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Opinion

Alternative Gaseous Fuels for Marine Vessels towards Zero-Carbon Emissions

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Abstract: The maritime industry is recognized as a major pollution source to the environment. The use of low- or zero-carbon marine alternative fuel is a promising measure to reduce emissions of greenhouse gases and toxic pollutants, leading to net-zero carbon emissions by 2050. Hydrogen (H_2), fuel cells particularly proton exchange membrane fuel cell (PEMFC), and ammonia (NH_3) are screened out to be the feasible marine gaseous alternative fuels. Green hydrogen can reduce the highest carbon emission, which might amount to 100% among those 5 types of hydrogen. The main hurdles to the development of H_2 as a marine alternative fuel include its robust and energy-consuming cryogenic storage system, highly explosive characteristics, economic transportation issues, etc. It is anticipated that fossil fuel used for 35% of vehicles such as marine vessels, automobiles, or airplanes will be replaced with hydrogen fuel in Europe by 2040. Combustible NH_3 can be either burned directly or blended with H_2 or CH_4 to form fuel mixtures. In addition, ammonia is an excellent H_2 carrier to facilitate its production, storage, transportation, and usage. The replacement of promising alternative fuels can move the marine industry toward decarbonization emissions by 2050.

Keywords: net-zero carbon emission; marine alternative fuel; green hydrogen; ammonia; greenhouse gas

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1. Introduction

More than 90% of the global trade commodities are transported by sea. Sea freight plays an important role in world trade. The consequent contribution of ships to air pollution and climate change cannot be ignored. Marine transportation is the most efficient mode of freight in terms of energy use per ton kilometer (tkm) transported [1]. As the volume of goods transported by sea increases, the amount of fossil fuel consumed by merchant ships also rises rapidly, leading to an increase in greenhouse gas emissions. The maritime industry consumes 330 million tons of bunker fuel every year [2], the largest portion (77%) of which is low-quality heavy fuel oil (HFO). About 3~6% of the world's CO_2, 14~31% of NO_x, and 4~9% of SO_x come from merchant vessels [3], which implies that ships are also one of the main sources of environmental pollution. In 2020, the number of global merchant vessels increased by 3%, reaching 99,800 ships. By January 2021, the shipping capacity reached an equivalent of 2.13 billion deadweight tons (DWT) [4,5]. The maritime shipping industry accounted for 7–8% of global greenhouse gas (GHG) emissions [6]. According to the International Maritime Organization (IMO) forecast for 2050, CO_2 emissions from ocean transportation will account for over 15% of global CO_2 emissions [7]. Therefore, the International Maritime Organization (IMO) has set a target to reduce CO_2 emissions from shipping activities. The goal is to reduce the CO_2 intensity of shipping activities by 40% by 2030 and by 70% by 2050, compared to the 2008 CO_2 emissions [8]. At the same time, the Marine Environment Protection Committee (MEPC) of the IMO approved the amendments to Annex VI of the International Convention for the Prevention of Pollution from Ships (briefly denoted as MARPOL). The use of alternative marine fuels has been identified as an effective strategy to reduce SO_x, NO_x, and CO_2 emissions and move towards the target of net-zero CO_2 emissions by 2050. One of the goals of IMO is to decarbonize marine diesel engines as soon as possible in this century. Two promising fuels that meet this requirement are hydrogen (H_2) and ammonia (NH_3). These fuels contain no carbon or sulfur; so, their fuel combustion produces no carbon emissions or SO_X. Ammonia (NH_3) is combustible and could be used directly as an alternative fuel in internal combustion engines or a mixture fuel by blending NH_3 with other fuels such as a NH_3/H_2 or NH_3/CH_4 mixture [9]. Han et al. [10] also found that ammonia can be used to produce propulsive power or heating energy by its direct combustion. H_2 in the fuel mixture can facilitate the control and promote the combustion characteristics of NH_3. Apart from its use as a clean fuel, NH_3 can be used as a superior H_2 carrier for the transport, storage, production, and use of H_2. For example, NH_3 can be partially dissociated to form NH_3/H_2 fuel mixtures [9].

Xing et al. [11] considered that hydrogen and ammonia could play an important role in shipping in coastal waters. In addition, although the current cost is relatively high and the infrastructure is not completely commercially mature, liquefied natural gas (LNG) seems to be the most promising alternative fuel for global shipping. The adoption of mature alternative marine fuels is a long-term proceeding. Therefore, achieving the goal of a clean maritime transport frame as early as possible is the consensus of the global maritime community. The technology development and construction of fueling infrastructure at shipping ports determine the fate of potential marine alternative gas fuels. The demand for hydrogen has more than tripled and has continued to grow since 1975. The currently used hydrogen is produced almost entirely from fossil fuels, although hydrogen can also be manufactured from biomass, coal, or water. Natural gas or methane is particularly the main feedstock of hydrogen production, accounting for about 75% of the world's dedicated hydrogen production of about 75 million tons per year [12]. There are many ways to produce hydrogen, but not all of them are green and environmentally friendly.

There are different classifications of hydrogen types according to the manufacturing processes [13]. These hydrogen types include (1) green hydrogen, (2) grey hydrogen, (3) blue hydrogen, (4) turquoise hydrogen, and (5) brown hydrogen. Non-carbon energy (such as wind or solar energy) is used to produce green hydrogen from water molecule dissociation. Grey hydrogen is manufactured by processing hydrocarbon fuel through reactions such as steam methane reforming (SMR). If the CO_2 emission from the separation of hydrocarbons for hydrogen production is accompanied by the CCUS (i.e., carbon capture, utilization, and storage) process, it is grouped with blue hydrogen. The CCUS technology captures, separates, and compresses the CO_2 emitted during the process of converting fossil fuels into hydrogen and then transports it to a suitable storage location, to isolate and reduce the amount of CO_2 emitted into the atmosphere. The definitions for various types of hydrogen are listed in Table 1 [14,15]. Grey hydrogen accounts for around 95% of today's global hydrogen production and has the highest carbon emissions. Because the boiling point of hydrogen is $-252.87\ ^\circ C$, hydrogen is gaseous at normal ambient temperature. But the volumetric energy density of gaseous hydrogen is very low (10.8 MJ/m^3 at a pressure of 1 bar); so, unless the volumetric energy density can be increased significantly, the volume of fuel storage tanks required to meet the energy needs of ship navigation will be too large for merchant vessels. There are two main ways to reduce the volume of hydrogen storage. One method is to store hydrogen in a high-pressure container in the form of gas (i.e., gaseous hydrogen, GH_2). It is generally believed that the maximum practical pressure is 700 bar, which can increase the energy density of hydrogen to 5040 to 7560 MJ/m^3 [16], but an additional complex infrastructure is required to maintain this high pressure. Another way is to store hydrogen as a liquid state (i.e., liquid hydrogen, LH_2) at temperatures lower than $-252.87\ ^\circ C$. However, maintaining this low temperature in cryogenic storage tanks will inevitably generate high energy consumption costs, which will increase the total energy demand by up to 30–40% [17]. However, compared to GH_2, LH_2 is more cost-effective for large-scale use because of its much higher energy density. For the above reasons, Balcombe et al. [18] proposed that liquid hydrogen fuel used in the internal combustion engines of ships navigating through fixed routes is more economical and feasible.

Table 1. Various types of hydrogen.

Type	Definition
Green hydrogen	Water molecule dissociation using non-carbon energy
Grey hydrogen	Steam Methane Reforming (SMR) from hydrocarbon fuel
Blue hydrogen	CO_2 produced from the hydrogen separation process from hydrocarbon fuel and treated with CCUS.
Turquoise hydrogen	Hydrocarbon pyrolyzed to hydrogen and carbon black. A variant type of blue hydrogen.
Brown hydrogen	Produced from coal gasification, thermal pyrolysis, or water dissociation.

Source: compiled by the authors from Refs. [14,15].

2. Application of Hydrogen in Marine Vessels

At present, the main fuel for shipping is mainly hydrocarbons derived from fossil fuels. Nevertheless, the amount of CO_2 emissions depends on the hydrogen/carbon (H/C) ratio in the fuel since a higher H/C ratio makes it a more energy-efficient fuel and produces lower CO_2 emissions. Human health and environmental safety must be the main considerations for all potential transportation fuels by maritime stakeholders. Hydrogen has a wide range of flammability, ranging from 4% to 77% in air [19], which means it is also highly explosive. In addition, hydrogen gas is odorless, nontoxic, and invisible; so, leaks are difficult to detect. The widespread use of clean hydrogen in the global energy transition still faces several challenges, such as the current high cost of producing hydrogen from low-carbon natural gas. Hydrogen is also an energy carrier that can be produced through electrolysis processes. The main challenge lies in the economic and robust hydrogen storage system and transportation issues, especially when it is used on maritime vessels. Hydrogen energy is expected to replace liquid fossil fuel for vehicles such as shipping vessels, airplanes, and automobiles in the future. It is anticipated that 35% of the vehicles in Europe in 2040 will be powered by hydrogen fuel, and there are around 457 hydrogen fuel stations in the world [20].

A fuel cell is another application for hydrogen energy. Due to its high efficiency and nonpollution advantages, its technology development has been actively moved forward. A fuel cell is sometimes regarded as the power generation system with the most potential. Hydrogen fuel cell ships need to carry a large amount of hydrogen to carry out electrochemical reactions to provide propulsion power for ships. Fuel cells are mainly divided into six types, which include proton exchange membrane fuel cells (PEMFC), molten carbonate fuel cells (MCFC), solid oxide fuel cells (SOFC), alkaline fuel cells (AFC), phosphoric acid fuel cells (PAFC), and direct-methanol fuel cells (DMFC) [21]. It is expected that in the short term, using fuel cells as propulsion power in ocean-going ships will still be more expensive than using internal combustion engines, which burn hydrogen directly. Hence, fuel cells will be preferentially used in offshore shipping [22]. Previous studies have found that PEMFC is a promising alternative energy source for ships because it can provide stable, green, and sustainable power for ships. PEMFCs have been successfully used in submarines and are ideal for smaller ships due to their smaller size [23,24]. Tronstad et al. [25], after adequate evaluation found that PEMFC and SOFC are the most promising fuel-cell types for ships. Some studies found that compared with PEMFC, direct use of hydrogen as a fuel for internal combustion engines (ICE) can achieve higher environmental benefits [26].

To achieve the goal of IMO, shipping companies began to pay attention to the use of ammonia, because ammonia (NH_3) is composed of carbon-free molecules. Al-Aboosi et al. [27] considered ammonia to be an attractive option for alternative vessel fuel due to its relatively low greenhouse gas emissions, high energy density, competitive cost, and well-developed infrastructure. Cheliotis et al. [28] showed that ammonia can be used as a fuel carrier for various propulsion powers such as fuel cells. In addition, ammonia can be produced from renewable substances. The low volumetric energy density of current alternative fuels implies a greater volume of storage tanks is required for the same DWT and thus loss of loaded freight space. The biggest bottleneck for the use of hydrogen as a ship fuel is the low energy density per unit volume of hydrogen. If hydrogen is stored or transported in the form of LH_2 (liquid hydrogen) or GH_2 (gaseous hydrogen), the additional cost is extremely high. In contrast, ammonia is a compound of hydrogen and nitrogen. This substance has many possible applications, most commonly used as an agricultural fertilizer. About 80% of the total global ammonia consumption is used for the production of fertilizers such as urea, ammonium nitrate, ammonium phosphate, or direct use of ammonia.

3. Opportunities of Using Ammonia as Alternative Vessel Fuel

The Harber–Bosch process, also termed the synthetic ammonia process or the Harber ammonia process, is considered the most economically feasible method for synthesizing ammonia in chemical industries. This method is used to directly synthesize ammonia from nitrogen in air and hydrogen, which might be produced from methane through steam reforming processes. The ammonia synthesis process is carried out under extremely high pressure ranging from 200 to 400 bar and moderately high temperature in the range between 400 and 650 °C under the assistance of a catalyst. Finely distributed iron attached to iron oxide carriers joining with promoters such as potassium oxide and calcium oxide is the major composition of the catalyst to reduce the reaction temperature and facilitate the hydrogenation of nitrogen toward a greater yield of ammonia [29]. Ammonia is a toxic substance, and if it is released into the atmosphere in high concentrations, it will pose a great health risk and can even be fatal in high concentrations or after exposure to ammonia for a long time. Emissions from burning ammonia are more likely to contain significant amounts of the greenhouse gas nitrous oxide (N_2O); therefore, additional equipment will be required on board to control NO_x emissions. Ammonia is far less hazardous in the case of accidental ignition or explosion than other available alternative fuels. Ammonia can be divided into three types according to its synthesis process and carbon footprint, namely brown ammonia, blue ammonia, and green ammonia. Brown ammonia is synthesized using raw materials such as methane, naphtha, and coal, while blue ammonia refers to the product synthesized using similar feedstocks but associated with proper carbon capture and storage compared to the brown ammonia [30]. Green ammonia is the option to achieve a zero-carbon footprint by using renewable energy for water electrolysis, electrochemical reduction, or photocatalytic reduction [31].

Although hydrogen has good performance and low emissions, its storage is still a hurdle for the maritime industry. Compared with hydrogen, ammonia is much easier to store and distribute, and it has a higher volumetric energy density; so, it is recognized as a more promising alternative fuel for ships. The vast majority of ships use diesel engines as the power source; so, most of the previous research on ammonia as an alternative fuel focused on its use as fuel for compression ignition (CI) engines [32]. The feasible ways to use ammonia as CI engine fuel may require modifying the engine design to incorporate a higher compression ratio, adding the equipment of intake-air preheating, using an adequate combustion oxidizer, or using dual-fuel combustion together with some hydrocarbon fuel. Ammonia has a low cetane number; so, it is not suitable for use in CI engines. Ammonia's high-octane rating is an important advantage in spark ignition (SI) engines, resulting in improved combustion performance and knock resistance. In addition, ammonia is also considered a "super battery" that can store excess renewable energy on a long-term and large-scale basis. Because of the low burning rate of pure ammonia, it is difficult to burn effectively. Hence, ammonia itself is not suitable for direct use as a fuel alone. An efficient and environmentally friendly method has been developed to convert ammonia into hydrogen. This implies that ammonia can play the role of an economical hydrogen carrier [33].

The density of anhydrous ammonia at atmospheric pressure is 0.86 kg/m^3, which is 0.589 times that of air. The accidental release of anhydrous ammonia into the atmosphere will not lead to accumulation of its concentration near ground level can cause harm to human health. However, ammonia is prone to be liquified because of its strong hydrogen bonding. Colorless ammonia liquid will be readily formed when its temperature is lowered to the boiling temperature −33.1 °C [34]. In addition, ammonia can be easily dissolved in water, and the maximum concentration of aqueous solution of ammonia is 0.88 g/cm^3. The volumetric energy density of liquid ammonia is 13.225 MJ/m^3, which is slightly higher than that of liquid hydrogen. The increase in the water content in aqueous ammonia retarded the ignition timing and reduced the reaction temperature of ammonia in the combustion chamber of the direct injection engine which can use hydrogen gas as a pilot-ignition fuel [35].

Ammonia has many desirable properties as a fuel, making it potentially attractive as a medium for storing hydrogen. The hydrogen mass contained in ammonia is higher than liquid hydrogen by 45% on the same volumetric base. This means that a larger mass of hydrogen in ammonia than of liquid hydrogen is contained in a liter of liquid ammonia or liquid hydrogen [36]. Ammonia with a lower heating value compared to LNG and methanol is usually stored in insulated and pressurized tanks, thus requiring larger vessel space to meet the same propulsion power of the navigation. Ammonia can be burned directly in internal combustion engines or used as a hydrogen carrier for fuel cells. Hence, the shipping industry is still highly interested in using ammonia as an alternative fuel. In addition, the low freezing point (−77.73 °C) of ammonia makes it an ideal choice for use in extremely cold conditions. Although the price of ammonia is much higher than that of MGO (marine gas oil) and LNG, its price is nearly the same as that of hydrogen. Hence, ammonia is competitive in alternative marine fuel markets. In comparison with hydrogen fuel, ammonia is much more energy efficient and requires no cryogenic storage or high-pressure tank. In addition, much less cost is needed for the production, storage, and delivery of ammonia fuel. Another advantage of ammonia over hydrogen fuel lies in the relatively lower global warming potential measured over 100 years (termed GWP_{100}), which is near zero for ammonia, compared to a GWP_{100} of 5.8 for hydrogen fuel [35]. The reduction percentages of greenhouse gas (GHG) emissions for various types of hydrogen and ammonia are compared in Table 2 [37,38]. Depending on the types of either hydrogen or ammonia, various reduction percentages in the range between 0% and 100% can be observed in Table 2. The reduction percentage of GHG emissions from using blue hydrogen is almost two times that of blue ammonia.

Table 2. Reduction in the greenhouse gas emissions for hydrogen and ammonia.

	Reduction (%) in Greenhouse Gas (GHG) Emission
Hydrogen	Grey hydrogen: 0%, blue hydrogen: 84%, green hydrogen: 75–100% (if renewable and non-carbon electricity is used for hydrogen dissociation)
Ammonia	Brown ammonia: 3%, blue ammonia: 42.8%, green ammonia: 79.2–100% (if renewable and non-carbon electricity is used for ammonia production)

Source: compiled by the authors from Refs. [37,38].

Ammonia, while not highly flammable, requires only 0.25% airborne concentrations to cause death. This implies that it is highly toxic to humans. Ammonia is considered one of the major options for non-carbon alternative marine fuels; it has not yet been applied to the shipping business model. However, according to MAN Energy Ltd., a German manufacturer specializing in the production of ship propulsion systems, they are working on the design for dual-fuel engines fueled with heavy fuel oils and ammonia [39]. At the same time, the company is also working with the American Bureau of Shipping (ABS) to develop container ships powered by such dual-fuel technology. In particular, green ammonia is regarded as a promising alternative fuel for container vessels for the decarbonization of international shipping in the future.

4. Conclusions

The maritime industry is anticipated to contribute over 15% of global GHG emissions in 2050. Hydrogen, ammonia, and fuel cells, especially PEMFC, are promising alternative gas fuels and power for ships. Ammonia can be used directly as a combustible fuel for combustors or as an excellent H_2 carrier. The fuel mixture of NH_3/H_2 can be burned together in internal combustion engines. The dissociated H_2 from NH_3 can power fuel cells or be an alternative fuel to heavy fuel oils burned in marine diesel engines. In consequence, those potential alternative gaseous fuels bear great potential to make a significant contribution to the decarbonization of shipping towards zero-carbon emissions in 2050.

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