Ammonia in Various Technologies

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Ammonia is a carbon-free fuel with promising applications as either a direct or indirect hydrogen carrier. Ammonia can play an important role in the decarbonization of the shipping industry, at least for deep sea routes. The key barriers to using green ammonia as an alternative fuel in maritime industry. are: (1) High production costs, due to the high capital costs associated with ammonia's supply chain; (2) availability, specifically the limited geographical locations available for ammonia bunkering; (3) the challenge of ramping up current ammonia production; and (4) the development of ammonia-specific regulations addressing issues such as toxicity, safety, and storage. These issues are further discussed in this topic review.

Keywords: green ammonia ; ammonia as an energy carrier

1. Introduction

Shipping represents about 3% of total global greenhouse emissions [1]; therefore, regulations regarding CO_2 emissions and harmful emissions, such as NO_x, SO_x, are "set to promote major technological changes in the industry" [2][3]. To put matters into perspective, if the shipping industry were a country, it would rank as the 6th-highest emitter, ahead of Germany and the UK [4]. The International Maritime Organisation (IMO) has set an ambitious decarbonisation target of reducing the CO_2 emissions from shipping by at least 50% by 2050 compared with the 2008 baseline [5]. Decarbonisation options for the maritime sector exist, such as green ammonia and green hydrogen technologies, but are limited due to the following key implementation barriers, namely: (1) cost, (2) fuel storage, (3) additional storage space demand, (4) technical maturity, (5) high fuel price, (6) limited availability, (7) lack of global bunkering infrastructure, (8) safety, and (9) lack of regulations [4]. Hence, using the currently available technologies, the most practical and pragmatic plan to achieve zero emissions includes the use of LNG and LPG as a bridge solution. On the other hand, transition fuels, such as LNG, still emit CO_2 when produced nonrenewably and, thus, we cannot ignore the potential of other alternative fuels, such as ammonia, despite their current drawbacks. Furthermore, fuels such as LNG can have a negative impact on the environment due to "methane slip." Methane is a much more potent greenhouse gas than CO_2 [6].

Current methods of producing ammonia typically use fossil fuels to create a hydrogen feedstock and then, via the energy-intensive Haber–Bosch process, combine hydrogen and nitrogen with the help of high temperatures, high pressures, and a catalyst [7][8][9]. Aziz et al. provided an overview of the production, storage, and utilization of ammonia [10]. In their review, they mention that ammonia can be produced either by renewable energy sources or fossil fuels and show that ammonia can be used directly, or effectively used a hydrogen energy carrier, due to its excellent physical properties. On the other side, air separation units are typically needed to isolate and provide the nitrogen feedstock. In 2020, global ammonia production accounted for 2% of total energy consumption and 1.3% of CO_2 emissions [11][12][13][14]. In recent years, the use of ammonia as a marine fuel has gained momentum [7][15][16]. Solar, wind, or hydropower is needed in order to produce green ammonia renewably. The quantities needed to supply the shipping industry with ammonia as a fuel will need to increase and, therefore, the corresponding CO_2 emissions could increase if ammonia is not produced renewably [7][17]. As a result, the production of ammonia by renewable energy is imperative. However, green ammonia production is not yet cost-effective compared to conventional fossil fuel-based ammonia. Presently, 90% of current ammonia production depends on fossil fuels such as natural gas [18].

Blue ammonia, which can be produced using carbon capture and storage (CCS) systems, can mitigate the increase in CO_2 emissions. However, CCS technologies are at an early stage of research and development, so not ready for commercialization, and are not cost-effective [6]. Currently, there is considerable activity in the research and development of ammonia-powered vessels. In fact, *Mapping of Zero Emission Pilots and Demonstration Projects*, a report by the Getting to Zero Coalition, identified 14 shipping technology concept studies, pilots, and demonstrations that focused on ammonia-powered shipping undertaken in Japan, China, South Korea, Greece, and Northern Europe, with an additional nine projects on production and fuelling infrastructure for ships [19]. These projects cover the whole value chain, "focusing on different elements for the transition of shipping to zero emission fuels” [19]. In this respect, studies such as the one performed by Dincer et al. [20] evaluating the lifecycle performance of ammonia production are necessary to determine the implications of the production process for the environment, in terms of global warming potential, and also to consider other factors impacting the environment. For example, in their study, considering the current capabilities and efficiencies, the green ammonia produced from PVs has a significant environmental impact in terms of toxicity, acidification, and eutrophication. This is because of the low efficiencies of current PV systems; hence, the large number of cells and corresponding area needed to produce the necessary power. Nonetheless, a more credible alternative for ammonia production may be wind-based electrolysis [20]. Furthermore, the authors mention that ammonia produced using biomass has the most “benign” impact on the environment [20].

Zero-emission shipping must be built on three pillars: (1) retrofitting and/or designing new vessels with the ability to use zero-emission, alternative fuels, so the design must incorporate safety, reliability, and proven performance in an operational context; (2) the use of zero-emission fuels that can be produced in sufficient (yet sustainable) quantities to satisfy the current and growing demand, and (3) financing and investment (in “existing and new infrastructure necessary to decarbonize shipping across the value chain”) [21]. Any measure or new technology involving ammonia as a fuel will need public acceptance. In a recent online survey conducted in the UK and Mexico, Guati-Rojo et al. [22] suggest that most participants support the development of green ammonia technologies; however, the corresponding perception is highly dependent on the associated risks and benefits. Consequently, public acceptance of an energy technology is complex and difficult to study [22].

2. Advantages and Disadvantages of Ammonia Versus Other Green Ship Fuels

Ammonia allows more hydrogen storage in liquid form without the need for cryogenic storage (−33.4 °C for ammonia compared to −252.9 °C for hydrogen), thus making NH_3 a suitable hydrogen carrier [18]. Hydrogen is far more expensive to store than ammonia, despite the fact that both fuels have similar energy densities [18]. There are numerous barriers to ammonia becoming a competitive fuel in shipping’s transition to decarbonisation, namely (1) an “appropriate ammonia-fuelled power generator, (2) appropriate system safety assessment tool, and (3) mitigating measures to address the hazards of ammonia” [23]. Hydrogen handling and safety are important issues to address. Ammonia storage is generally simpler than that of hydrogen [23]. Another limitation of hydrogen, is that it has a low energy density (4.7 GJ/m^3) in gaseous form compared to liquefied hydrogen (8.5 GJ/m^3); however, liquefying hydrogen is an energy-intensive process [24]. In the longer term, “zero-carbon energy carriers” such as hydrogen and ammonia offer the most promising pathways to decarbonize shipping; however, biofuels, in the short to medium term, are most suitable for “retrofits and existing infrastructure” [25]. In addition, the NoGAPS project concluded that it is envisioned that ammonia synthesized from green hydrogen “represents a credible long-term, zero-emission fuel” [21]. The NoGAPS project also concluded that “the potential of ammonia-powered shipping to contribute to the decarbonization of the maritime sector is significant, and ammonia carriers present a logical starting point for demonstrating this potential” [21]. However, and most importantly, government support and public finance can accelerate investment now, which can improve the long-term prospects for ammonia deployment as a shipping fuel [21].

In addition to hydrogen, there are other alternative fuels that compete with ammonia. These are alcohols (ethanol and methanol), natural gas, biodiesel, and, to a lesser extent, biogas. There has been interest in methanol as a marine fuel [7], with notable examples being the retrofitting of a Stena Line ferry [26] and the recent order from A. P. Moller-Maersk of a container ship operating with e-methanol [27], with MAN Energy Solutions developing dual-fuel engines [28]. Natural gas (which is 90% methane) is the most competitive alternative to traditional marine fuels. Methane (whose properties are considered identical to natural gas) has the highest volumetric energy density (23.4 GJ/m^3). Methane has the added benefit of lower CO_2 and NOx emissions, almost nonexistent PM emissions, and zero Sox emissions. Ethanol and methanol are competitive alternative fuels due to their relatively high volumetric energy density (21.1 GJ/m^3 and 15.8 GJ/m^3, respectively). Note that ethanol methanol and liquid ammonia, compared to liquid methane, have almost half the energy density, which means that, to achieve the same power output, twice the amount of fuel is required [23], which implies higher storage costs and less space on vessels to transport goods. The situation is even worse for liquefied or compressed hydrogen, despite having the largest energy density on a LHV basis. It is worth mentioning that ethanol and methanol can be produced from renewable energy sources, whereas natural gas is extracted from fossil fuels [23]. In the short term, transition fuels such as LNG and LPG are necessary due to the low availability of green fuels such as ammonia and hydrogen, which are expected to be dominant in the longer term.

3. Ammonia in Various Technologies

Ammonia can be used as a drop-in fuel in diesel in internal combustion engines and gas turbines and as a primary fuel in fuel cells, making it a very appealing and competitive alternative [6][18][23]. However, as Imhoff et al. suggest in their study, “naval vessels are less likely to adopt ammonia powertrains without significant redesigns” [29]. They further state that, if ammonia can be used as an alternative marine fuel, the powertrain design concept must prove that it is practically possible. Note that, in the study by Imhoff et al., the powertrain includes an engine, a waste heat recovery (WHR) heat exchanger (HX), an exhaust aftertreatment system, a fuel tank, a fuel heater, and an ammonia cracker [29].

3.1. Internal Combustion Engines

Combusting ammonia in internal combustion engines (ICEs) is not a new concept, but is an attractive option because of the absence of carbon and sulphur in ammonia’s chemical formula. Thus, emissions of CO_2, CO, UHC, PM, and SOx are virtually eliminated. Ammonia and hydrogen have higher octane ratings than gasoline, are favourable at higher compression ratios [30], and thus are ideal for diesel engines [30]. Ammonia has a high autoignition temperature, so the dual-fuel approach [31] may be the way forward [6].

Ammonia has several limitations that inhibit its commercial exploitation [32]. These are:

- Poor ignition
- Slow flame propagation speed compared to other fuels.
- High toxicity and corrosiveness, thus the requirement for sustainable safety and storage solutions.
- High NOx emissions, unless these are controlled either by after-treatment such as Selective Catalytic Reduction or by optimizing the combustion process.
- High costs in production by considering the supply chain and life-cycle considerations, especially if ammonia is produced renewably.
- Lack of regulations if ammonia is to be used as a marine fuel.

3.2. Fuel Cells

The most efficient method for extracting energy from ammonia is via a fuel cell [7][33][34] with less noise, reduced air pollutants, and a lower space requirement compared to ICEs [17]. Fuel cells, compared to batteries, provide higher energy density with fewer repercussions for the environment (i.e., lower toxicity) [34]. The fact that fuel cells can be powered with green fuels such as ammonia and hydrogen has made this type of technology very promising [23]. In fact, interest in using ammonia as a fuel for fuel cells in maritime applications is growing [35]. An example is ShipFC, which is a funded project by the Fuel Cells and Hydrogen Joint Undertaking (FCH JU) under the EU’s Horizon 2020 research and innovation program. The project is to install and test fuel cells using green ammonia in Viking Energy, an offshore vessel owned and operated by Eidesvik [36]. Compared to ICEs, cost-wise, fuel cells are more expensive, which is the main hurdle to their adoption in shipping [4][17][37]. “The most promising fuel cell types for the maritime sector are proton exchange membrane fuel cells (PEMFC) and solid oxide fuel cell (SOFC)” [17] because the former is already used in road transportation with relatively high maturity. The latter can use ammonia directly (PEMFC ammonia is used as a carrier for hydrogen) with resulting high power densities [38]. Afif et al. [38] rightfully mention that SOFC technology is not yet at the commercialization stage. A recent study by Kim et al. [39] examined the environmental and economic performance of ammonia as a possible fuel on a 2500 Twenty-foot Equivalent Unit container feeder ship for the following propulsion technologies: (1) main engine, (2) generators, (3) PEMFC, and (4) SOFC. The systems were compared with equivalent heavy fuel oil, and they determined that SOFC is the most environmentally friendly option although it has high lifecycle costs. However, case studies are required on all ship types to reach universal conclusions.

4. Economic Performance of Ammonia Compared to Other Shipping Fuels, and Projected Development by 2030 and 2050

Despite ammonia’s excellent properties as either a hydrogen carrier or a direct fuel, the current cost of green ammonia is higher than that of fossil fuels. This is a major barrier to the “widespread adoption” of ammonia “as an energy vector” [40][41]. Blue ammonia will inherently be more expensive than green ammonia due to the extra processing required [40] and the additional infrastructure needed to capture and store CO_2. The competition between ammonia and hydrogen, in economic terms, was more comprehensively examined by Cheliotis et al. [23]. The operating expenditure (OPEX) and capital expenditure (CAPEX) of hydrogen and ammonia were examined and compared against diesel fuel as a benchmark. Cheliotis et al. [23] have shown that the CAPEX for an ammonia-based power system is slightly more expensive than that of hydrogen. On the other hand, Zamfirescu and Dincer [16] reported that “ammonia cost per volume of stored energy is three times less expensive than that of hydrogen." Cheliotis et al. [23] further mention that the CAPEX is predicted to be lower compared to the corresponding hydrogen-based power system due to the increasing maturity of the technologies and reduced complexity of ammonia-based systems. CAPEX for diesel fuels is relatively stable compared to ammonia and hydrogen, while the OPEX cost increases due to IMO's deep decarbonization targets. Cheliotis et al. [23] further conclude that it is envisioned that ammonia-powered systems will be the most favourable in economic terms by 2030.

IRENA [42] reported that green ammonia production costs are currently much higher than those of conventional marine fossil fuels. However, as the technologies mature it is expected that the production cost and renewable electricity costs will continue to decrease, so ammonia technologies will become competitive by 2050 [42]. Wang and Wright [43] conclude that hydrogen, which is one of the main competitors of ammonia, has "high capital costs and uncertainty in fuel supply," whereas ammonia has "several technical key hurdles and safety issues." Moreover, Wang and Wright [43] mention that the dominant driver for conventional ammonia is the price of feedstock in a particular geographical area, which is related to the availability of ammonia's supply chain, similarly to the production costs of hydrogen and methanol.

5. Regulations Impacting Ammonia's Use as a Shipping Fuel

A key barrier for ammonia as a maritime fuel is the lack of ammonia-specific rules for its use as a maritime fuel. These rules will need to address issues of toxicity, safety, and storage. There are regulations and protocols in place for ammonia as it is trans-ported as cargo; however, some amendments in existing regulations regarding ammonia as a fuel are required. "Class Rules will likely be the earliest regulatory framework in place for using ammonia as a fuel" [21]. For example, "one of the important barriers for new fuels such as ammonia and hydrogen is the storage and bunkering infrastructure. This means regulatory actors (Class and Flag) need to collaborate with original equipment manufacturers (OEMs) to enable the uptake" [44].

Until regulations for using ammonia as a fuel are in place, the relevant statutory legislation adopted by the IMO, Flag Administrators, and associated Recognised Organisations for designs on ammonia-powered vessels will need to be based upon the Alternative Design Assessment [21].

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