carbon and hydrogen emission;
(2) The combustion of LPG is more stable, so it can effectively reduce the emission of unburned hydrocarbon;
(3) LPG has a high octane number, which can improve the thermal efficiency of the engine;
(4) The flame temperature of LPG is low, so it can reduce the NO_X emission.

In order to explore the feasibility of LPG as an alternative fuel, many scholars have studied the combustion flame characteristics of LPG in burners [85–89]. Among the researches, Elbaz et al. [89] studied the LPG combustion flame with annular swirl and outer swirl in the staged swirl burner, and found that mixing LPG into mixture could improve the stability of flame, and reasonable swirl number could reduce flame temperature, residence time and NO emission. LPG is used in three forms in engines: single fuel method, dual fuel method and ignition improver method. Single fuel method is that LPG is injected into the cylinder and fully burned by spark plug ignition. LPG is a mixture of propane and butane, and the ratio of propane to butane has a certain influence on LPG combustion [90,91]. And by comparing the combustion performance of LPG, LNG and diesel in engines, it can be found that LPG has better combustion characteristics [92–94]. Moreover, LPG combustion can be improved by lean combustion technology. Kim et al. [95] found that LPG with stratified lean combustion can improve brake specific fuel consumption (BSFC) by up to 27.5 % and reduce NO_X emission by up to 83.4 %, and using EGR technology can further reduce NO_X emissions, but for BSFC slightly increased. Similarly, Kim et al. [96] found that stratified lean combustion could improve thermal efficiency and reduce NO_X and CO emissions, but the particulate matter emissions increased. Hence, they proposed a multicharged ignition strategy to reduce particulate matter emissions while ensuring combustion stability. For the dual fuel method, it is LPG and other fuel mixing combustion, and is commonly used in ships. According to the different mixed fuel, it can be divided into LPG-diesel dual fuel method, LPG-dimethyl ether (DME) dual fuel method, LPG-methanol dual fuel method, LPG-pure hydrogen dual fuel method and other methods. Table 8 demonstrates the studies of LPG on dual fuel engines. These studies mainly focus on engines with small cylinder diameters, and few studies on ships with large cylinder diameters. Therefore, in order to use LPG as alternative fuel for ships, it is necessary to strengthen the research on LPG in marine engines. As an alternative fuel, LPG can effectively reduce the greenhouse gas emissions of ships, and have better economic performance. Fig. 7 illustrates the reduced annual fuel consumption and cost of using LPG in South Korea, showing that by 2022, fuel consumption can be reduced by up to 10.4 % and fuel cost can be reduced by up to 25.9 %. LPG, with its advantages of wide sources and low pollution, has excellent development prospects as well as LNG. However, LPG also has the disadvantages of easy leakage and strong corrosivity, so LPG cannot be used as the ultimate ideal alternative fuel for future ships.

Methanol

Methanol is also one of the low-carbon alternative fuels for ships. Methanol contains oxygen element, and the ratio of carbon to hydrogen is 1/4, which can realize the complete combustion of self-supplied oxygen and reduce the emissions of CO and HC [107,108]. Methanol has many advantages, such as extensive sources, convenient storage, convenient transportation and filling, etc. As an alternative fuel, methanol has important significance on energy conservation and emission reduction of ships. Methanol can be produced from a wide range of sources, such as coal, natural gas, coke oven gas, biomass and even carbon dioxide. Coal and coke oven gas are the main ways of methanol generation at present, and pure methanol is carried out through gasification, purification and synthesis of raw materials, but there are environmental pollution problems due to the use of fossil fuels. In addition, natural gas is also the main raw material for methanol preparation. Steam conversion method is used to crack natural gas and synthesize methanol with CO_2. At present, the market supply and demand of methanol basically maintains a balance, but as an intermediate substance of other products, methanol still has a high market demand. Meanwhile, methanol engines have been used in ships. Wartsila and

Table 8
Researches of LPG addition to dual fuel engine.

Author	Fuel	Method	Work	Outcomes
Ngang [97]	LPG and diesel	Experiment and simulation	The combustion and emission of LPG and diesel dual fuel engines	Increasing the proportion of LPG in mixture will improve engine efficiency, power and torque and reduce NO_X and HC emissions
Simsek [98]	LPG and gasoline	Simulation	The optimal mixing ratio of LPG via response surface methodology	35 % LPG mixed with gasoline can achieve the best dual fuel combustion conditions
Rimkus [99100]	LPG and diesel	Experiment and simulation	The combustion and emission of LPG and diesel dual fuel engines	Diesel blended with 60 % LPG and properly advanced injection advance angle can ensure engine efficiency and reduce exhaust emissions
Gong [101102]	LPG and methanol	Experiment	Effects of LPG addition on methanol engine	The addition of LPG can effectively improve the cold start of methanol engine, and reduce HC and unburned methanol emissions
Kacem [103]	LPG and hydrogen	Experiment	Effects of hydrogen addition on LPG engine	Mixing 20 % hydrogen with LPG can achieve higher brake torque and reduce CO and NO_X emissions
Pastor [104]	LPG and hydrotreated vegetable oil	Experiment	Effects of adding LPG to hydrotreated vegetable oil fuel on combustion and emissions	With the addition of LPG, the ignition delay and lift-off length of the mixture increased and SOOT emission decreased
Wang [105]	LPG, DME and diesel	Experiment	LPG and DME blend on DME-Diesel dual fuel engines	The increase of LPG ratio would delay combustion, shorten combustion duration, and slightly reduce thermal efficiency and NO_X emissions

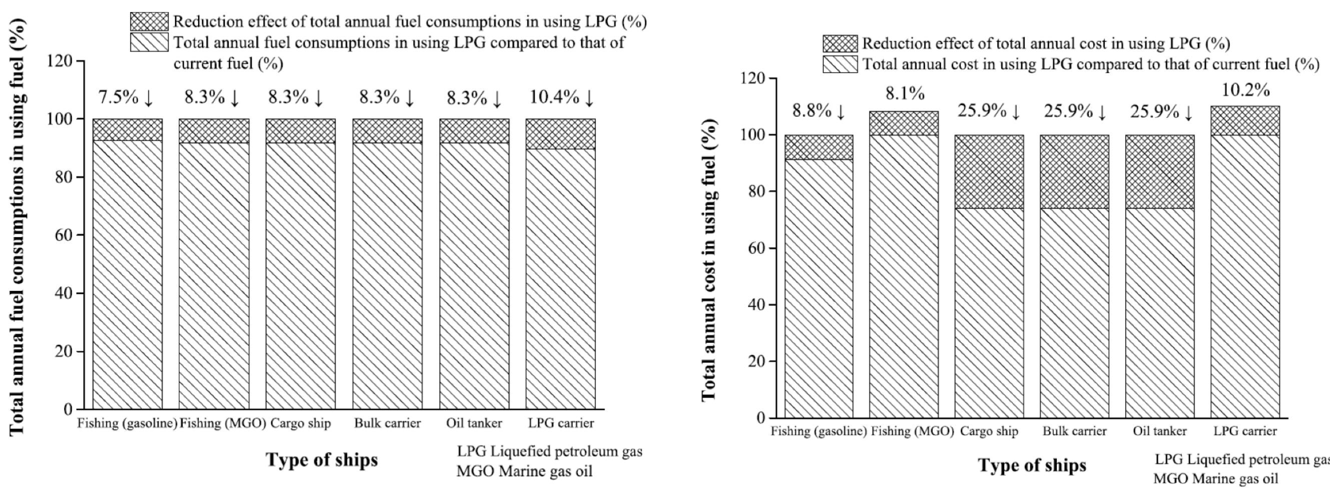

Fig. 7. Reduction effects of LPG on fuel consumption and cost (Until 2022) [106] (with permission).

MAN have launched low-speed and medium-speed methanol fuel engines, which have been applied in real ships, and Mercedes also plans to use methanol-fueled ships [109]. However, the number of methanol fuel ships in the world is still small at present, it is worth developing vigorously as a way to achieve low-carbon emissions of ships.

The application of methanol in ships mainly includes the following ways: methanol-diesel dual-fuel engine, pure methanol engine, methanol fuel cell, and so on, among which the methanol-diesel dual-fuel engine is the most widely studied and used mode at present. Fig. 8 demonstrates the research strategies of methanol fuel. Among them, marine methanol fuel cell, as a new type of power device, is still in the theoretical research stage of pure methanol engine in the world. Most methanol diesel engines on the market are modified on the basis of existing diesel engines, adding a set of methanol fuel supply system. Methanol is pumped to the storer through high-pressure oil pump and sent to the methanol injector through the fuel supply system, and the whole fuel supply system is controlled by the fuel management system [110]. The current research also illustrates that methanol fuel is one of the most promising liquid alternative fuels for internal combustion engine, as the studies of methanol in the engine shown in Table 9. There are two ignition modes of methanol as fuel in the engine, spark ignition (SI) and compression ignition (CI). As methanol has low cetane value and high spontaneous combustion temperature, it usually needs other pilot fuels to compression ignition [119]. And SI methanol engine also has difficulty in cold start at low temperature, but it can be improved by fuel blending [102,103]. Furthermore, methanol combustion has the problem of formaldehyde emission, which is a harmful or even fatal to human body, so how to improve methanol combustion and reduce the emission of pollutants is also the focus of research. In addition, methanol has also been experimentally studied in Marine engines. Xuan et al. [120] studied the combustion experiment of methanol blended diesel in 4190ZLC-2 marine medium-speed engine, and showed that methanol blended diesel could reduce in-cylinder pressure and NO_X and SOOT emissions. Similarly, Zincir et al. [121] explained that compared with diesel, methanol partially premixed compression combustion can achieve higher thermal efficiency and lower CO2, NO_X and SO_X emissions at medium and low loads in a 4-stroke marine engine. These studies have fully proved the feasibility of methanol as an alternative fuel for ships, but the large-scale application of methanol in ships still needs to be studied and explored.

Methanol, as a low-carbon alternative fuel for ships, still needs to be improved in many aspects. For example, the calorific value and theoretical air–fuel ratio of methanol are low, the dynamic viscosity of methanol is much lower than that of diesel, the corrosive nature of methanol is strong, and so on. Therefore, how to improve the thermal efficiency of methanol and the corrosion resistance of methanol injection system is the focus of future research.

Carbon neutral fuel

Biodiesel

Biodiesel, also known as fatty acid methyl ester (FAME), is a new

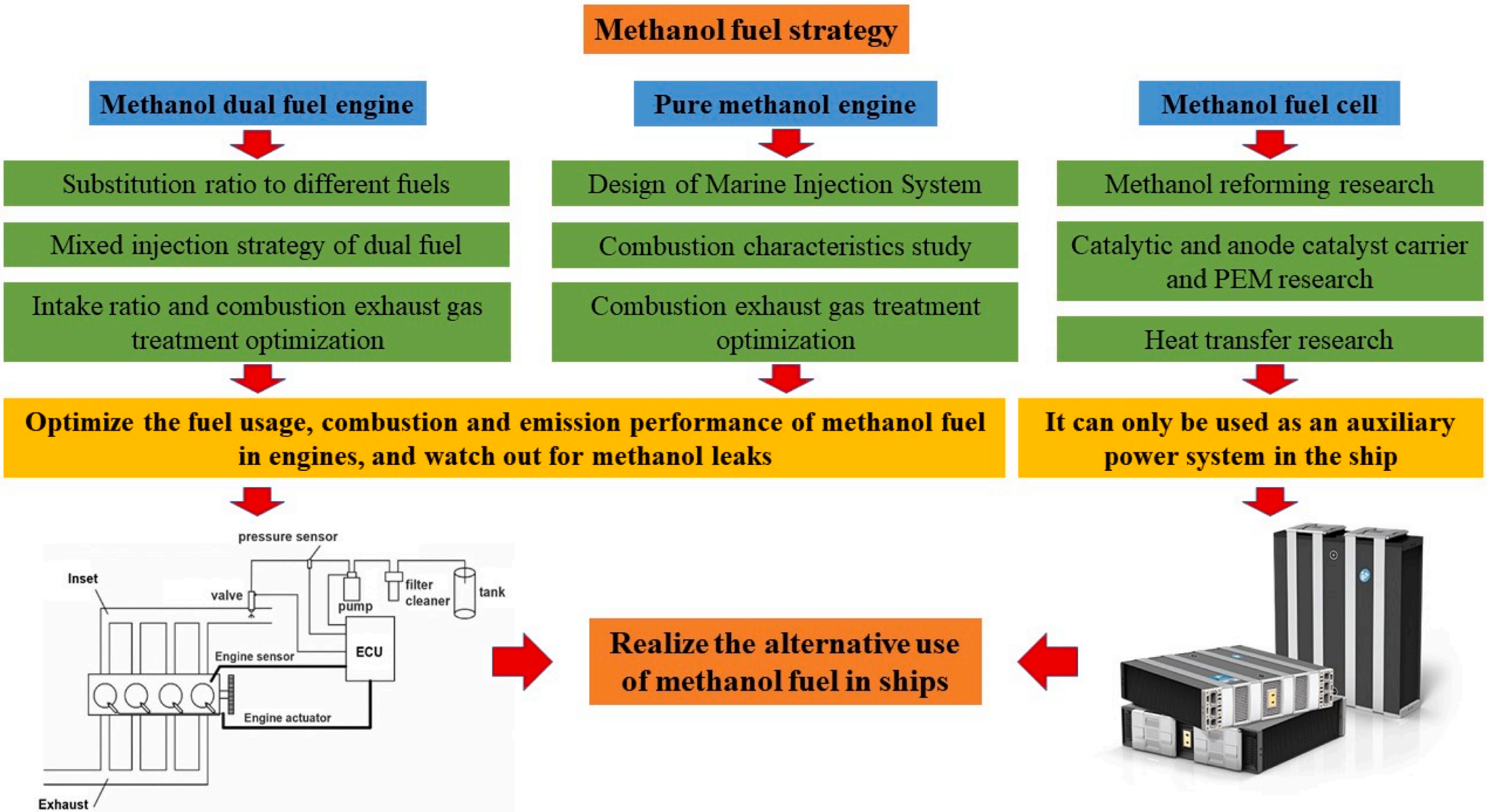

Fig. 8. Strategies of methanol fuel (The methanol engine figure on the lower left is from the literature [98]).

Table 9
Researches of methanol dual fuel engine.

Author	Fuel	Ignition Type	Research
Wu [111]	methanol and diesel	CI	Effects of methanol substitution ratio and injection strategy on combustion and emissions
Xu [112]	methanol and *n*-heptane	CI	Effects of ambient temperatures on dual fuel spray combustion via large eddy current
Ning [113]	methanol and diesel	CI	Effects of fuel injection time and methanol substitution rate on combustion and emissions at full load
Li [114]	methanol and diesel	CI	Effects of injection timing of diesel and methanol on combustion and emissions
Wang [115]	methanol and diesel	CI	Exploring the reason for the high efficiency and low emission of diesel-methanol dual fuel engine
Chen [116]	methanol and nature gas	SI	Effects of air–fuel ratio and methanol injection timing on low-load combustion and emissions
Maurya [117]	methanol and ethanol	CI	Studying the combustion and emission of HCCI engine fueled with ethanol and methanol
Liu [118]	methanol and gasoline	SI	Studying the knock suppression of methanol-gasoline dual fuels in gasoline engines with high compression ratio

type of fuel obtained from vegetable oil, animal oil, waste gas oil and other chemical processing reactions. The oxygen content in the chemical composition of biodiesel is about 10 %, which is much higher than that of traditional fossil fuel diesel. The self-oxygen supply effect can be realized after ignition, so that the combustion speed is higher than that of diesel, and the combustion duration is short and the combustion perfection degree is good [122,123]. Compared with diesel, HC and CO are reduced by about 25 % and 29 %, soot emission is reduced by more than 50 %, and PM emission is not significantly changed [124]. Biodiesel can effectively improve the energy supply, greenhouse effect and other issues. The European Union, the United States, China and other countries have also adopted various drafts to promote the development of biodiesel [125]. And the standards of the EU are relatively strict, because biodiesel in the EU is mostly used as automotive fuel, while biodiesel in the USA is mainly used as power fuel for heavy equipment [126]. Due to the different types of raw materials, the composition of biodiesel products is also differentiated, which can be divided into esters and hydrocarbons. The production technologies mainly include transesterification (the first generation), catalytic hydrogenation (the second generation) and gas synthesis (the third generation) [127], and the techniques are shown in Table 10. Compared with the first generation biodiesel, the second and third generation biodiesels have higher cetane number and similar properties to diesel, which are the ideal alternative diesel fuel. Algae technology is also a way to produce biodiesel, but it cannot be produced on a large scale because of its high cost. Moreover, as the low-carbon alternative fuel for ships, biodiesel has the following advantages [128]:

(1) Diversity. The sources of raw materials are more extensive, and the types of biodiesels are more diverse;
(2) Materiality. Biodiesel can be used to produce physical products like oil and coal;
(3) Recyclability. Biodiesel is the use of natural carbon cycle production of fuel, does not consume the earth's carbon storage;
(4) Economy. Biodiesel can expand the field of agricultural production, promote the development of rural economy and increase farmers' income.

The main component of biodiesel is long-chain fatty acid methyl esters (FAME) with ester functional groups. These FAME are mainly composed of hydrocarbon groups with 12 to 24 carbon atoms and ester functional groups with one carbon atom. According to the different FAME, it can be considered that the main components of biodiesel include methyl stearate, methyl linolenic acid, methyl palmitate, methyl oleate and methyl linoleate [129]. Due to the multi-carbon and complex composition of biodiesel, combustion and oxidation processes need chemical kinetics models to describe. As early as 2000, Fisher et al. [130] first proposed methyl butyrate (MB) to replace biodiesel. However, due to the short carbon chain of MB, it cannot well match the long carbon chain structure of biodiesel. In order to match the long carbon chain structure of biodiesel, Herbinet et al. [131] used methyl decanoate (MD) as a substitute, and showed that MD had better combustion simulation effect than MB for biodiesel, and could well simulate the formation process of early low temperature CO_2 of biodiesel. In 2010, Herbinet et al. [132] from Lawrence Livermore National Laboratory (LLNL) used three mixtures of MD, 9 - decanedioic acid methyl ester (MD9D) and *n*-heptane to replace biodiesel, and developed a detailed mechanism, including 3299 species and 10,806 reactions. This mechanism has a profound reference significance for the subsequent research of other people. Moreover, Table 11 shows the chemical kinetic mechanisms of biodiesel, they are perfected to achieve the physicochemical

Table 10
Production technology of biodiesel [128].

	Raw Material	Production Process	Ingredients	Method	Technology	Cetane Number	Low calorific value (J/g)
First-generation biodiesel	Animal or vegetable oils	Transesterification	Fatty acid methyl ester, glycerin	Acid-base homogeneous catalysis Acid-base heterogeneous catalysis	Acid catalysts convert FA into FAME, and base catalysts convert triglycerides into FAME	Around 51	38,000
				Supercritical method	Convert free FA and oils with higher water content into biodiesel under high temperature and high pressure		
Second-generation biodiesel	Animal or vegetable oils	Catalytic hydrogenation	Alkanes	Direct hydrodeoxygenation	Deep hydrogenation of grease under high temperature and high pressure	Around 90	44,000
				Hydrodeoxy isomerization	Hydrodeoxygenation and hydroisomerization		
				Diesel blending	Use traditional diesel hydrogenation equipment to blend animal and vegetable oils		
Third-generation biodiesel	Agricultural and forestry wastes such as straws	Gas synthesis	Alkanes	Gasification synthesis	Catalysis, hydrogenation, Fischer-Tropsch Synthesi and other technologies	Around 80	44,000

Table 11
Studies on chemical kinetic mechanism of biodiesel.

Author	Year	Proportion	Species	Reactions	Temperature (K)	Pressure (bar)	Equivalence Ratio
Sarathy [133]	2011	MD	648	2998	900–1800	0.1, 1	0.25–2.0
Lancheros [134]	2012	methyloctanoate, large alkanes, and 1-methylnaphthalene	1975	7865	700–1200	20, 40	0.5–1.5
An [135]	2014	MD MD9D NH	112	498	700–1800	1, 10, 100	0.5, 1, 2
Rodriguez [136]	2015	MS MO ML	461	18,217	1026–1388	7	0.75, 1.25
Cheng [137]	2015	MD MD9D NH	92	360	650–1350	10–60	0.5, 1, 1.5
Liu [138]	2016	MD MD5D ND ML	106	263	700–1500	10, 60	0.5, 1, 2
Jiaqiang [139]	2016	MD MD5D ND ML	134	475	700–1500	20, 60, 100	0.5, 1, 2
Lele [140]	2018	MB	89	560	850–1100	10–40	0.5–1.5
Li [129]	2019	MHD MOD ND	140	890	900–1310	10, 20	0.25, 0.5, 1, 1.5
Alviso [141]	2020	MD	521	1861	500–1280	1, 10, 100	0.5, 1, 1.5
Zhang [142]	2020	MD MD9D NH	156	598	700–1800	1–100	0.5–2
Wu [143]	2021	MHD, MOD, MOD9D12D, MD5D, ND	187	982	1280–1990	7.6–9.1	0.25, 1, 2
Bai [144]	2021	1,4-hexadiene, MD, methyl *trans*-3-hexenoate, *n*-hexadecane	98	314	909–1400	10	0.25

properties of biodiesel. Compared with fossil diesel, biodiesel has little difference in power performance during the combustion process, and the traditional diesel engines can directly burn biodiesel without any mechanical changes [145]. There are many studies on biodiesel as an alternative fuel in marine engines [146–151], and it can be found that biodiesel, as a substitute fuel for diesel, can reduce the in-cylinder peak pressure and effectively reduce HC and CO emissions, but also cause an increase in fuel consumption and NO_X emissions under the same load condition. For the NO_X emission, it can be reduced by HCCI combustion mode or EGR, SCR and other post-treatment technologies. In addition, biofuel also includes, in addition to biodiesel, other fuels processed from biooil. They can also be used in carbon-reducing engines and improve engine combustion performance and reduce pollutant emissions [152–157].

However, due to the large volume of marine engine and the high fuel consumption during operation, it is necessary to carry a large amount of fuel with the ship in actual navigation, which involves the complexity of storage, transportation, filtering and other equipment, and the application of real ship is less. In addition, the fuel needed for large-scale production of biodiesel is also the focus of future applications in ships. Biofuels have a bright future, but in fact, the production process of biofuels is very expensive. The large-scale cultivation of the same species of plants will cause pests, and using pesticides by human beings will pollute water, which is equal to chronic suicide. Therefore, this will also become a problem that needs to be solved in the future development.

Carbon-free fuel

Hydrogen fuel

Hydrogen is a colorless gas. One gram of hydrogen can produce 142 KJ of heat, which is three times as much as gasoline. The product of complete combustion of hydrogen is only water, with emissions of NO_X, and has less pollution to the environment. Hydrogen as an alternative fuel is characterized by non-pollution, high efficiency and recycling [158]. Hydrogen is considered to be the most ideal energy in the 21st century, but due to its extremely light weight, it is inconvenient to carry and transport. There is a lot of hydrogen in methanol, methanol can be cracked into CO and H_2 through high temperature catalytic reaction, and then mixed with diesel to form alcohol-hydrogen mixed fuel for injection into the engine. It can solve the storage problem of hydrogen. Therefore, methanol can be used as the medium for hydrogen storage. Fig. 9 shows the schematic diagram of an alcohol - hydrogen fuel system [159]. Hydrogen is produced by pyrolysis of methanol from high temperature exhaust gas, and stored in buffer tank by filtration and cooling through pipeline. Furthermore, natural gas is also one of the main sources of hydrogen production, the technology mainly uses waste heat to catalyze and reform natural gas and its part of exhaust gas [160–163]. It can not only produce hydrogen, but also realize the utilization of ship waste heat, which is beneficial to realize ship carbon emission reduction.

Hydrogen can be used for power propulsion in two main ways,

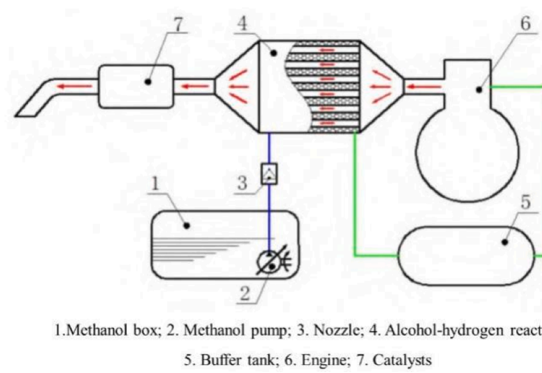

Fig. 9. The schematic diagram of an alcohol - hydrogen fuel system [159].

proton exchange membrane fuel cells (PEMFC) and hydrogen engines [164]. PEMFC works as an “inverse” device for hydroelectricity, and the oxidation and reduction reaction between hydrogen and oxygen can produce sufficient electricity for energy. Current researches on PEMFC mainly focus on the selection of catalyst, optimization of proton exchange membrane and overall thermal management of battery pack [165], and other descriptions of PEMFC are presented in Chapter 4.1. Hydrogen combustion has the characteristics of wide ignition range, fast flame propagation speed and low ignition energy, and the heat release of hydrogen combustion is high, which is three (times) than gasoline, so hydrogen can be used as a fuel in the engine. Hydrogen engines are divided into port injection engines and direct injection engines according to different fuel supply modes [166], as shown in Fig. 10. The fuel and air mixing modes of hydrogen engine are divided into internal mixing and external mixing [167]. Port fuel injection is hydrogen and air through the port together into the cylinder to achieve the external mixing. In this way, hydrogen and air are mixed for a longer time, so the mixture is more uniform and the combustion effect is better. However, it is also prone to premature combustion and tempering under high load or high compression ratio conditions [168]. Direct injection means that hydrogen is sprayed directly into the cylinder through an injector. According to the different state of hydrogen, gaseous or liquid, it can be divided into two forms: low pressure premix and high pressure direct injection, which are similar to the in-cylinder direct injection of natural gas. Compared with port injection, direct injection can achieve higher energy density and reduce exhaust emissions [169]. And a summary of specific hydrogen engine researches is given in Table 12. Wartsila (Finland), Andrew (Belgium), CMB (Belgium) and other companies have also carried out a series of studies on marine hydrogen engines [178–180]. It can be found that hydrogen engines are mainly mixed with natural gas in dual-fuel operation. In addition, the mixing of ammonia gas and hydrogen gas is also the focus of current marine engine research, which is summarized in Chapter 3.6.

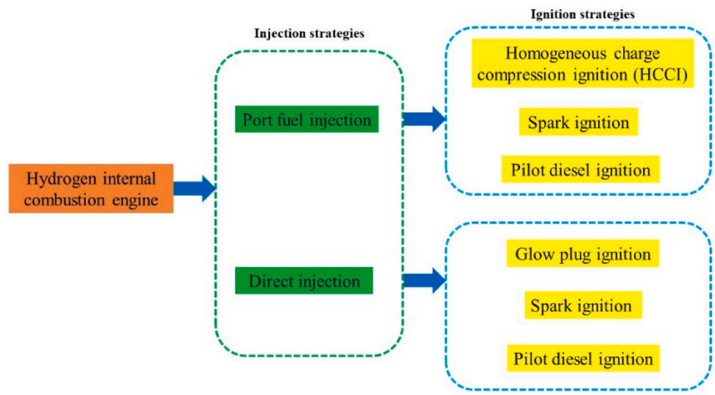

Fig. 10. Categorization of hydrogen internal combustion engine.

Table 12
Researches of hydrogen engines.

Author	Fuel	Injection Strategy	Ignition Strategy	Work
Caton [170]	hydrogen	Port injection	HCCI	To verify the feasibility of homogeneous charge compression ignition of hydrogen in the engine
Santoso [171]	hydrogen and diesel	Port injection	Pilot ignition	Combustion characteristics of hydrogen with pilot diesel in a dual fuel engine at low load
Arslan [172]	hydrogen and nature gas	Port injection	Pilot ignition	Effect of hydrogen enriched natural gas on combustion and emission of compression ignition engine
Bao [173]	hydrogen	Direct injection	Spark ignition	Effect of injection strategy on engine polytropic index, which is measured as a function of the crank angle reflects the extent of heat transfer of the engine.
Qu [174]	hydrogen	Direct injection	–	Effect of hydrogen injection valve angle on mixture uniformity and hydrogen escape for a low speed two stroke marine engine
Liu [175]	hydrogen and diesel	Direct injection	Pilot ignition	Experimental verification of hydrogen-diesel engine operation feasibility
Nguyen [176]	hydrogen	Direct injection	Spark ignition	Effect of supercharger system on power enhancement of hydrogen engine under low-load condition
Ye [177]	hydrogen	Direct injection	Spark ignition	Effect of injection timing on knock characteristics in a direct-injection hydrogen engine

As an alternative fuel for ships, hydrogen has high heating value, high combustion efficiency, and the product of complete combustion only has water, so hydrogen is an ideal alternative fuel. However, in the actual using process, the costs, safety, storage and transportation of hydrogen is a problem to be solved, and nitrogen oxides will be generated in the actual combustion products of hydrogen, how to solve nitrogen oxides is also the focus of future research. And there are fewer regulations on hydrogen and less social attention to hydrogen fuel. As a result, there is still a long way to reach a hydrogen-based economy.

Ammonia fuel

Ammonia as a decarbonization fuel is also suitable for the replacement of marine fuel, and has a good development prospect [158,181–183]. China is a big ammonia producing country, accounting for about 1/3 of the world ammonia production [184]. In recent years, ammonia has been used as a renewable and environmentally friendly alternative fuel for engines [185]. Ammonia is a colorless but irritating gas at room temperature, it does not contain carbon, and when it is completely burned, the products only contain water and nitrogen, without other polluting gases [186,187]. So ammonia is an ideal marine alternative fuel. As the fuel of the engine, ammonia is easy to obtain, store, and has high octane number [188]. At present, ammonia is mostly synthesized by Haber-Bosch process, in which hydrogen and nitrogen are pressurized to synthesize ammonia through catalyst [189]. According to the source of hydrogen, ammonia synthesis processes can be divided into the generation 1 (hydrogen production from fossil fuels) and the generation 2 (hydrogen production from renewable energy) [190]. Fig. 11 demonstrates the two production processes, by comparison, it can be found that the generation 2 can almost achieve carbon-free ammonia production, which is more in line with the goal of zero-carbon emissions. In addition, N_2 can be electrically reduced to ammonia by direct or indirect means (generation 3). Different from the Haber-Bosch process, the electric reduction process has lower requirements on N_2 purity and higher energy utilization efficiency [190]. However, the generation 3 is still under development, which promises clean and efficient ammonia production in the future.

At present, governments and enterprises around the world are vigorously developing marine ammonia fuel. In Europe, Eidesvik, Waziland and Norwegian National Oil, launched the development of ammonia fuel ships in 2020. Asiatic Lloyd signed four 7100 TEU container ships with reserved ammonia power at Dalian shipyard in 2021. In South Korea, EMEC started the research and development of ammonia fuel ship in 2020, Dayu Shipbuilding launched the design of ammonia fuel 23,000 TEU container ship in the same year, and The Korea Register of Shipping released the report on Ammonia-fueled Ships in 2021. In Japan, 23 international enterprises, classification societies and institutions, such as Itochu, formed an alliance in 2021 to jointly develop ammonia fuel for ships, and Kawasaki Heavy Industries expects to launch an ammonia-fueled engine in 2025. In China, the Shipyard launched the 180,000 - ton ammonia fuel bulk carrier design in 2019, and jointly developed ammonia fuel ships with the Italian Classification Society in 2021. Jiangnan Shipbuilding launched the design of ammonia fuel 40,000 square medium-sized liquefied ship in 2021. Meanwhile, MAN developed the first two-stroke marine dual-fuel ammonia engine in 2019, Fig. 12 showing the main principles of the ammonia engine and the dual-fuel fuel supply system [192]. When the engine is in dual fuel operation, ammonia fuel should be supplied to the engine through the supply system. In order to maintain the combustion conditions of the

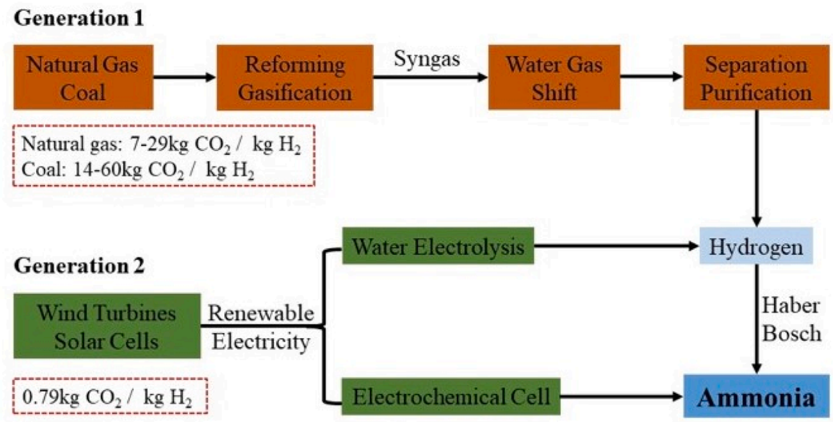

Fig. 11. Schematics of ammonia production in renewable approaches and traditional approaches [191] (with permission).

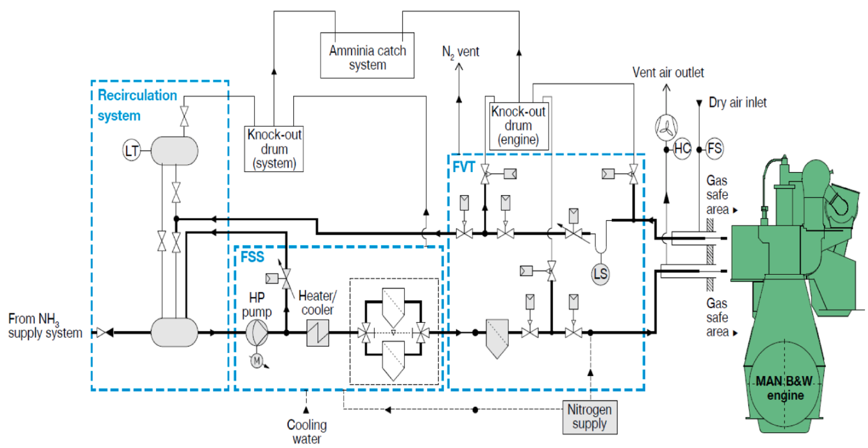

Fig. 12. The structure of the ammonia dual fuel ship [192].

engine, a small part of ammonia is recycled to the fuel supply system (FSS) through the recirculation system. The fuel valve train (FVT) can completely isolate the ammonia fuel supply system from the engine, and clean the engine with nitrogen. FVT ensures the safety hazard after the engine is closed.

The problems existing in the application of ammonia fuel in engines are also obvious, mainly reflected in the following parts. Firstly, the combustion mechanism is not complete, the combustion technology is not mature, and the calorific value of ammonia is low, which will lead to more fuels for combustion. Secondly, the flame speed is slow, the ignition is difficult, and the compression ratio of the engine is high, which leads to the overall size of the engine. At present, ammonia fuel is only used in large marine engines, which is difficult to be used in small space and high power engines. Thirdly, NO_X content in combustion products is high. In the future development, ammonia fuel can combust with other fuels, such as hydrogen fuel [193–196]. Ammonia fuel also can use spark ignition technology, by changing the injection timing, multiple injection, combustion mode and other strategies, to improve the thermal efficiency while reduce the NO_X emission [197], while Table 13 shows the researches of ammonia with other fuels in the engine. And the existing engine model is not very suitable for ammonia fuel, it is necessary to improve the engine structure. In addition, ammonia fuel in the production and transportation is also the focus of future research, the current widespread use of brown ammonia production process will also develop in the direction of green ammonia. Overall, ammonia fuel needs to improve the combustion mechanism, optimize the combustion strategy, develop new engine structure, so that ammonia can be fully burned and become the mainstream of alternative fuel for ships in the future.

The use of ammonia that is an alternative fuel for ships can effectively reduce the generation of CO_2 and achieve zero carbon emissions of ships. However, the heating value of ammonia is low. Compared with diesel, more fuel is needed to release the same heat, and it is difficult to store due to the low point of ammonia. In practice, incomplete combustion of ammonia can also cause the formation of nitrogen oxides, resulting in excessive emissions of nitrogen oxides and polluting the environment. How to improve these problems is the key to the future use of ammonia in ships.

Comparative analysis of marine alternative fuels

Alternative fuel is an important direction to achieve zero carbon emissions of ships in the future. Table 14 shows the current available alternative fuel for ships, it can be found that the energy density of zero-carbon fuel is lower than that of other low-carbon alternative fuels. Zero-carbon fuel is the most effective way to achieve zero-carbon emission of ships. At present, the most suitable alternative fuel is natural gas, but there are still emissions of carbon-containing compounds in the combustion process. In the next decade, zero carbon fuels such as ammonia, hydrogen and biodiesel will gradually replace natural gas, and dual fuel technology is also the transition to achieve this carbon free fuel. However, once considering the multidimensional standards including technology, economy, environment and sustainable raw materials, there is no clear ideal alternative fuel for ships.

Each alternative fuel has its own characteristics, advantages and disadvantages, and has developed to varying degrees. For the selection of alternative fuels for ships, on the one hand, it is necessary to consider

Table 13
Studies on co-combustion of ammonia and other fuels.

Author	Fuel	Workouts
Chen [198]	NH_3/H_2	Adding hydrogen to pure ammonia can shorten ignition delay time.
Wang [199]	NH_3/H_2	Ideal working conditions of ammonia and hydrogen mixed fuel: mixed calorific value 1.0–1.05, hydrogen fraction 40 %-60 %.
Zhu [200]	NH_3/H_2	With the decrease of ammonia concentration, the combustion flame is accelerated and the detonation is advanced.
Khateeb [201]	NH_3/H_2	The increase of ammonia content promotes the dilution injection, but decreases the flame tempering tendency, especially when the ammonia content is higher than 70 %.
Shrestha [202]	NH_3/H_2	Increasing the initial temperature, fuel hydrogen content or oxidant oxygen content will lead to an increase in laminar flame velocity, while increasing the initial pressure will decrease the laminar flame velocity.
Zhu [203]	NH_3/H_2	Under the rarefied condition, the emission of NO in the exhaust gas is as low as 100 ppm.
Hashimoto [204]	NH_3/CH_4	With the addition of methane, the flame propagation limit increases.
Xiao [205]	NH_3/CH_4	With the increase of methane, the diffusion stability of the flame decreases.
Teramoto [206]	NH_3/CH_4	When ammonia is added to methane, the dilute burning limit equivalent ratio increases and the flame tempering tendency decreases.
Tay [207]	NH_3/ Diesel	With the advance of injection timing, the heat release from the main peak increases.
Reiter [208]	NH_3/ Diesel	The ignition delay increases with increasing ammonia content.
Boretti [209]	NH_3/ Diesel	They proposed a new dual-fuel combustion system with direct injection of NH_3 and diesel.
Gross [210]	NH_3/DME	The addition of ammonia increases the ignition delay of the engine and limits the load conditions of the engine.
Yapicioglu [211]	NH_3/ Gasoline	The addition of ammonia increases the combustion temperature of the engine, reduces the power, but reduces the CO_2 emission.
Han [212]	NH_3/H_2 + CO	They proposed a mechanism for the combustion of ammonia with hydrogen and carbon monoxide.

whether the emissions of alternative fuels after combustion meet the requirements; on the other hand, it is also necessary to consider the economy, accessibility, constructiveness and environmental protection.

Economy

Price determines the economic application of alternative fuels in ships, and also determines the future development trend of alternative fuels. Based on the price of marine diesel, the prices of several alternative fuels are compared. As the popular alternative fuel for ships, LNG has been cheaper than marine diesel in the past decades, which is one of the reasons why LNG is widely used. LPG is produced from crude oil, and the price tends to be consistent with the price of crude oil. But the market price of LPG has declined since shale gas was produced in the United States, and is between the price of marine diesel and LNG. Methanol as a ship fuel, it is generally produced by natural gas, which leads to a higher price of methanol than LNG. Biodiesel has raw material sources and production constraints, so the price of biodiesel is higher than the price of marine diesel. Marine hydrogen fuel is mainly produced by electrolytic water or natural gas, so the price of hydrogen fuel is generally high, far above the price of marine diesel fuel. Marine ammonia fuel has a wide range of sources, which can be synthesized from fossil fuels and renewable fuels, so the price is relatively low. In general, LNG, LPG and ammonia fuels have higher economy.

Accessibility

For marine alternative fuels, the sufficient output is the key to determine its price and the basis for large-scale application. At present, the output of marine diesel is almost saturated, which can fully meet the needs of the shipbuilding industry. LNG is from natural gas and the output of LNG accounts for only about 10 % of the total output of natural gas. Therefore, the future output of LNG will be sufficient to replace the supply of marine diesel, and the availability is high. The output of LPG is lower than that of LNG, but the current trend is good, and the annual output can increase by about 2 %, which is also sufficient to meet the requirements of the shipbuilding industry in the future. Methanol production process is relatively complex, and the energy density is lower than that of marine diesel, which also leads to the future methanol cannot become the mainstream fuel. The current production of biodiesel is low and cannot meet the requirements of the shipbuilding industry. The global production of hydrogen fuel is about 5000 tons per year. Since hydrogen can be directly obtained through electrolysis of water, it also determines the high availability of hydrogen fuel, but the cost problem is also the limitation of large-scale application of hydrogen fuel. The current output of ammonia fuel is about 180 million tons, enough to meet the requirements of the shipping industry, it has high availability. According to the accessibility characteristic of various fuels, a comparison between the availability of various fuels is compared in this paper. In general, LNG and ammonia fuels have higher availability.

Constructiveness

The volume of the ship is large, and ships are generally necessary to supplement and maintain fuel in the port. Therefore, the development level of port facilities also represents the constructive quality of the ship. Marine diesel as a marine fuel has developed for decades, infrastructure has been very perfect. As an early proposed marine alternative fuel, LNG has developed early and rapidly. At present, 85 ports have already built or planned to build LNG filling stations. Table 15 shows the distribution of global LNG filling stations [213]. Although LPG is not as perfect as

Table 14
Main physical and chemical properties of marine alternative fuels.

Fuel		LNG	LPG	Methanol	Biodiesel	Hydrogen	Ammonia
Content		Methane	Propane	Methanol	FAME	Hydrogen	Ammonia
Molecular formula		CH_4	C_3H_8	CH_3OH	C_{12}-C_{18}	H_2	NH_3
Relative molecular weight		16	44	32	-	2	17
Element %	C	0.75	0.818	0.375	-	-	-
	H	0.25	0.182	0.125	-	1	0.176
	O	-	-	0.5	-	-	-
	N	-	-	-	-	-	0.824
Phase		Liquid	Liquid	Liquid	Liquid	Gas	Gas
Density (kg/m^3)		448	495	796	870-880	0.089	0.771
Cetane number		low	low	<5	47 - 65	-	-
Boiling point (k)		109	230.9	337.7	627	20.38	239.5
Flash point (k)		98	169	285	423 - 433	-	284
Autoignition temperature (k)		923	739	736	643 - 723	844	903
Low calorific value (MJ/kg)		48.28	46.39	19.94	35 - 37	120	22.5
Energy density (kWh/L)		7.99	9.97	7.04	-	4.11 (liquid)	6.07 (liquid)

LNG facility construction, it can be used for offshore fuel supplement by LPG vessels or for facility maintenance at ports when sailing on the sea. In addition to LNG and LPG, the infrastructure construction of methanol, biodiesel, hydrogen fuel and ammonia fuel is basically blank, which needs to be supplemented in the future. In general, LPG and LNG fuel construction is relatively perfect.Table 16..

Environmental protection

Although several alternative fuels can reduce greenhouse gas emissions, the degree of reduction is different, so the degree of emission reduction is also the key to selecting alternative fuels. On the one hand, for carbon dioxide emission reduction, LNG, LPG and methanol can achieve 10 %–30 % emission reduction, and biodiesel, hydrogen fuel and ammonia fuel can achieve zero carbon emission. On the other hand, for NO_X emissions, the NO_X emissions of several alternative fuels during combustion will exceed the Tier III standard, but the NO_X emissions can be reduced by SCR, EGR and other technologies, which need not be considered. In general, biodiesel, hydrogen fuel and ammonia fuel have good environmental protection.

Summary

Fig. 13 provides the overall comparison of several alternative fuels. In the short term, LPG, LPG, methanol technology is more mature, which can be applied to ships, and LNG is the mainstream fuel. IMO plans to reduce greenhouse gases by 50 % in 2050, while LNG, LPG and methanol have limited emission reduction capacity for carbon dioxide, so the factor will limit development. From the perspective of long-term development, the technologies of biodiesel, hydrogen fuel and ammonia fuel are gradually mature, and the fuels have outstanding emission reduction capabilities for carbon dioxide, which will inevitably become the mainstream of alternative fuels for ships. Among them, ammonia fuel will become the primary choice of alternative fuel for ships in the future due to its low price, wide source and strong emission reduction. Notably, in the view of the World Bank, the short-term outlook for LNG is not good either. On the one hand, LNG is a fossil fuel that reduces only one-fifth of carbon dioxide emissions; on the other hand, the emission of LNG includes methane, which will cause global warming dozens of times more than carbon dioxide. Similarly, IMO's fourth GHG study showed that methane emissions increased by more than 150 percent between 2012 and 2018 as LNG usage increased by 28–30 percent, which was also a direct cause of the greenhouse effect. Therefore, ammonia fuel will become the mainstream of alternative fuel for ships in the future.

New power system on ships

The renewable energy sources, such as solar energy, wind energy and marine energy, are also carried out in the direction of ship power. However, due to the low energy density, intermittent and random characteristics of these types of energy, the large-scale application in ships is limited [214]. And these new power systems are mainly used in small inland river ships or the auxiliary equipment of ocean-going ships.

Table 15
The distribution of global LNG filling stations [213].

Area	Existing	Plan	Suggestion	Summary
Asia	2	4	5	11
Europe	26	20	12	58
Middle East	0	2	1	3
North America	3	7	0	10
Oceania	2	0	0	2
South American	1	0	0	1

Fuel cell power

Fuel cell is a kind of chemical device which converts the chemical energy of fuel into electrical energy. The fuel cell is not limited by the Carnot cycle, so the thermal efficiency of fuel cell can reach 50 %–80 %, which is much higher than that of marine engine about 40 % [215]. The composition of fuel cell power generation system is relatively complex, which is mainly composed of fuel supply system, thermal management system, DC/DC converter, inverter, battery and so on [216], as the structure illustrated in Fig. 14. The fuel cell system is the main source of ship, which provides energy for the power device of the ship. And it is composed of a large number of small fuel cells. The thermal management system is the key to ensure the normal operation of the battery system, which can monitor the state of the stack. The auxiliary equipment, such as converter and inverter, can play a role in power isolation, voltage-current conversion and power distribution. Although fuel cells can produce high energy, they cannot store the energy, so the energy is generally collected into storage power batteries. At present, lithium-ion power battery, lead-acid power battery, nickel–cadmium power battery and nickel-hydrogen power battery are the four most important power batteries. Compared with other power batteries, lithium-ion power batteries have the characteristics of high energy density, no memory and long-term stable discharge, and have broad application prospects. Among them, lithium iron phosphate batteries have been certified by China Classification Society and can be used as energy sources in marine power systems [217].

Fuel cell has been invented for more than one hundred years. In 1839, British scientist Grove put forward the concept of fuel cell for the first time, and in the 1960 s, fuel cell was first used as an auxiliary power for the American Apollo spacecraft. According to the different types of electrolytes, fuel cells can be divided into alkaline fuel cell (AFC), phosphoric acid fuel cell (PAFC), molten carbonate fuel cell (MCFC), Solid oxide fuel cell (SOFC), proton exchange membrane fuel cell (PEMFC) [218], while the performance parameters and characteristics of these fuel cells are given in Table 16. And PEMFC is widely used because of its high power density and low pollution. For the combination of fuel cells and ships, Canada Ballard, Germany Siemens, Germany Proton Motor and Finland Wärtsilä manufacturers have reached significant applications [219,220]. However, the development of fuel cells in ships is limited by the high cost of fuel cells, incomplete regulations on marine battery power, thermal management, thermal runaway and etc. Moreover, fuel cells, which use hydrogen as fuel, also have the danger of inflammable and explosive when operating at sea. Although fuel cells have many problems, it is expected that fuel cells will be widely used in the shipbuilding industry, and will lead the replacement revolution of ship power system.

Sail power

Sail as a ship's power device has existed for a long time. Modern ships mainly use diesel engines as the main power device, but with the concept of energy conservation and environmental protection deeply rooted in the hearts of the people, the concept of sail power has returned to the scope of people's research. The role of sail from the ship's main propulsion power device into the use of wind energy generated auxiliary power device. Now with the research of fluid mechanics, aerodynamics, automatic control and so on, sail as a ship's auxiliary propulsion device has become increasingly mature. There are several types of ship sails, such as wing sail, sky sail, rotor sail and suction sail, as shown in Fig. 15. The wing sail is shaped like an aircraft wing, and the common wing sail shapes are rectangular sail and triangular sail [221]. The sky sail, shaped like rammed parafoils, can use the most stable and powerful wind in the upper layer to pull the ship forward. The rotor sail is composed of a rotating cylinder and an endplate at both ends of the cylinder. When used, a transverse force perpendicular to the airflow direction is generated by rotating the cylinder, which promotes the ship to move

Table 16
The distribution of global LNG filling stations [218].

Type	AFC	PAFC	MCFC	SOFC	PEMFC
Power (kW)	0.3 ~ 5	200	2000 ~ 10000	1 ~ 100	0.5 ~ 300
Fuel	H_2	H_2, NG	H_2, NG, gas	H_2, NG, gas	H_2, NG, CH_3OH
Oxidant	O_2 / H_2O_2	Air	Air	Air	Air
Plate (anode–cathode)	Pt/Ni-Pt/Ag	Pt/C-Pt/C	Ni/Al-Li/NiO	Ni/YSZ- Sr/LaMnO3	Pt/C-Pt/C
Electrolyte	KOH solution	H_3PO_4 solution	Alkali metal carbonate melt mixture	Oxygen ion conductive ceramics	Fluorinated proton membrane
Efficiency (%)	60–70	45–55	50–65	60–65	40–60
Temperature (k)	323–473	433–493	893–933	1073–1273	333–353
Startup time	A few minutes	A few minutes	>10 min	>10 min	A few seconds
Example	Spacecraft motor vehicle	Portable power source for power station	Power station	Combined cycle power generation	Vehicles, power stations, ships, etc.

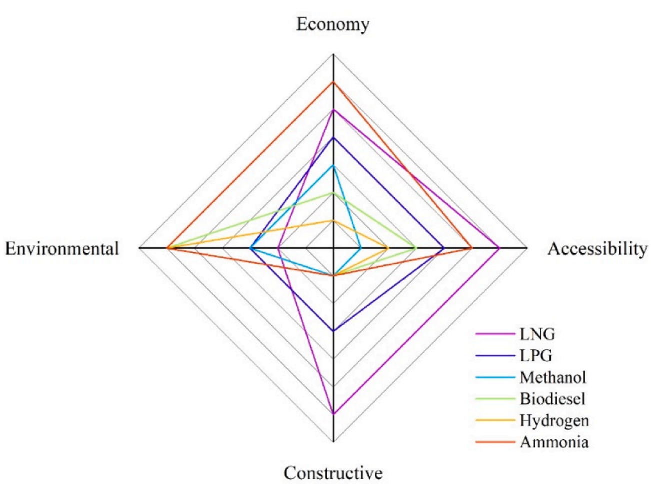

Fig. 13. The overall comparison of several alternative fuels.

forward. The suction sail is composed of a rotating elliptical cylinder and end plates on both sides of the rear edge. The suction is controlled by wind speed, wind direction, ship speed and other conditions, so that the sail achieves the best propulsion efficiency.

Among all kinds of sails, wing sail has become the most commonly used modern sail because of excellent aerodynamic and simple structural. When the wind sail works, the flow velocity on the upper surface is larger than that on the lower surface, so the pressure on the upper surface is smaller than that on the lower surface, and the pressure difference will be generated. By adjusting the windward angle of the sail, the pressure difference can be transformed into the propulsion power [224]. According to the profile curve shape, the wing sail can be divided into laminar flow type, arc type, common type and horizontal back type. And the research shows that the aerodynamic characteristics of the laminar wing are the best, followed by the arc wing, and the dynamic performance of the ordinary wing and the leeward wing is poor [225]. In recent years, with the research on sail wings, people have understanded the sail power, and successively introduced a variety of sail power systems. All kinds of sail power systems have their own advantages, but no matter what kind of sail can effectively reduce the fuel consumption of the ship. After considering various factors such as energy-saving efficiency, installation layout, safety and stability of ship power auxiliary equipment, different ship types will choose different sail power systems according to the actual situation to minimize the use cost.

Conclusion

From the current means of low-carbon emission of ships, there is no exact solution at present. In order to meet the IMO carbon reduction targets, the existing technical measures include alternative fuels such as LNG and ammonia, battery power, sail power, etc. The main conclusions can be summarized as follows:

(1) For the alternative fuels, LNG and LPG are the most widely used alternative fuels with high heat release. The technologies have been relatively mature and can meet the requirements of ship operation, but there are still high pollutant emissions. Therefore, how to solve the problems of storage, filling station and methane emission are the focus of future research.

(2) Alcohol fuels includes methanol, biodiesel, etc., the combustion products are only water vapor and a small amount of carbon compounds, which are extremely clean fuels. Therefore, alcohol fuels are one of the most promising liquid alternative fuels for internal combustion engines. However, the heating value of alcohol fuels is low, and a large amount of fuel is often needed in

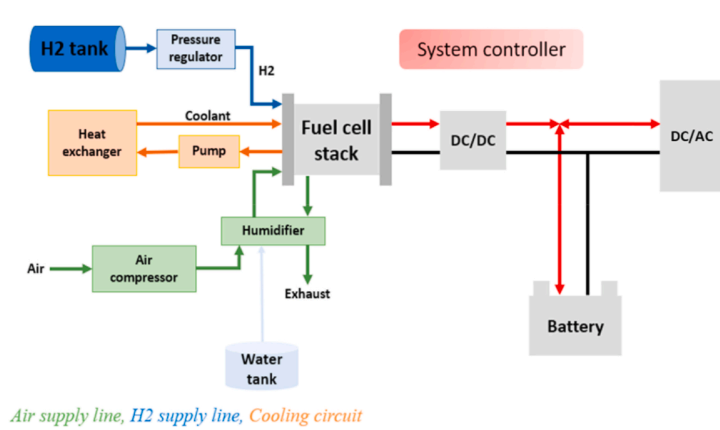

Fig. 14. Schematic of a typical hybrid fuel cell system [216] (with permission).

(a)The wing sail (b)The sky sail

(c)The rotor sail (d)The suction sail

Fig. 15. Structures of four kinds of sails [222,223] (with permission).

use. Therefore, the production of biodiesel and methanol should be considered in the future. In addition, methanol is highly corrosive, and the research of corrosion resistance device is also the direction of methanol alternative fuel research.

(3) Decarburized fuels, such as hydrogen, ammonia, can emit high heat during combustion, and there is no carbon in the molecule, so the combustion products are non-pollutant, which are the most ideal alternative fuels. However, the combustion technologies, such as mechanism and combustion characteristics, have not been perfected, which are the focus of future research. And due to the low-temperature storage problem, ammonia and hydrogen cannot be applied on a large scale in ships. How to solve the storage problem of ammonia and hydrogen is also an important research direction of marine engine alternative fuel in the future.

(4) New power systems, such as battery power and sail power, can achieve zero pollution. However, due to their own power shortage, they can only be used in some small ships or used as auxiliary power equipment for ships, and cannot be widely promoted.

(5) At present, the most suitable alternative fuel is natural gas, which has reduced greenhouse gas emissions from ships by 20 %. Alcohol fuel will reduce ship greenhouse gas emissions by 50 % over the next three decades. And at last, zero-carbon fuel is the most effective way to achieve zero-carbon emission of ships.

CRediT authorship contribution statement

Yang Wang: Conceptualization, Resources, Writing – review & editing. **Qun Cao:** Conceptualization, Methodology, Software. **Long Liu:** Conceptualization, Resources, Writing – review & editing, Supervision. **Yue Wu:** Conceptualization, Software. **Hongyu Liu:** Conceptualization, Software. **Ziyang Gu:** Conceptualization, Software. **Cunxi Zhu:** Conceptualization, Software.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

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