AMMONIA AS A MARINE FUEL

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Master's Thesis

MSc: Sustainability and Quality in Marine Industry

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May 2022, Piraeus

Abstract

Due to climate change the International Maritime Organization (IMO) has set limits to the shipping sector in order for emissions to be mitigated. The marine industry will see a quick energy and technology shift that would have a greater influence on asset values, earning capacity and costs than previous transitions. Shipowners are already under increasing pressure to minimize marine transportation's greenhouse gas footprint. The use of an alternative fuel seems to be a strong solution so as to achieve the sustainable targets of the Paris Agreement. This thesis evaluates the potential of ammonia as a marine fuel, a promising energy carrier and carbon free combustible fuel, in comparison with other alternative fuels like Hydrogen, Methane, LNG, LPG, Bio-Fuels and Batteries. It also uses multi-criteria decision analysis (MCDA) to solve serious shipowners concerns. In addition, it takes into account all the aspects of ammonia as a hydrogen carrier, as well as the relevant legislation and rules, port infrastructure, cost and environmental efficiencies, technological maturity and scalability. The findings of this thesis suggest that various alternative fuels have potential, but more research is needed before definite conclusions can be drawn about ammonia's potential as an alternative marine fuel.

Keywords: Ammonia, International Maritime Organisation, Alternative Fuels, Renewable Energy, CAPEX, OPEX

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Abbreviations

AFC – Alkaline fuel cells

Atm - Atmosphere

CAPEX – Capital expenditures

CO – Carbon monoxide

CO_2 – Carbon dioxide

CI – Compression Ignition

CII – Carbon Intensity Indicator

CCS – Carbon Capture and Storage

CR – Compression ratios

DCS - Fuel Oil Data Collection System

DMFC – Direct methanol fuel cells

ECAs – Emission control areas

EEA – European Environment Agency

EEDI – Energy Efficiency Design Index

EEOI - Energy Efficiency Operational Indicator

EEXI – Energy Efficiency Existing ship Index

EGR – Exhaust Gas Recirculation

EU – European Union

FC – Fuel Consumption

FC – Fuel Cell

GHG – Greenhouse gas

GRT – Gross Registered Tonnage

GT – Gross Tonnage

GWP – Global Warming Potential

H_2- Hydrogen

H_2O - Water

HB process – Haber-Bosch process

HFO – Heavy fuel oil

HVO – Hydrogenated vegetable oil

ICE – Internal combustion engine

IGC Code – International code of safety for ships using gases or other low-flashpoint fuels

IGF Code – International code of safety for ships using gasses or other low flashpoint fuels

IMO – International Maritime Organization

IRENA – International Renewable Agency

Kg - Kilograms

LBG- Liquefied biogas

LFSS – Liquid fuel supply system

LHV – Lower heating value

LNG - Liquid natural gas

LPG – Liquid petrol gas

MARPOL - Maritime Regarding Oil Pollution

MBM - Market- Based- Measures (MBM)

MCFC – Molten carbonate fuel cells

MDO – Marine diesel oil

Mg - Milligrams

MJ – Megajoules

MRV - Monitoring, reporting and verification of emissions

NECAs – NITROGEN EMISSION CONTROL AREAS

MGO – Marine gas oil

N_2- Nitrogen

N_2O – Nitrous oxide

NH_3 - Ammonia

NO- Nitric oxide

NO_X - Nitrogen Oxides

ODS- Ozone depleting substance

OPEX - Operating expenses

PAFC - Phosphoric acid fuel cells

PEMFC - Proton exchange membrane fuel cells

PM- Particulate Matter

PPM - Parts Per Million

PV - Photovoltaics

SCR - Selective Catalytic Reduction Technology

SECAs - Sulfur emission control areas

SEEMP - Ship Energy Efficiency Plan

SFC - Certified Specific Fuel Consumption

SI – Spark ignition

SMR - Steam Methane Reforming

SOEC – Solid oxide electrolysis cell

SOFC- Solid oxide fuel cells (SOFC)

SO_x – Sulfur oxides

TRL – Technical readiness level

UN – United Nations

US – United States

VLSFO – Very low sulfur fuel oil

VOC- Volatile organic compounds

1 Introduction

1.1 Background

The shipping industry contributes significantly to the global economy, since it transports more than 80% of the world's total trade volume. In comparison with other ways of cargo transportation, shipping permits the intercontinental transfer of large quantities of cargo in the most fuel and cost-efficient way.

Since the 1950s heavy fuel oil has predominantly been used in shipping sector because of its broad availability and low cost. But, the sustainability of using heavy fuel oil in shipping is questioned.

In line with the Paris Agreement from the UN Climate Change Conference 2015, the International Maritime Organization (IMO) has adopted a strategy for the progressive reduction of greenhouse gas (GHG) emissions by the shipping sector, aiming to halve it by 2050 compared to 2008 figures. The strategy proposed by the IMO includes different paths for the progressive reduction of GHG emissions, including short-, mid- and long-term measures, but the target set by the IMO for 2050 cannot be achieved without the adoption of alternative carbon-neutral fuels. The term carbon neutral refers to a source of energy that has no net GHG emissions. The Energy Efficiency Design Index (EEDI) for new ships, the Ship Energy Efficiency Management Plan (SEEMP) for the existing ships and Emission Control Areas (ECAs) are some examples of IMOs strategy (Brynolf et al., 2014).

Shipping activities have a great impact on climate change, environment and health. By introducing alternative fuels like ammonia (NH_3) could significantly reduce fuel emissions and impacts, as well as environmental risk associated with spills of heavy fuel oil (HFO) and other marine oils.

Ammonia is gaining a growing interest as one of the potential fuels candidates for the decarbonization of the shipping industry. There are significant technical and safety challenges related to ammonia as a marine fuel which can be surmounted. If there are any obstructions in adopting the use of ammonia in the shipping sector are its source and the future cost of green ammonia.

Today ammonia, made from hydrocarbons, does not only reduce the carbon footprint in the air but it also adds costs. On the contrary, green ammonia - produced by electrolysis powered by renewables or nuclear – is a promising source of zero emission fuel, on the condition that are handled appropriately.

Ammonia (NH_3) is a carbon-free molecule and therefore burning it in an internal combustion engine leads to zero CO_2 emissions from the stack. Additionally, ammonia becomes a carbon-neutral fuel when it is produced from renewable energy sources like electricity, wind and solar generation (green ammonia) or from fossil sources associated with carbon capture and storage technologies (blue ammonia).

Ammonia is also a sulfur-free fuel. Therefore it does not require any SO_x removal system on the exhaust to comply with environmental limitations on sulfur emission. Furthermore, any NO_x generated from ammonia combustion can be removed from exhaust gases with selective catalytic reduction (SCR) technology.

Ammonia seems to be a sustainable solution for carbon and sulfur neutrality and can also play a strategic role in the transition phase. A greater use of renewable energy will lead to an abundance of affordable renewable power production on land. This energy can be used for production of green ammonia that means an existence of a zero emission fuel.

Since the green ammonia production is in negligible amounts, it is imperative to adopt a massive investment programme, so that we can be able to produce not only a meaningful supply of green ammonia, but also to reduce the operational costs. Thus, the fuel can become financially viable for the shipping industry.

1.2 Aim

The overall ambition of this thesis is to estimate the value of ammonia as an alternative fuel in shipping industry in comparison with other fuels and how can eliminate greenhouse gas emissions from it. In addition, the purpose is to assess the commercial and operational viability of other alternative marine fuels and if ammonia can be a cost and environmental effective choice against them. The main target of this thesis work is to focus on estimating the environmental, economic, social and technical impacts of ammonia as a fuel in shipping sector, more specifically in internal combustion engines (ICE), fuel cells (FC) and gas turbines and make a comparison with other alternative fuels using information and data from existing studies. It also points out that the major problem of CO_2 emissions footprint will not move to the electricity generation or fuel production process. Moreover, it covers the concerns of shipowners about the options to be viable at a moderate carbon price and without too great an increase to the capital cost of the ship.

1.3 Literature review

To obtain information and data about ammonia as a marine fuel and its efficiency, a literature review is carried out. Furthermore, the literature review is a helpful tool that can be used to discover vital information regarding the levels of emissions, the regulations and the environmental targets in the shipping industry, other alternative fuels and their characteristics, as well as the systems and technology are being utilized. All that referred above, can be accomplished by gathering data from research papers, scientific reports, books and journal articles.

1.4 Methodology

Ammonia is under research and development and only theoretical framework is used to highlight the feasibility of being an alternative marine fuel. The comparison with other fuels, the technology that ammonia can be burned, the regulation, cost and energy efficiencies and maturity are considered in a multi criteria decision analysis (MCDA) (Hansson et al., 2020).

The most acceptable approach for this thesis is a multi - criteria decision analysis (MCDA). This strategy is often utilized to solve challenges related to sustainable energy production, where possibilities with contradicting impacts are common and different quantitative and qualitative measures. This also seems to happen with the choice of alternative marine fuels based on their performance, making it much more difficult for decision makers to evaluate and compare them properly (Hansson et al., 2020).

2 Emissions and Regulations

2.1 Emissions

Global warming is a severe environmental problem issue that the globe is grappling with. The release of toxic gases and air pollutants continues to disturb the ecosystem and contribute to climate change. Greenhouse gases (GHG), sulfur oxides (SO_x), nitrogen oxides (NO_x), carbon monoxide (CO) and Particulate Matter (PM) are the gases released by burning fuel. The major component of greenhouse gases is carbon dioxide (CO_2), which is mostly produced by the combustion of fossil fuels (Ji et al., 2021).

Greenhouse gases (GHG) are mainly CO_2, methane (CH_4) and nitrous oxide (N_2O) and other gases include water vapor and ozone (O_3). The CO_2 produced from energy use and deforestation, CH_4 from agriculture, waste and energy use and N_2O from agriculture. The presence of greenhouse gases in the atmosphere causes climate change by trapping heat. They contribute to respiratory problems caused by smog and air pollution. Other implications of climate change produced by GHGs include extreme weather, food supply shortages, increasing wildfires, ice fields and glaciers are receding and permafrost is melting (Selin, 2020),(NUNEZ, 2019). Maritime transportation emits roughly 940 million tons of CO_2 each year, accounting for about 2.5 percent of worldwide GHG emissions (Commission, 2021).

Sulfur oxide emissions (SO_x) are due to the presence of sulfur compound in the fuel and the main air pollutant that induces acidification. SO_2 produced from the use of marine fuels in main and auxiliary engines, as well as other combustion apparatus on board, such as oil-fired boilers, is the principal source of SO_x emissions from ships (Agency, 2021). Human health, visibility and climate are all impacted by SO_x emissions, but the latter is owing to a cooling influence. Other negative consequences of SO_x emissions include considerable damage to buildings and infrastructure, which results in financial expenses. According to reports, the maritime transport industry emits 11.3 million tons of SO_x per year (Wei et al., 2018).

Nitrogen Oxide Emissions (NO_x) that are measured in the exhaust duct of a marine diesel engine, they usually consist 95% of nitric oxide (NO) and 5% of nitrous oxide (NO_2). NO_X contributes to a range of environmental effects when released into the atmosphere, including eutrophication, acidification and as a precursor to the creation of ground level ozone and secondary particulate matter (Lindgren et al., 2016).Also, long term exposure to NO_2 has been linked to an increase in bronchitis symptoms and causes extent damage to the lungs (W.H.O., 2021).

Particulate matter (PM) is made up of a wide range of solid and liquid particles, some of which are visible like smoke, dust, pollen and others which are minuscule (Agency, 2021). PM_{10} and $PM_{2.5}$ are well known terms that refer to the masses of particles having diameters of smaller than 10 and 2.5 µM, respectively (Lindgren et al., 2016). Acute lower respiratory infections, cardiovascular illness, chronic obstructive pulmonary disease and lung cancer are all linked to high PM levels.

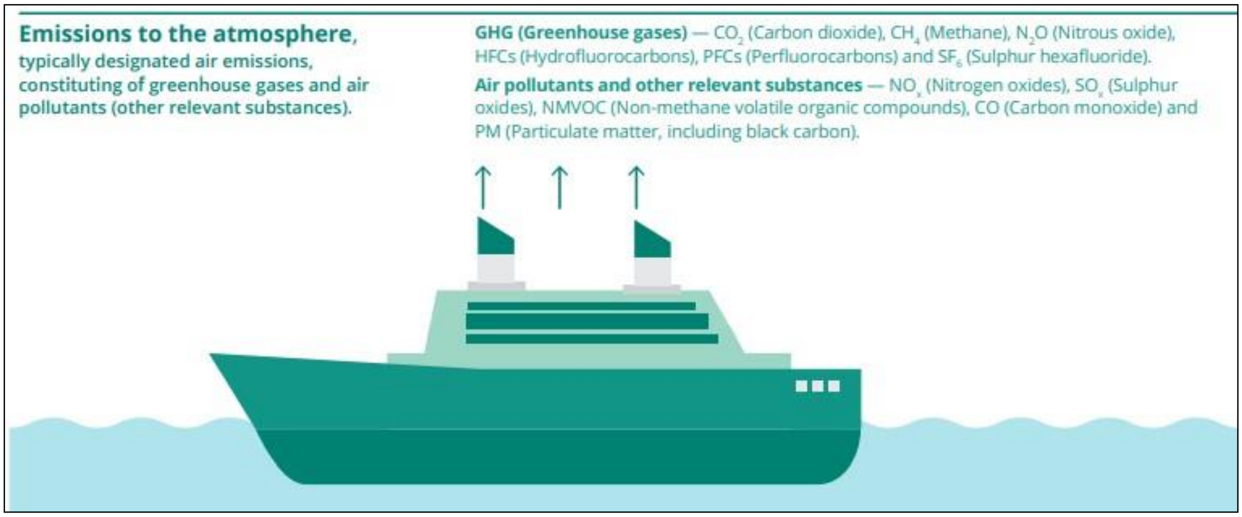


Figure 1: Pollutant emissions to the atmosphere from a generic ship (Agency, 2021).

2.2 Life cycle emissions

The term ‘tank-to-wake’ referred to the emissions from burning or using an energy source and not the fuel or getting it to the ship, while the term ‘’well-to-tank’’ referred to the emissions from production and transportation, Figure 2. The most important is the measurement of net carbon impact. The ‘’well-to-wake’’ emissions should be considered for alternative fuels because the life cycle of a fuel includes production, transportation and use (ABS, 2020b). For example, Hydrogen is carbon free at the moment of use when utilizes as a fuel (tank- to- wake). However, if it is made from non- renewable energy, the process (well- to- tank) might result in considerable emissions. On the other hand, it may also be made by electrolysis of water using renewable energy, which eliminates emissions from the feedstock and the manufacturing process.

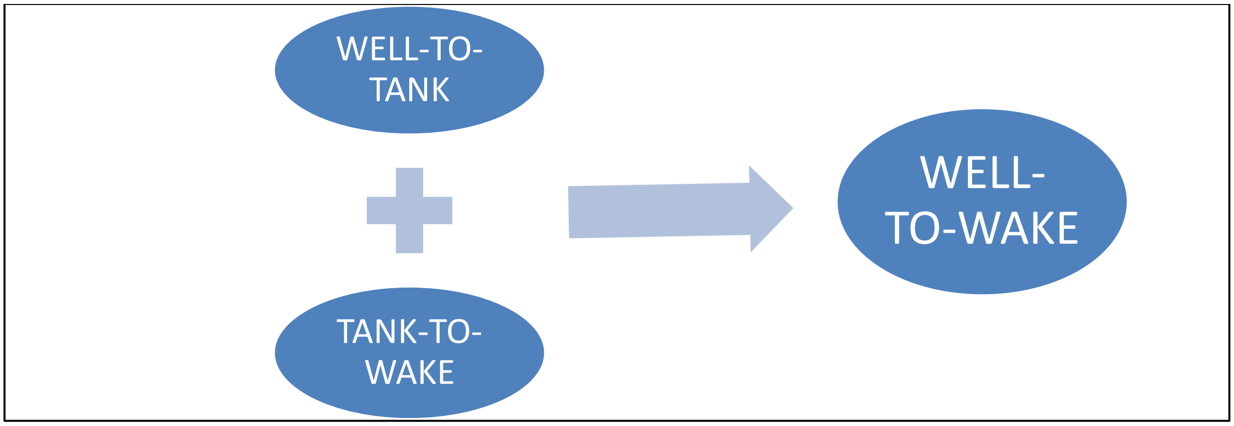


Figure 2: Life Cycle Emissions (ABS, 2020b).

The shipping sector must drastically decarbonize and make significant adjustments to accomplish climate change goals and reduce GHG emissions in order to move towards a better, greener and sustainable future (Romano and Yang, 2021). Policymakers and stakeholders are urged to make major efforts to discover and implement solutions that will reduce shipping's carbon impact. The IMO's goal of reduction in emissions is ambitious and it will almost certainly necessitate broad adoption of lower and zero carbon fuels, as well as other energy efficiency measures, both operational and market based (Serra and Fancello, 2020).

2.3 Regulations

The International Maritime Organization (IMO) is a United Nations organization specialized in charge of maritime safety and security, as well as the prevention of a ship related to marine and atmospheric pollution. The activity of the IMO contributes to the UN's Sustainable Development Goals (SDGs). About 90% of global trade is transported by international shipping to individuals and communities all over the world. For most stuff, shipping is the most efficient and cost effective way of international transportation because it provides a dependable, low cost means of carrying goods throughout the world, promoting business and contributing to the development of nations and peoples. It is clear that one of IMO's top tasks will be to promote sustainable shipping and marine development (I.M.O., 2014).

International shipping accounts for roughly 2.2 percent of worldwide yearly CO_2 emissions, according to the IMO's Third GHG Study and emissions from international shipping might climb by 50 % to 250 % by 2050, owing to the development of global trade. Furthermore, IMO projections for 2050 show that shipping transportation will account for 15 % of overall CO_2 emissions. According to 2019 forecasts, demand for seaborne trade would expand by 39% by 2050. The deep sea section, in particular, is anticipated to account for more than 80% of global fleet CO_2 emissions, emphasizing the need of finding technically feasible and cost effective emission reduction solution for this segment (I.M.O., 2015).

The 2015 Paris Climate Agreement set forward specific goals for reducing GHG emissions and the International Maritime Organization (IMO) has adopted a strategy for the progressive reduction of greenhouse gas (GHG) emissions by the shipping sector, aiming to halve it by 2050 compared to 2008 figures. There is also an additional goal of reducing CO2 emissions per unit of transportation work by at least 40% by 2030 (I.M.O., 2020b).

International Convention for the Prevention of Pollution from Ships, initially enacted in 1997, sets limitations, named Maritime Regarding Oil Pollution (MARPOL) Annex VI, on the principal air pollutants found in ship exhaust gas, including as sulfur oxides (SO_X), nitrous oxides (NO_x) and Particulate Matter (PM), as well as forbids intentional emissions of ozone depleting substances (ODS). Shipboard incineration and the emissions of volatile organic compounds (VOC) from tankers are likewise restricted by MARPOL Annex VI (I.M.O., 2019d).

By 2020, MARPOL Annex VI put the limit of sulfur content in marine fuel in 0.5%, instead of 3.5% that was in previous years and 0.1% in sulfur emission control areas (SECAs) as stated in Figure 3. Whereas these restrictions are aimed at reducing sulfur emissions from ships, they are likely to have an impact on GHG emissions, partly because the sulfur regulation may be thought as an implicit carbon price: it raises the costs of carbon intensive shipping transportation. Cost hikes in container transportation may vary from 20 to 85 %, based on oil prices and ship dimensions (Forum, 2018). Most ships were utilizing heavy fuel oil (HFO) before the new restriction went into effect. HFO, which was derived as a leftover from crude oil distillation, had a substantially greater sulfur concentration, which ended up in ship emissions after burning in the engine. To comply with the new requirement, the great majority of ships now use very low sulfur fuel oil (VLSFO).

Vessels may also fulfill SO_x emissions standards by employing permitted options, such as Exhaust Gas Cleaning Systems (EGCS) or ''scrubbers'', which ''purify'' pollutants before they are discharged into the atmosphere. Closed-loop EGCS keep harmful emissions on board, but they are only practical for short distance travel. Despite ongoing advances in scrubber technology, shipowners are hesitant to invest in EGCS due to their cost. Implementation can take up to 20 days, resulting in revenue losses due to downtime, and they do not truly reduce sulfur, instead transferring it from the air to the sea (open-loop EGCS). Furthermore, given that the IMO is enforcing emissions limits, there is a chance that discharging pollution into the sea may be outlawed as soon as standards are enacted (Serra and Fancello, 2020). The revised restriction is expected to result in a 77 % decrease in total sulfur oxide emissions from ships or 8.5 million metric tonnages of SO_x (I.M.O., 2020a).

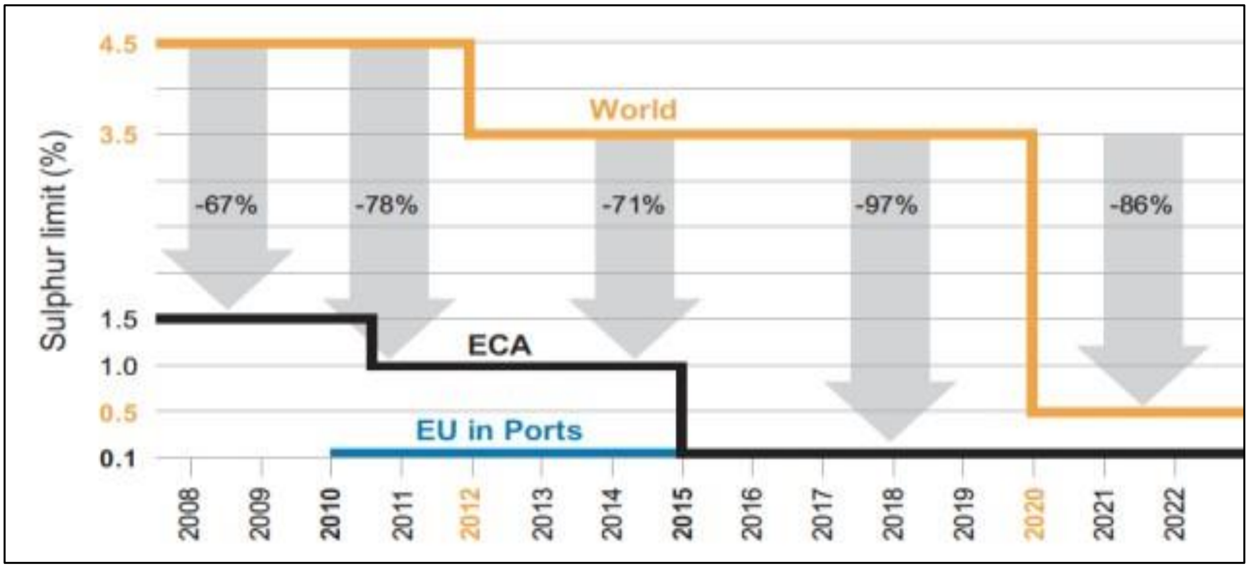
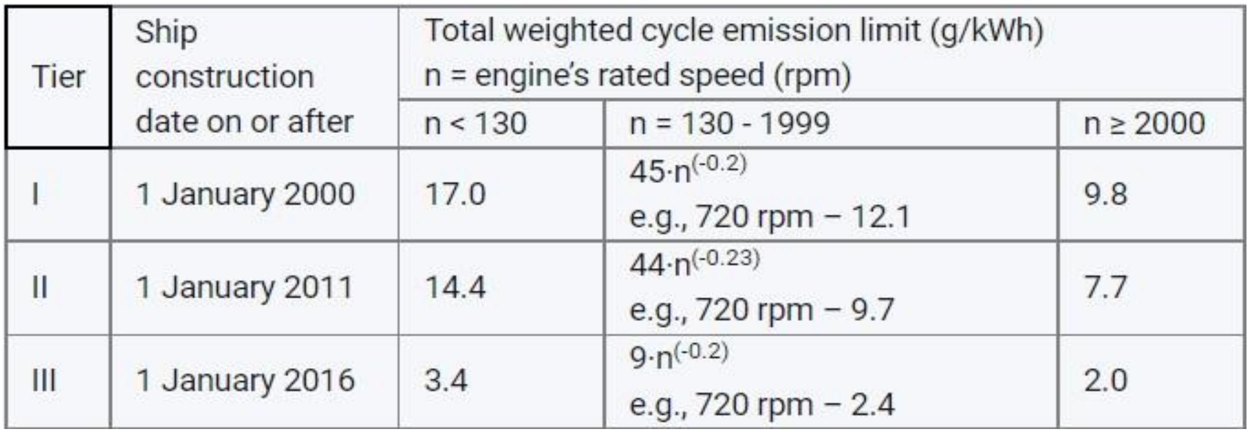


Figure 3 : IMO MARPOL Annex VI sulfur limits timeline (Minic, 2019) .

Alongside, the NO_x vulnerable areas named nitrogen emission control areas (NECAs) are protected by tier standards. The Tier 1 NO emission standard, which went into effect in the year of 2000, set emission regulations (9.8 – 17 g/kWh) for ships built between 1 January 2000 and 1 January 2011, were up to 10% harsher than those implemented before 2000. Tier 2, applied in 2011, imposed up to 15 % higher regulations (7.7 – 14.4 g/kWh) than Tier 1 for ships built after 1 January 2011. Tier 1 and Tier 2 regulations apply to all new marine diesel engines. Tier 3 of the regulations, implemented in 1 January 2021, is 75 % stricter than Tier 2 (2.0 – 3.4 g/kWh) as is stated in Table 1 and only applies to newly built ships travelling inside designated NECAs like North America and North and Baltic Sea (Karl et al., 2019).



Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130 - 1999	n ≥ 2000
I	1 January 2000	17.0	$45 \cdot n^{(-0.2)}$ e.g., 720 rpm − 12.1	9.8
II	1 January 2011	14.4	$44 \cdot n^{(-0.23)}$ e.g., 720 rpm − 9.7	7.7
III	1 January 2016	3.4	$9 \cdot n^{(-0.2)}$ e.g., 720 rpm − 2.4	2.0

Table 1: NO_x regulations (I.M.O., 2019c).

As stated by Annex VI of the 1997 MARPOL Protocol, emission Control Areas (ECAS) are marine zones in which stricter limitations were implemented to prevent airborne emissions from ship. Current and possible future ECAs areas are in Figure 4.

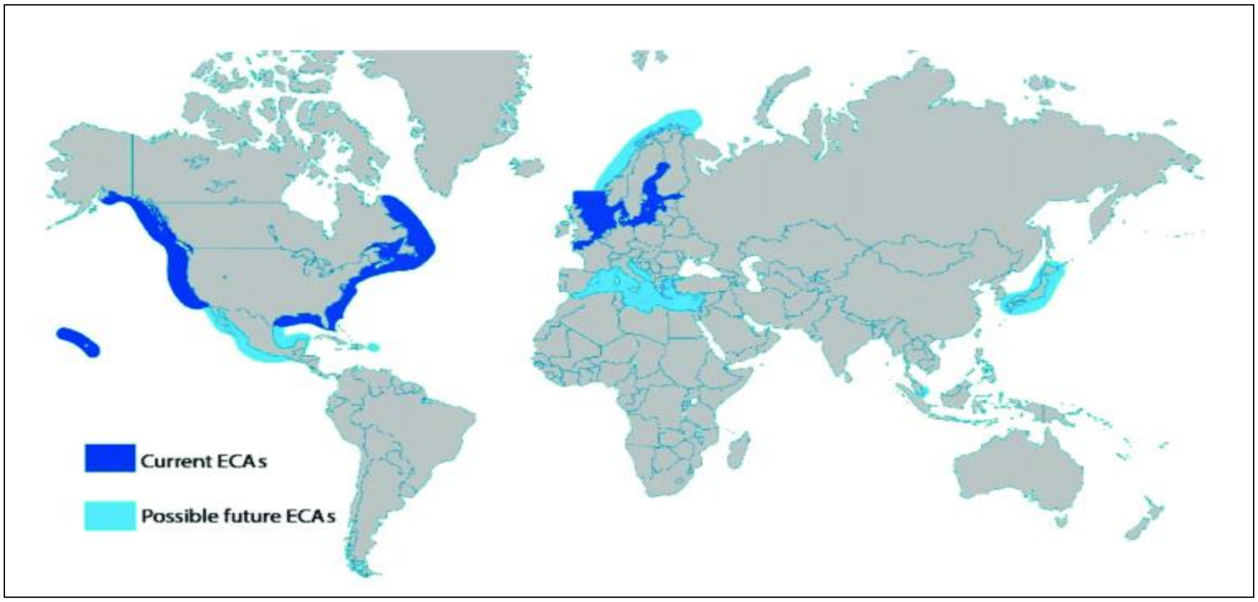


Figure 4 : Global ECAs areas map (Vaferi et al., 2020).

With the enactment of revisions to MARPOL Annex VI, the Energy Efficiency Design Index (EEDI) was made necessary for new ships and the Ship Energy Efficiency Management Plan (SEEMP) was declared mandatory for all ships at MEPC 62 (July 2011). EEDI is the most significant technical measure for new ships and it tries to encourage the adoption of more energy efficient (lower polluting) systems and engines. For different ship types and size parts, the EEDI specifies a minimum energy efficiency standard per capacity mile and measures CO_2 emissions per tonne-mile, too. It may be calculated as the ratio of ''environmental cost'' divided by "Benefit for Society'' as is stated in Figure 5 (IRCLASS). The lower the EEDI rating, the more energy efficient the vessel's technical and design is. Maritime designers and developers have complete freedom in selecting technologies to meet EEDI standards in a given ship design, resulting in the evolution of ship systems toward those that are more energy efficient over time.

$$\text{EEDI}=\frac{\text{Impact to environment}}{\text{Benefit for society}}=\frac{\text{CO2 Emission}}{\text{Transport Work}}=\frac{\text{Power}*\text{SFC}*\text{FC}}{\text{Deadweight}*\text{speed}}$$

EEDI is a function of a) Installed power b) Speed of vessel c) Cargo carried

Parameter	Description
SFC	Certified Specific Fuel Consumption in g/kWh
FC	Fuel Consumption in g/kWh

Figure 5: EEDI function (IRCLASS).

All new ships constructed after 1 January 2013 are required to display an EEDI in order to meet minimum statutory energy efficiency performance criteria, which increase in three phases. The first phase started from 2015 to 2020 with the reduction of 10 % grams of CO_2 per tonne mile emissions, the second one from 2020 to 2025 with the reduction of 20 % of CO_2 emissions and the third one will start from 2025 to 2030 with the reduction of 30 % of CO_2 emissions, as Figure 6 shows. During 2019, the IMO's MEPC adopted revisions to MARPOL Annex VI to tighten the current EEDI standards for various new ship types such as gas and LNG carriers, container ships and general cargo ships. As a result of these revisions, ship categories that account for about 85 % of CO_2 emissions from international shipping are now covered under the international regulatory framework (I.M.O., 2019a). The enhanced measures are projected to have a major positive effect to the environment and on people's health, especially for residents of port cities and coastal regions.

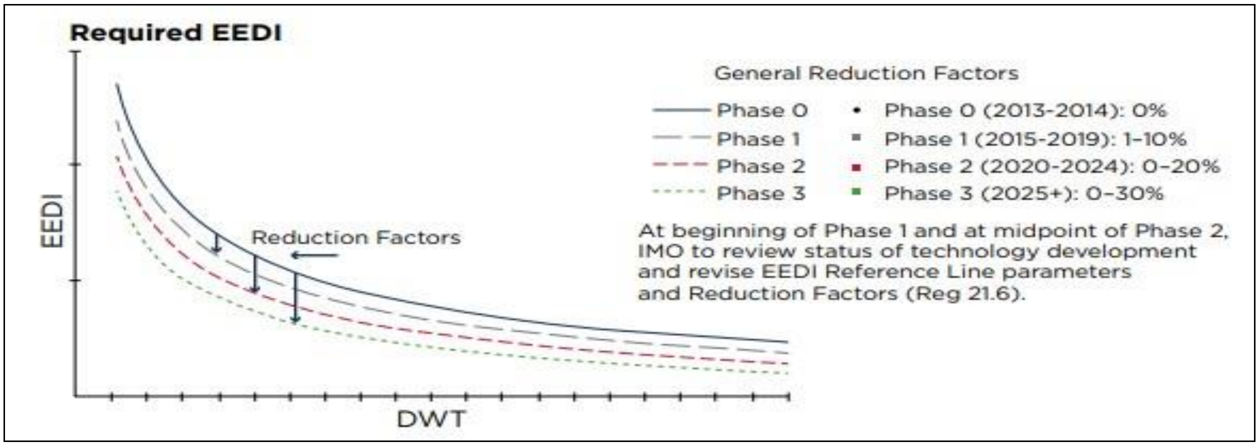


Figure 6: Energy Efficiency Design Index (EEDI) (ABS, 2020a).

The Ship Energy Efficiency Management Plan (SEEMP) is a cost effective operational measure that develops a framework to increase of all ship's energy efficiency (I.M.O., 2019a). The Energy Efficiency Operational Indicator (EEOI) was proposed as a tool for SEEMP implementation, but only on a temporary basis and primarily for evaluating the individual ship performance (Panagakos et al., 2019). In comparison to other management system standards like ISO 9001 for quality management or ISO 14001 for environmental management, the SEEMP demands very little from a shipping firm to meet the regulations. Weather navigation, optimal trim, just in time arrival and waste heat recovery are all suggested targets in the SEEMP guide lines, however certain goals are not appropriate for all types of vessels (Hansen et al., 2020). The corporation must create a SEEMP that aims to increase the ship's energy efficiency following the Plan- Do- Check- Act- Cycle (PDCA), Figure 7.

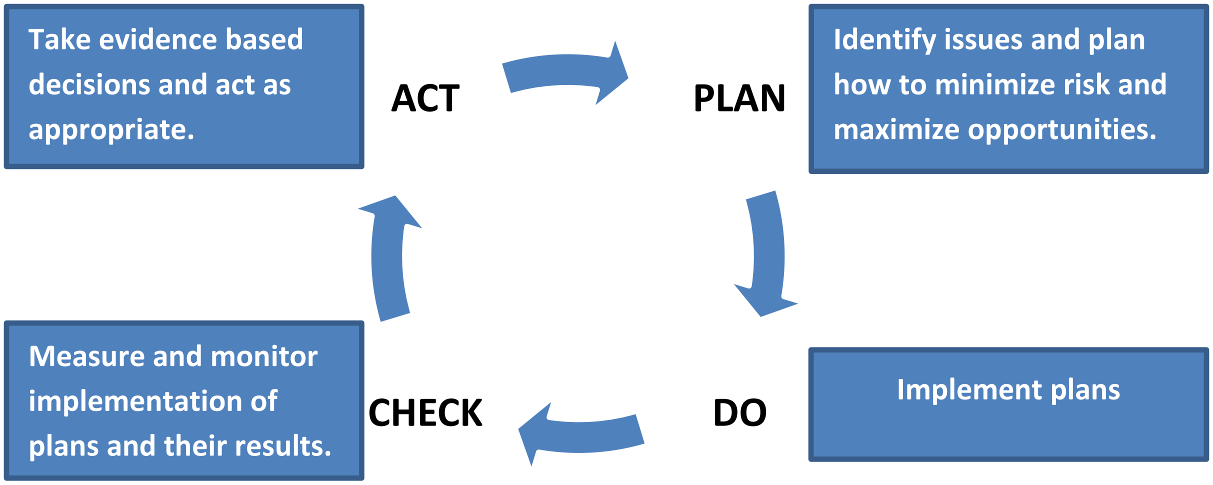


Figure 7 : Plan- Do- Check- Act- Cycle (PDCA) (Lindgren et al., 2016).

Provided that the EEDI and SEEMP initiatives from 2011 were deemed insufficient, the Commission suggested a report in 2013, which was adopted as the EU Monitoring, Reporting and Verification (MRV) Regulation and came into force on 1 July 2015 (Regulation 2015/757). The strategy is broken into three steps as stated in Figure 8. It applies to ships greater than 5,000 GT, despite of flag and port of registry. It requires companies to monitor, report and verify their ship's fuel consumption, CO_2 emissions and energy efficiency on voyages to, from and within EU ports, as well as evaluate annual indicators, such as EEOI, which are then released by the Commission in order to promote emission reductions by presenting energy efficiency information to the concerned markets. According to the Commission's impact assessment, the MRV system is predicted to reduce CO_2 emissions from covered travels by up to 2 % compared to a ''business as usual'' scenario. In 2030, the system may save owners up to €1.2 billion per year in net costs (shipping, 2019b). Table 2 shows the differences in monitoring and reporting obligations on a per-voyage and annual basis.

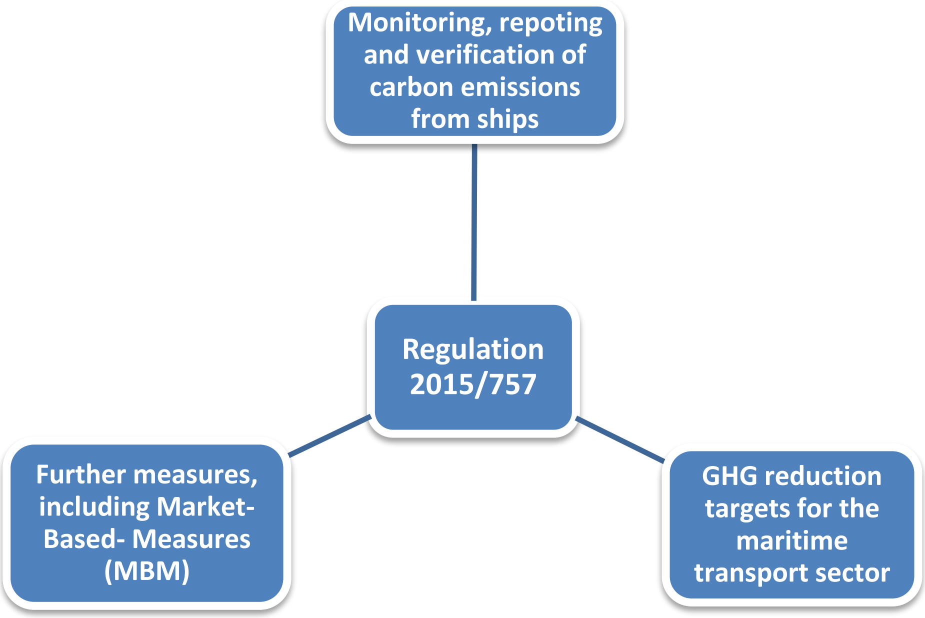
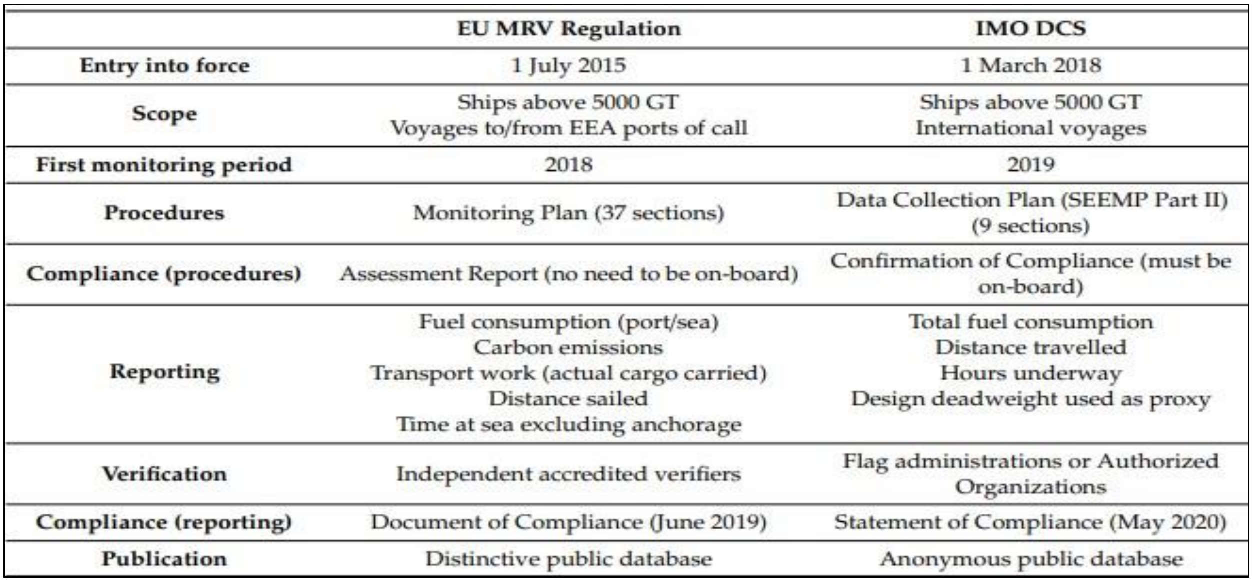


Figure 8 : Regulation 2015/757 consists of three consecutive steps (shipping, 2019b).

Annual reporting requirements	**Per voyage reporting requirements**
Aggregated annual CO_2 emissions from all voyages between, from and to ports under a Member State's jurisdiction during the reporting period.	Port of departure and arrival including the date and times in and out.
Aggregated annual CO_2 emissions from all voyages between, from and to ports under a Member State's jurisdiction during the reporting period.	
Details of the method used for emissions monitoring.	
Technical efficiency of the ship (EEDI or EIV as applicable).	
Vessel identification	
Total annual amount/weight of cargo carried	
Annual average efficiency (e.g. EEOI, fuel consumption per distance and cargo carried)	
Total annual fuel consumption	
Total CO_2 emitted	CO_2 emitted
Total distance travelled	Distance travelled
Total time spent at sea and at berth	Time spent at sea

Table 2 : EU MRV monitoring requirements (Bazari and Moon, 2016).

In 2019, the IMO announced an obligatory Fuel Oil Data Collection System (DCS) for international shipping, mandating ship with a gross tonnage of 5,000 or more to begin collecting and reporting data to an IMO database. The DCS is a document that details the ship's specifications, as well as the methods, systems and duties for recording fuel consumption, hours at sea and distance traveled. The DCS must be developed as part of the SEEMP and kept onboard the ship. It is important to mention that the decision to establish a ship data gathering system was mostly reached in 2014 (MEPC 67), one year after the European Commission's MRV proposal. Table 3 shows the main differences between the EU Monitoring, Reporting, and Verification (MRV) and International Maritime Organization (IMO) Data Collection System (DCS) (shipping, 2019c).



	EU MRV Regulation	IMO DCS
Entry into force	1 July 2015	1 March 2018
Scope	Ships above 5000 GT Voyages to/from EEA ports of call	Ships above 5000 GT International voyages
First monitoring period	2018	2019
Procedures	Monitoring Plan (37 sections)	Data Collection Plan (SEEMP Part II) (9 sections)
Compliance (procedures)	Assessment Report (no need to be on-board)	Confirmation of Compliance (must be on-board)
Reporting	Fuel consumption (port/sea) Carbon emissions Transport work (actual cargo carried) Distance sailed Time at sea excluding anchorage	Total fuel consumption Distance travelled Hours underway Design deadweight used as proxy
Verification	Independent accredited verifiers	Flag administrations or Authorized Organizations
Compliance (reporting)	Document of Compliance (June 2019)	Statement of Compliance (May 2020)
Publication	Distinctive public database	Anonymous public database

Table 3 : Main differences between the EU Monitoring, Reporting, and Verification (MRV) and International Maritime Organization (IMO) Data Collection System (DCS) (shipping, 2019c).

The IMO is coming up with new and various standards that will apply to all ships, like a technical need to reduce carbon intensity based on a new energy efficiency existing ship index (EEXI) and a new operational carbon intensity indicator (CII). The IMO has developed the EEXI index extension of EEDI for current ships above 400 Gross Registered Tonnage (GRT), built before 2013, which only takes into account the vessel's design criteria and not operational parameters, in order to meet GHG reduction targets and ultimately make shipping Carbon neutral. Just before the shipping sector can transition to alternative zero-carbon fuels, ships must comply with the EEXI requirements. Decreasing the power of engines is the simplest approach to achieve compliance, but ships should not dip below their optimal speed, which might result in higher total fuel consumption and carbon emissions. As an outcome, ships need to use a mix of Engine Power Limiters and expensive Energy Saving Devices to enhance their EEXI, which necessitates quick action to assess the most cost effective compliance solutions. Every ship must have had an EEXI computed, which would then show its energy efficiency in comparison to a baseline (Shipping, 2019a).

In addition, the CII is a measure of vessel efficiency in terms of CO_2 emitted when carrying cargo or people. It is represented in grams of CO_2 per deadweight nautical mile. The CII would estimate the yearly damping ratio needed for ships above 5000 GT (Gross tonnage) to support continuous and sustainable improvement in the ship's operating carbon intensity within a defined rating level. The ranking would be given on a scale of major superior, minor superior, moderate, minor inferior or inferior performance level –A, B, C, D or E. The SEEMP would keep track of the performance level. In other terms, ships are rated an energy efficiency grade, with A being the best. A ship that uses low carbon fuel receives a better rating than one that uses fossil fuel. The revisions to MARPOL Annex VI are planned to take effect on 1 November 2022, with the EEXI and CII certification requirements entering into force on 1 January 2023. So, the first annual reporting will be performed in 2023 and the first rating will be issued in 2024 (*I.M.O.*, 2021).

3 Alternative fuels

If the IMO targets are to be met, it is of high importance the use of low- and zero-carbon emission technologies to start on large ocean-going ships in the near future. Alternative fuels are considered to have lower or zero ship emissions when used for ship propulsion. This section examines a variety of prospective alternative fuel and energy choices as well as their costs and emission reduction potential. It is noted that some of these alternative fuels have not yet reached commercial maturity.

3.1 Hydrogen

Hydrogen (H_2) is a potential marine fuel that emits zero carbon dioxide (CO_2), zero sulfur oxide (SO_x) and only negligible amounts of nitrogen oxide (NO_x) (Forum, 2018). The use of hydrogen as an energy vector and as a green fuel is attractive and can be one of the drivers for the energy transition. H_2 can be produced from various and different energy sources and technologies and can be used directly in internal combustion engine or fuel cells. Most of global hydrogen production comes from the use of fossil fuels. On the other hand, much research has focused on methods of sustainable hydrogen production (IEA, 2019a).

Moreover, hydrogen can also be produced from biomass or from water. It needs 275 Mtoe (million tons of oil equivalents) of energy, in order to be produced, which corresponds to two percent of the global total primary energy demand. The main sources of hydrogen production is natural gas and the steam methane reforming (SMR) about 75 %, from coal about 23 % and from oil and electric power about 2 %, which means, hydrogen is very carbon intensive, Figure 9 (ABS, 2020a).

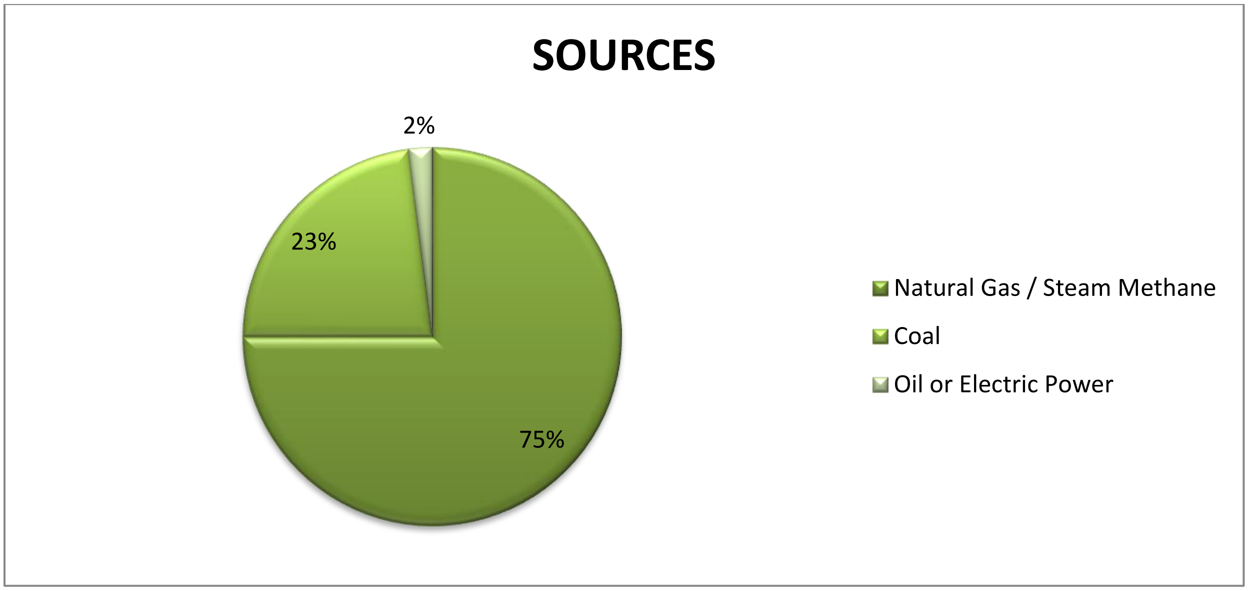


Figure 9: Main sources of hydrogen production (ABS, 2020a).

An emerging alternative pathway for a low-carbon hydrogen production is from water and electricity via electrolysis, from fossil fuels with carbon capture, utilization and storage (CCUS) and from bioenergy via biomass gasification. Carbon Capture and Storage (CCS) is the process of capturing CO_2 before it enters the earth's atmosphere and storing it underground or reusing it (Research, 2022). Solar, wind and hydropower sources can provide the electricity required for the electrolysis method's production process. This greatly improves total mitigation potential when considering its whole production life cycle. According to a study by Bicer (2018), hydrogen produced from hydropower emits 10 times less CO_2 than HFO across its full life cycle. Furthermore, combining hydrogen with HFO (50 % of total fuel) can cut CO_2 emissions by up to 43 % per tonne kilometer. This demonstrates that CO_2 and other GHG emissions can be significantly reduced even when present conventional marine fuels (HFO) are largely replaced by hydrogen (Forum, 2018).

About 55% of the hydrogen is used for ammonia synthesis and 10 % for methanol production. Also, hydrogen is used by other industry sectors, such as producers of iron and steel, glass, electronics, specialty chemicals and bulk chemicals. A disadvantage with the use of hydrogen as an alternative fuel in shipping industry is the lack of storage because it requires cryogenic storage at very low temperatures about -253 ° C or be pressured between 350 bar to 700 bar, associated with large energy losses during conversion, logistic steps and it needs very well insulated fuel tanks (ABB JIANGJIN TURBO SYSTEMS, 2019). This has a result the loss of cargo space because of the size of the storage tanks. The high cost of fuel, the energy intense for production and the expensive fuel cell technology with low power density leads to the conclusion that it is unlikely to play a major role in propulsion of shipping in the next ten to twenty years (Maritime Knowledge Centre, 2017).

3.2 Liquefied natural gas

Liquefied natural gas is already commercially used to reduce the carbon footprint of vessels. LNG for long term could play a vital role in shipping sector because of its adequacy and could achieve the IMO GHG emission reduction target in 2050 (Thepsithar et al., 2020). It was used as a fuel by LNG carriers in the 1960s, taking advantage of the fuel available on board in the form of boil-off gas and was enabled by virtually zero fuel costs when the vessels were loaded (Moirangthem and Baxter, 2016). The first LNG-powered vessel was a ferry built in Norway in 2000. In 2020, 173 LNG-powered vessels were constructed and 227 confirmed orders for new vessels. It is estimated that the consumption of LNG as fuel will grow five times from 2018 to 2022, due to larger vessels using it for propulsion (DNV, 2020). 6.5 million tons of LNG is consumed by ships which means around 2 % of the total marine consumption. Three main types of internal combustion engines are commercially available for the combustion of LNG: Dual Fuel- diesel cycle employed in large two – stroke engines, Dual Fuel- Otto cycle employed in medium - speed four - stroke engines and gas engines (Lindgren et al., 2016), (Fernández et al., 2017).

LNG as a marine fuel has a lot of environmental benefits, such as a reduction of SO_x and NO_x emissions and particulate matter up to 85 %, as well as small reduction in greenhouse gas emissions up to 20 – 25 % (Dnv, 2014). It reduces NO_x emissions tremendously and meets the IMO NO_X tier III standard. On the other hand, an increase will be emerged in the shipping-related contribution of GHGs when there is an existence of spills and slippage of methane (CH_4). Methane slip occur when the fresh fuel air – mixture escapes unburned from the cylinder to the exhaust or from incomplete combustion. Table 4 shows that methane is a potent GHG with high Global Warming Potential (GWP). The GWP of a compound is a relative measure comparing the relative amount of heat trapped in the atmosphere to an equivalent mass of CO_2 (GWP=1). The larger the GWP, the more than a given gas warms the Earth compared to CO_2 over that time period (Lindgren et al., 2016).

	Lifetime (Years)	**GWP over 100 years (kg CO2 eq./kg)a**	**GWP over 20 years (kg CO2 eq./kg)a**
Carbon dioxide	-	1	1
Methane (CH_4)	12.4	28(34)	84(86)

Table 4: Global warming potentials of Methane over various horizons (Lindgren et al., 2016).

LNG requires cryogenic storage conditions onboard about -162 °C and has a high energy density (Laval et al., 2020). The energy density of a fuel partly determines how applicable the fuel is for certain ship types and ship operations (Dnv, 2019). The use of LNG is increasing, but certain challenges need to be addressed because of the bunkering infrastructure is limited, new building and conversion costs are high. The real reason LNG is seen as a transition fuel is the potential to move from natural gas to biofuel and synthetic LNG showing a pathway to net zero outcomes by 2050 (Research, 2022).

3.3 Liquefied petroleum gas

Liquefied petroleum gas (LPG) is any mixture of propane (C_3H_8) and butane (C_4H_{10}) in liquid form, with small fractions of propylene and other light hydrocarbon species (GL, 2019a),(ABS, 2020a). The composition of LPG, like natural gas, varies depending on the source and season. More than 60 % of it is generated as a byproduct of natural gas production, giving it as a significant transportation advantage over other gaseous fuels (Yeo et al., 2022), (ABS, 2020a).

LPG provides further advantages in terms of pollution emissions. Because the carbon -to-hydrogen of LPG is lower than that of oil- based fuels, it emits less CO_2 and the life cycle of greenhouse gas emissions of LPG are 17 % lower than those of heavy fuel oil, as Table 5 shows. It essentially eliminates sulfur emissions and may be used to comply with local and international sulfur standards. The engine technology employed determines how much NOx is reduced.

	HFO	MGO	LPG	LNG (QATAR)
Well- to -tank	9.79	12.69	7.15	9.68
Tank-to-propeller	77.70	74.40	65.50	61.80
Total	87.49	87.09	72.65	71.48

Table 5: GHG emissions (kg CO_2 eq/ GJ) of HFO, MGO, LPG and LNG (ABS, 2020a).

When compared to the usage of HFO, NO_x emissions from a two- stroke diesel engine can be predicted to be reduced by 10 – 20 %. However, for a four-stroke Otto cycle engine, the projected reduction is bigger and may be below Tier III NO_x requirements. Exhaust Gas Recirculation (EGR) or Selective Catalytic Reactors (SCR) systems are to be installed on two - stroke LPG engine to meet these specifications. In addition, the use of LPG as a fuel will reduce particulate matter and black carbon emissions to a great extent (WLPGA, 2017).

LPG's advantages make it a good choice for maritime applications. It is non –toxic, does not affect soil or water, and is easy to be handled as a liquid. Its combustion might give a short- to – medium- term option for satisfying IMO emission standards. In addition, handling LPG decreases evaporative emissions of volatile organic compounds (VOCs), which is a new requirement in port all over the world (ABS, 2020a).

Because LPG is heavier than air, it flows to the bottom surface, concentrates in low places, and does not disperse as effectively as LNG into the environment following a leak. To permit external discharge, LPG should be kept in a well-ventilated location. Furthermore, due to propane's lower boiling point, the propane concentration of LPG for use as a fuel in cold areas should be greater than in warmer climates (Yeo et al., 2022).

3.4 Methanol

Methanol (CH_3OH) as a fuel delivers climate benefits according to IMO. At room temperature and pressure, it is a light, volatile, colorless, flammable liquid with a strong odor (Ming, 2021). Up to 90% of methanol produced worldwide from natural gas through reformation of the gas with steam to produce syngas and then converting and distilling the syngas to produce methanol, and the rest 10 % from coal, Figure 10 (Research, 2022). Nowadays, up to 95 % of total methanol is used in the shipping sector. Because of its potential to GHG emissions, simplicity of handling, operational safety, and engine compatibility, methanol has received a lot of interest as a marine fuel (Ming, 2021).

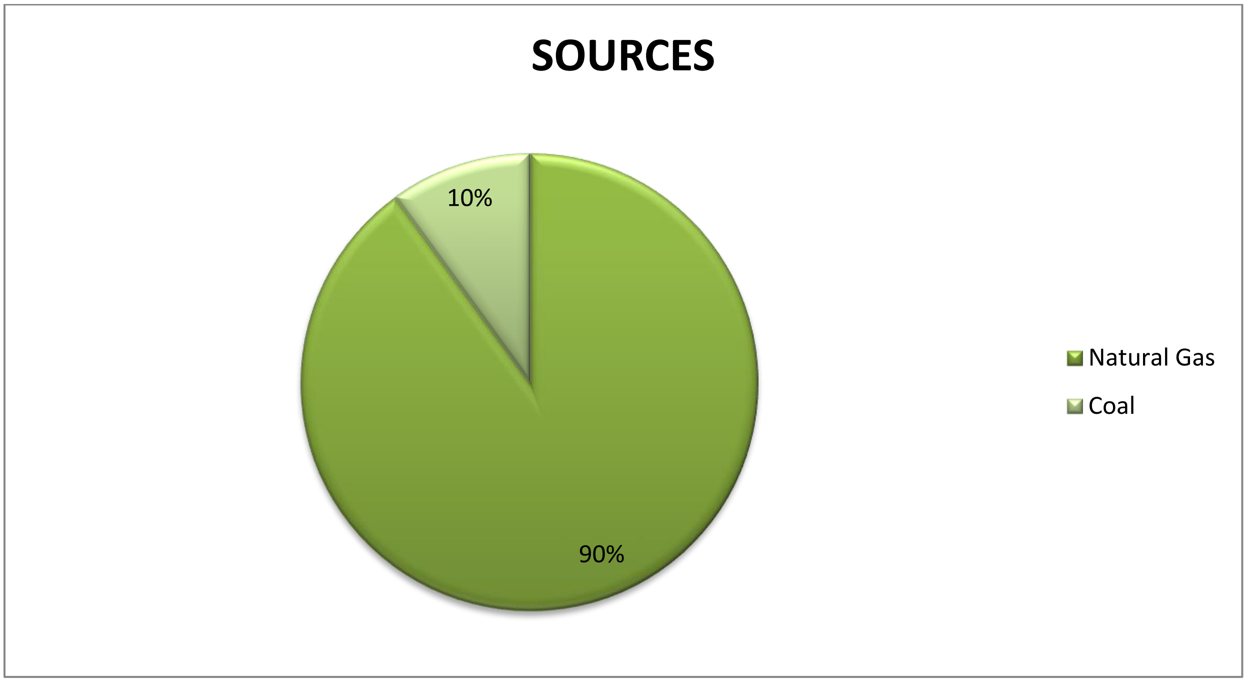


Figure 10: Main sources of methane production

Methanol is an oxygen– rich fuel that combusts in an internal combustion engine emitting no sulfur oxides (SO_x), a negligible amount of particulate matter (PM) and nitrogen oxides (NO_x). It can also be considered as a low carbon fuel because under special production processes 'blue' and 'green' methanol exists. 'Blue' methanol is produced through the utilization of Carbon Capture and Storage (CCS) and natural gas. 'Green' methanol or renewable methanol in the form of bio-methanol derived from biomass or e-methanol derived from renewable energy has the potential to produce a zero-carbon fuel (Research, 2022).

Methanol's energy density (15.7 Mj /L) is less than the half of traditional fossil fuels (40Mj/L), necessitating more fuel storage capacity on board a vessel than conventional fuels. Moreover, it is corrosive to a variety of materials. As a result, the material compatibility of tank coatings, pipes, seals must be carefully studied. Because of its low flash point (60°C) and toxicity, methanol is classified as a hazardous chemical. However, it requires special considerations when used as a ship fuel (Thepsithar et al., 2020).

Additionally, it is seen to be the safest alternative fuel, with a long history of use in transportation and a variety of other energy uses. It is a transparent, biodegradable liquid that, when spilt in water, soon dilutes to non - toxic levels with no adverse effects on the environment or harm to marine ecosystems. Methanol's safety was reaffirmed in November 2020 when the IMO approved rules for its usage as a safe ship fuel (Research, 2022).

With a few alterations, which increase the capital cost, methanol could be burned in internal combustion engines. These methanol- fueled engines are commercially accessible. Also, the use of methanol in fuel cells to generate electricity power for vessel propulsion is also technically viable. Ultimately, the abundance of feedstock determines the availability of methanol fuel. Coal and natural gas will continue to be the primary sources of feedstock for methanol manufacturing for a long time. When it comes to life cycle CO_2 emissions, renewable feedstock's including biomass, captured carbon dioxide, and renewable hydrogen are projected to play a bigger role (van der Maas, 2020).

3.5 Biofuels

3.5.1 Hydrotreated vegetable oil

Hydrotreated vegetable oil (HVO) or renewable diesel is an advanced synthetic liquid biofuel generated by hydro treating and refining plants oils, usually in the presence of a catalyst, considered for marine application (ABS, 2020a), (Tyrovola et al., 2017). It is a blend of sulfur-free paraffin's, aromatics and esters. HVO is a high quality fuel that has had the oxygen removed by hydrogen, giving it long term stability, and with high cetane number, Table 6. The fuel possesses properties that allow it to be used as a 'drop-in' fuel in place of fossil fuels (GL, 2019a).

Chemical Composition	**HVO**
Density at 20° C (kg/m3)	780
Lower Heating Value (MJ/kg)	44.0
Viscosity at 40° C (mm2 /s)	3.0
Cetane Number (CN)	80-99
Aromatics Content (% vol.)	0
Oxygen Content (% vol.)	0
Sulfur Content (ppm)	<10

Table 6 : Properties of HVO (ABS, 2020a).

By mixing 10 % HVO with marine distillate fuel, purity is not affected while exhaust emissions are reduced and engine performance is improved. In reality, the fuel mixes have been demonstrated to be of premium quality since the cetane number has been enhanced while the aromatic content has been lowered, resulting in lower exhaust emissions and good cold start performance (Tyrovola et al., 2017). Because HVO fuel has nearly no sulfur, SO_x emissions are almost non-existent. It decreases the sulfur level of mixes when combined with marine distillate fuel in increasing quantities.

Moreover, it is thought that a greater cetane number of HVO leads to a shorter ignition delay, resulting in lower peak combustion temperatures and pressures, and hence lower NO_x levels. Due to its advantageous hydrogen / carbon ratio (0.18), HVO also produce less CO_2. It is assumed that HVO's chemical composition/ structure, which is devoid of aromatics and double carbon chains, facilitates soot oxidation, resulting in decreased PM mas emissions (Ushakov and Lefebvre, 2019).

The findings clearly show that renewable fuels, such as HVO, can be used as a primary engine fuel in the marine sector. However, using them as additives to conventional fuels is a more practical and simple approach. This does not need any additional hardware upgrades and will result in immediate reductions in non- renewable CO_2 emissions.

3.5.2 Liquefied biogas

Liquefied Biogas (LBG) or Bio LNG is made from biomass. LBG is predominantly made up of methane and does not include significant amounts of other hydrocarbons like ethane or propane. It is most commonly generated by anaerobic digestion; however it may also be created through biomass gasification (Lindgren et al., 2016). Also, it is an intriguing fuel to help with the transition from fossil fuels to renewables and the reduction of greenhouse gas emissions.

Because LBG is chemically equivalent to fossil LNG, it is gaining popularity in the shipping industry, as well as it may profit from the expanding LNG infrastructure. It is often regarded as the most CO_2- friendly of all the fuels (Maritime Knowledge Centre, 2017). As LBG has a lower energy density than standard fuels, it must be kept in cryogenic tanks. This particular storage requirement may have an influence on the amount of space available aboard. LBG may be utilized in ICEs similarly to LNG and has a similar SO_x, NO_x and PM emissions. Due to changes in fuel composition, LBG contributes more methane to the GWP than LNG, whereas LNG emits more hydrocarbons than LBG. Also, LBG has a lower life cycle GWP than LNG since the CO_2 released comes from biomass rather than fossil fuels (Brynolf et al., 2014).

LBG has a very strong Overall Fuel Performance in terms of WTP CO_2 and LHV Fuel Efficiency, and can be regarded as a highly attractive alternative maritime fuel. It is a plug and play technology that provides carbon neutral paths for gas engines and the LNG distribution infrastructure. The material qualities are quite close to LNG, and it may be regarded identical in all practical ways (GL, 2019a). Unfortunately, LBG is not currently manufactured in sufficient quantities, and significant expenditures are necessary to achieve the numbers required by the shipping sector.

3.6 Batteries

A battery is an electrical storage device. As a result, unlike traditional fossil fuels, it is not a unique source of energy. Batteries are used to make an all-electric ship (one that uses batteries in the same manner as diesel does) or a hybrid ship (one that uses batteries to augment the other fuels and allows the system to run as efficiently as possible). All electric ships are largely practical for short sea transport, coastal trade, small ferries, and riverine uses due to the poor energy density of battery- based solutions. The electrification of a ship can totally eliminate CO_2, SO_x, NO_x and PM. When compared to a ship powered by conventional fossil fuels, this is a situation with an all-electric ship. The decrease in emissions from hybrid vessel will be determined by the degree of hybridization (Agency, 2021). Onboard electrical power production or an onshore power supply (OPS) can both be used to charge batteries. It can also be charged using renewable energy sources.

Battery applications in ships face problems because to the extremely high energy density and amounts of power needed for ship activities such as propulsion or operating high – powered auxiliary systems. Large battery systems are difficult to install aboard ships due to their weight or volume, notably if traditional propulsion and fuel tanks rooms are included into the system. Half of all ships with batteries that are constantly operating are hybrid ships, while around 18 percent are all-electric ships. Passenger ships and ferries are the ship kinds that consume batteries much more at the moment (Agency, 2021).

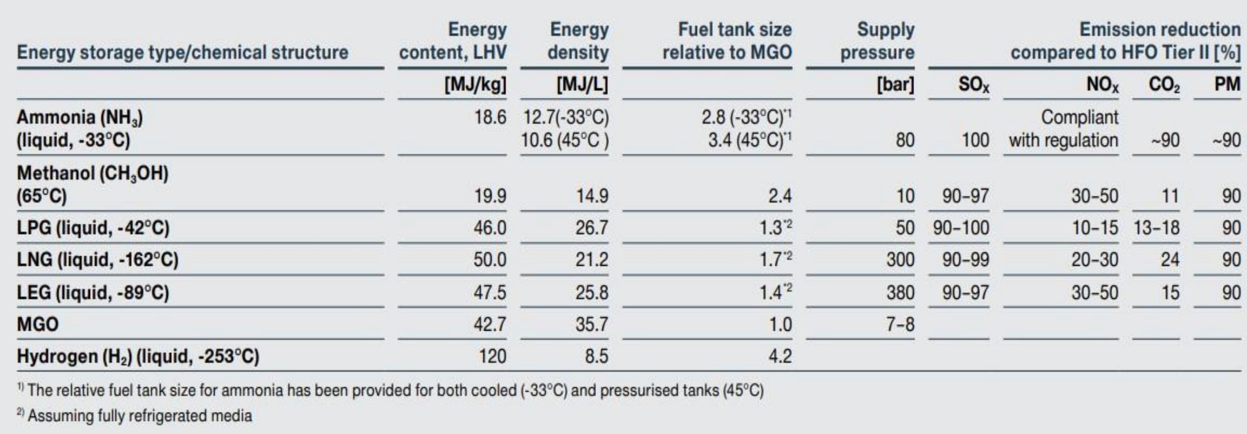
3.7 Ammonia

Ammonia (NH_3) is a compound of nitrogen and hydrogen and used commercially is usually named anhydrous ammonia, alleviating some of the problems of hydrogen storage. It is essentially a hydrogen carrier, but it has a greater energy density, making it a better fuel source. The volumetric hydrogen density of liquid ammonia is around 45 percent greater than that of liquid hydrogen, implying that liquid ammonia can contain more hydrogen in the same volume as liquid hydrogen. It is produced by the Haber-Bosch process, which combines nitrogen gas and hydrogen gas at high pressures and elevated temperatures to form ammonia. It is a colorless gas under ambient conditions with a lower density than air (DNV, 2020) . NH_3 has a boiling point of -33.3°C, and must be stored under pressure, or at low temperatures. If the pressure is raised to around 10 bars at a temperature of 20 – 25 degrees of Celsius, the ammonia stays liquid.

3.8 Comparison and conclusion

Hydrogen has the highest mass energy density, but its volumetric energy is poor and fuel storage tanks are around 7.6 times the size of conventional fossil fuel tanks. While delivering fuel to the internal combustion engine or fuel cell, the fuel temperature must be increased, complicating the dual supply system setup. Hydrogen is more likely to be employed in coastal operating boats than in ocean going ships due to these qualities. Methanol has a volume energy density of less than half that of conventional fossil fuels, although it can be kept at room temperature and pressure. As a result, as compared to certain other carbon neutral fuels, its storage tank is very small. Methanol fuel may be utilized with existing fuel supply systems and storage tanks without requiring significant modifications.

NH3 is carbon and sulfur free, resulting in a clean combustion with almost no CO_2 or SO_x emissions. NH_3 has a greater volumetric energy than liquid Hydrogen, as Table 7 shows, does not explode and has more viable storage conditions in terms of pressure and temperature. In addition, it is already a financially attractive commodity because of its broad application in industrial operations and as an agricultural fertilizer. Ammonia has a heating value of around 18.6 MJ/Kg, which is comparable to methanol. Most of alternative fuels, NH_3 has lower energy density per unit volume (12.7 MJ/L) than MGO (35 MJ/L), which means, if the ammonia tank is chilled, it will take about 2.8 times the capacity to transport the same amount of energy as MGO.



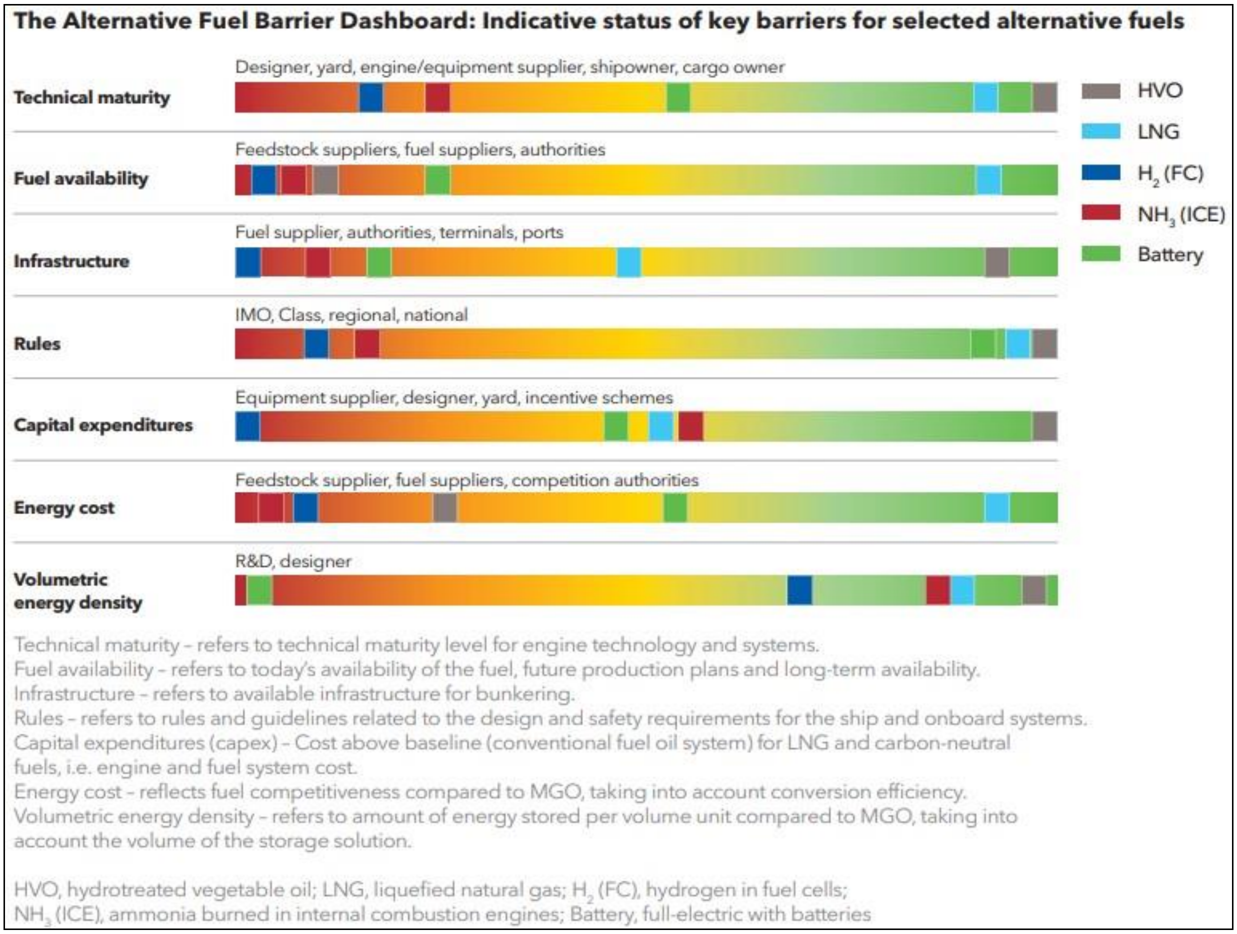
Energy storage type/chemical structure	Energy content, LHV	Energy density	Fuel tank size relative to MGO	Supply pressure	Emission reduction compared to HFO Tier II [%]			
	[MJ/kg]	[MJ/L]		[bar]	SO_x	NO_x	CO_2	PM
Ammonia (NH_3) (liquid, -33°C)	18.6	12.7(-33°C) 10.6 (45°C)	2.8 (-33°C)[1] 3.4 (45°C)[1]	80	100	Compliant with regulation	~90	~90
Methanol (CH_3OH) (65°C)	19.9	14.9	2.4	10	90–97	30–50	11	90
LPG (liquid, -42°C)	46.0	26.7	1.3[2]	50	90–100	10–15	13–18	90
LNG (liquid, -162°C)	50.0	21.2	1.7[2]	300	90–99	20–30	24	90
LEG (liquid, -89°C)	47.5	25.8	1.4[2]	380	90–97	30–50	15	90
MGO	42.7	35.7	1.0	7–8				
Hydrogen (H_2) (liquid, -253°C)	120	8.5	4.2					

[1] The relative fuel tank size for ammonia has been provided for both cooled (-33°C) and pressurised tanks (45°C)

[2] Assuming fully refrigerated media

Table 7: Properties of other alternative fuels (Solutions, 2020).

The fuels LNG and HVO have an advanced technical maturity -the maturity of engine technology and systems- and perform very well on most aspects, as Figure 11 shows. On the other hand, ammonia’s technological maturity is limited and fuel availability, rules, infrastructure and energy costs are significant obstacles to deployment. NH_3 outperforms hydrogen in terms of capital investment and volumetric energy density, providing it a strong benefit.



Technical maturity – refers to technical maturity level for engine technology and systems.
Fuel availability – refers to today's availability of the fuel, future production plans and long-term availability.
Infrastructure – refers to available infrastructure for bunkering.
Rules – refers to rules and guidelines related to the design and safety requirements for the ship and onboard systems.
Capital expenditures (capex) – Cost above baseline (conventional fuel oil system) for LNG and carbon-neutral fuels, i.e. engine and fuel system cost.
Energy cost – reflects fuel competitiveness compared to MGO, taking into account conversion efficiency.
Volumetric energy density – refers to amount of energy stored per volume unit compared to MGO, taking into account the volume of the storage solution.

HVO, hydrotreated vegetable oil; LNG, liquefied natural gas; H_2 (FC), hydrogen in fuel cells; NH_3 (ICE), ammonia burned in internal combustion engines; Battery, full-electric with batteries

Figure 11 : The alternative fuel barrier dashboard (GL, 2019b).

Ammonia and hydrogen, both zero carbon fuels, offer a lot of potential reducing shipping's carbon impact. Because NH_3 is a more volumetric efficient Hydrogen carrier, it might be a feasible zero carbon transportation alternative fuel. Along with its flexibility of transport, storage and bunkering compared to hydrogen and compatibility with present and upcoming technologies for propulsion end energy production, ammonia is predicted to rise in popularity as fuel. Figure 12 depicts the predicted consumption of marine fuels through 2050, as the shipping sector seeks to fulfill the IMO's GHG emission reduction standards (ABS, 2020b).

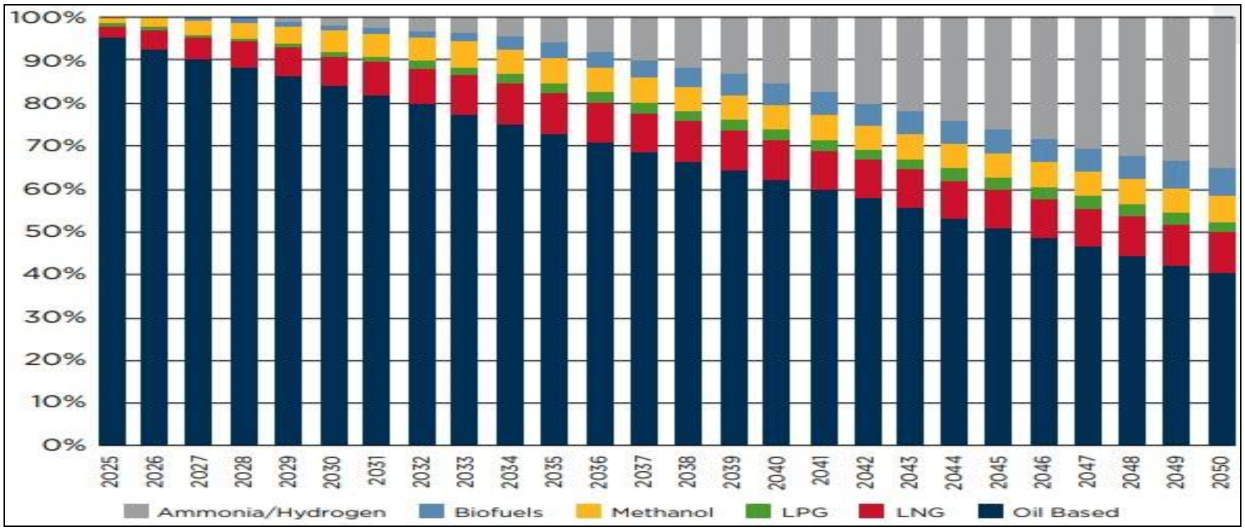
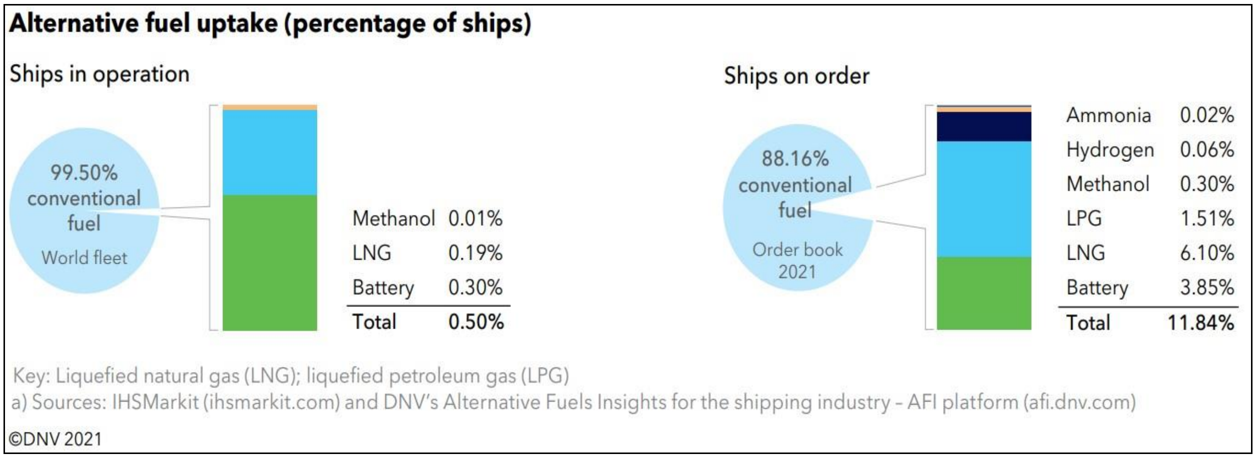


Figure 12 : Projected marine fuel use to 2050 (ABS, 2020a).



Key: Liquefied natural gas (LNG); liquefied petroleum gas (LPG)
a) Sources: IHSMarkit (ihsmarkit.com) and DNV's Alternative Fuels Insights for the shipping industry – AFI platform (afi.dnv.com)
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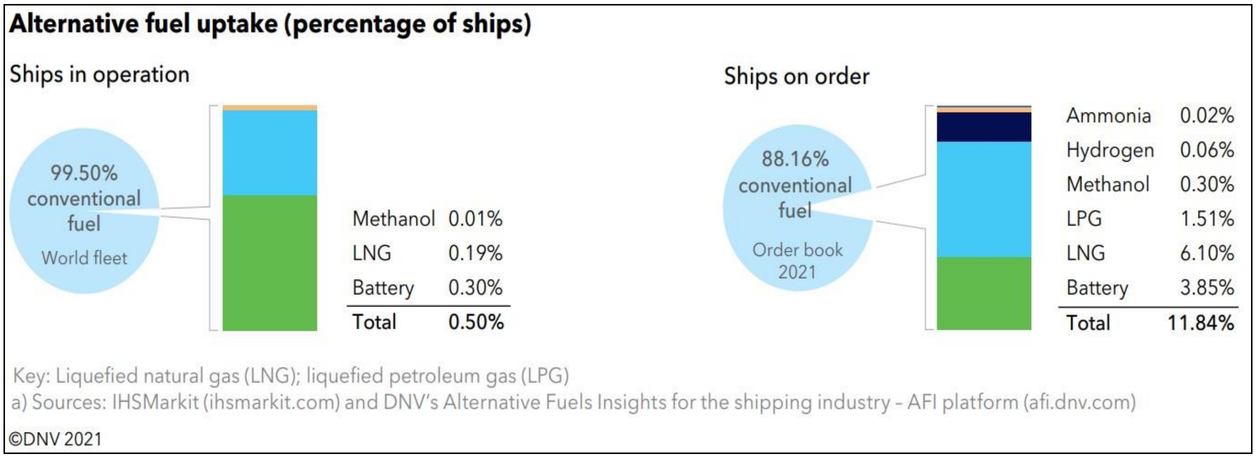
Methanol, ammonia and hydrogen are emerging as alternative fuels in the world fleet, as shown in Figure **13**. The fleet comprises of approximately 110,700 vessels with a displacement of more than 100 GT, excluding inland waterways, non-merchant and non-propelled vessels. Alternative fuels are used by less than 1 % of ships in operation, primarily in the short sea segment and non-cargo ships and they have negligible impact on total maritime emissions. However, the alternative fuel systems are specified in about 12 % of new constructions nowadays (DNV, 2021). This is nearly double the 6 % anticipated in (GL, 2019b), Figure 14. It is noticeable that there is an increase in deep- sea LNG fueled ships internationally, as well as batteries for full electric or part electric operations in the short sea segment, in bookings for newbuild ships during the next years.



Key: Liquefied natural gas (LNG); liquefied petroleum gas (LPG)

a) Sources: IHSMarkit (ihsmarkit.com) and DNV's Alternative Fuels Insights for the shipping industry – AFI platform (afi.dnv.com)

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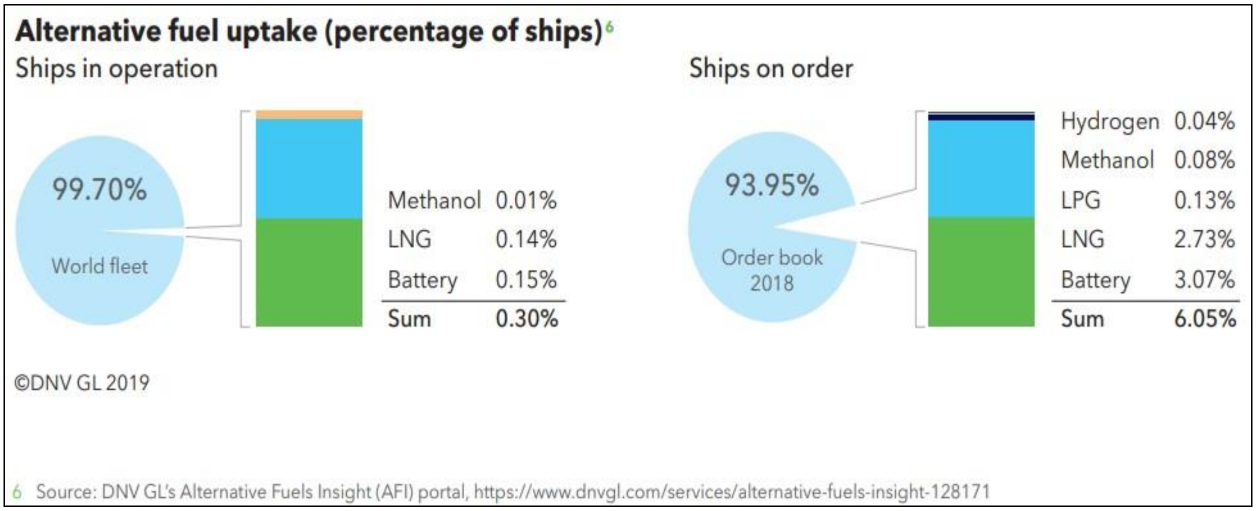
Figure 13: Uptake of alternative fuels for the world fleet as of June 2021 including ships in operation and on order (DNV, 2021).



©DNV GL 2019

6 Source: DNV GL's Alternative Fuels Insight (AFI) portal, https://www.dnvgl.com/services/alternative-fuels-insight-128171

Figure 14: Status of uptake of alternative fuels for the world fleet as of May 2019 including ships in operation and on order (GL, 2019b).

Storage capacity is a major obstacle to many alternative fuels in deep-sea applications and the present possibilities for deep- sea trade are LNG and LPG, which are not carbon- neutral but are the only alternative fuels that are scalable commercially, or biofuels which are significantly more expensive and not yet generally available. The variation of fuel options make it difficult to pick obvious winners across all circumstances, although ammonia is one of the most promising carbon- neutral fuels in the long run (DNV, 2021).

Each fuel has advantages and disadvantages, but fuel flexibility, or the ability to convert an engine to run on an alternative fuel will be crucial. Because the average ship has a life span of 25 to 30 years, each shipowner would have to make key investments decisions concerning its fleet numerous times in the next few decades. Some ships will have new propulsion system installed while others will be demolished and replaced.

4 Ammonia

4.1 Ammonia as hydrogen carrier

Ammonia has the chemical formula NH_3, present in gaseous state. In a gaseous state, it has one Nitrogen atom and 3 Hydrogen atoms attached to it. The chemical reaction known as the ammonia equation is as shown below:

$$N_2 + 3H_2 \rightarrow 2NH_3$$

As ammonia contains no carbon does not emit any CO_2 when used as a fuel in an internal combustion engine. This creates the potential for truly zero carbon propulsion. An additional small quantity of pilot fuel is required for combustion. However, what must be considered is that most ammonia today is produced from natural gas and so from a lifecycle perspective it is not zero-carbon, which is something that the industry needs to address if ammonia is pursued. Ammonia is also a sulfur-free fuel and it does not require any SO_x removal system on the exhaust to comply with environmental limitations on sulfur emission.

4.2 Types of ammonia

The following categories are used to distinguish the various techniques of manufacturing ammonia:

Brown ammonia: Ammonia produced using a fossil fuel source as the feedstock, such as natural gas, LPG, naphtha and coal. 400 Mt annually of CO_2 are emitted into the atmosphere during this process. Other feedstocks have lower efficiency for latest technological innovations for brown ammonia than natural gas, with 53 percent for naphtha, 49 percent for HFO and 44 percent for coal. Coal, naphtha and HFO have high carbon dioxide emissions between 2.5 and 3.8 tonnes CO_2/ tonne ammonia compared to 1.6 tonnes CO_2/ tonne ammonia for natural gas. Natural gas as a feedstock also offers a greater efficiency as well as lower capital expenditure (CAPEX) and operating expenses (OPEX) than coal (Society, 2020), (DNV, 2020).

Blue ammonia or low carbon ammonia: Ammonia from fossil sources (brown ammonia) that has been manufactured using carbon capture and storage technology (CCS) (DNV, 2020). Whereas up to 90% of carbon dioxide can be absorbed, upstream greenhouse gas emissions related with natural gas production restrict life cycle emission reductions up to 60 – 85% for paired steam methane reforming and carbon capture and storage. This level of carbon emission is remarkable, but current forecasts show that this method could only be a piece of a shift to a zero carbon strategy for net zero carbon hydrogen generation. If there is a significant rise in hydrogen and ammonia production in conjunction with efficient energy storage, it becomes extremely important (Society, 2020).

Green ammonia: Ammonia with no carbon footprint produced using renewable energy (electricity), water, and air. Green ammonia's CO_2 footprint approximated to be zero, despite the fact that a full lifecycle assessment should include plant building and transportation to the bunkering location. The life cycle emission reduction for green ammonia is estimated to be 90 percent for wind- powered ammonia and >75 percent for photovoltaic- powered ammonia. With the increased use of renewable energy in the manufacture of wind turbines and photovoltaics, the reduction will rise over time as the life cycle emissions from renewables fall (Laval et al., 2020).

Hybrid ammonia: Ammonia generated in hybrid plants that are partially powered by fossil fuels and partially by renewable electricity is known as hybrid green ammonia. Renewable energy, which is not yet available everywhere, has as a result to be useful in the transition from brown to green production.

Despite the fact that green and brown ammonia have vastly different carbon footprints, the final product is the same. From an operational standpoint, brown or green ammonia, or any combination of the two, can be used as a maritime fuel. Because brown ammonia is a commercial commodity sold in vast amounts, this fact considerably reduces any risk associated with investing in a ship that runs on NH_3 as a fuel. A ship owner could begin with brown NH_3 and progressively raise the amount of green ammonia mixture as economics, standards and regulations dictate, as well as the necessity or willingness to contribute to more carbon neutral and sustainable maritime sector.

NH_3 is a zero carbon fuel, which means that a ship runs on it, whether brown or green, no CO_2 is released. The manufacturing of ammonia and its delivery to the bunkering site account for the whole CO_2 footprint associated with NH_3 fuel. In reality, the ship owner or operator can utilize any of kinds of ammonia listed above, which are literally identical but have distinct production origins and as a result, have varied CO_2 footprints.

4.3 Haber-Bosch process

The German Chemist Fritz Haber was the first person who proposed the process of ammonia production from nitrogen and hydrogen. Carl Bosch, Alvin and other chemists made huge efforts to develop the required high pressure and temperature equipment to set up a commercial viable plant through Haber - Bosch process by using over 2500 catalysts (Berwal et al., 2021).

Haber tried to combine feed gas recycling under high pressure and an effective catalyst in order to achieve sufficiently high conversions of nitrogen which had a result a large –scale production of artificial fertilizers (Kandemir et al., 2013). About 90% of total production of ammonia globally is produced by this process. The Haber-Bosch process operates at high temperatures of 400 °C - 500°C and pressures of 150 - 300 bars which means that it is an energy – intensive process (Aziz et al., 2020).

Fossil fuels are used in the Haber-Bosch process as a source to produce hydrogen. The amount of hydrogen that is required for the HB process now can be produced through the electrolysis of water based on renewable energy, Figure 15 (Berwal et al., 2021). Most recent, greener ways are emerged on producing ammonia such as solar, wind or hydro power, giving ammonia a competitive edge over HFO synthesis. Is it feasible to revive one of the traditional manufacturing processes? Yes, since the atmospheric air, water, feedstock and renewable energy are all abundant and sustainable in many regions and some of the important cost drivers, such as electrolysis and power generation, have lately seen significant cost reductions (Laval et al., 2020). On a broad scale, such a process would normally have 68 percent efficiency. An air separation device is used to extract nitrogen. The efficiency of the entire process, from electricity to ammonia, is said to be around 52 percent.

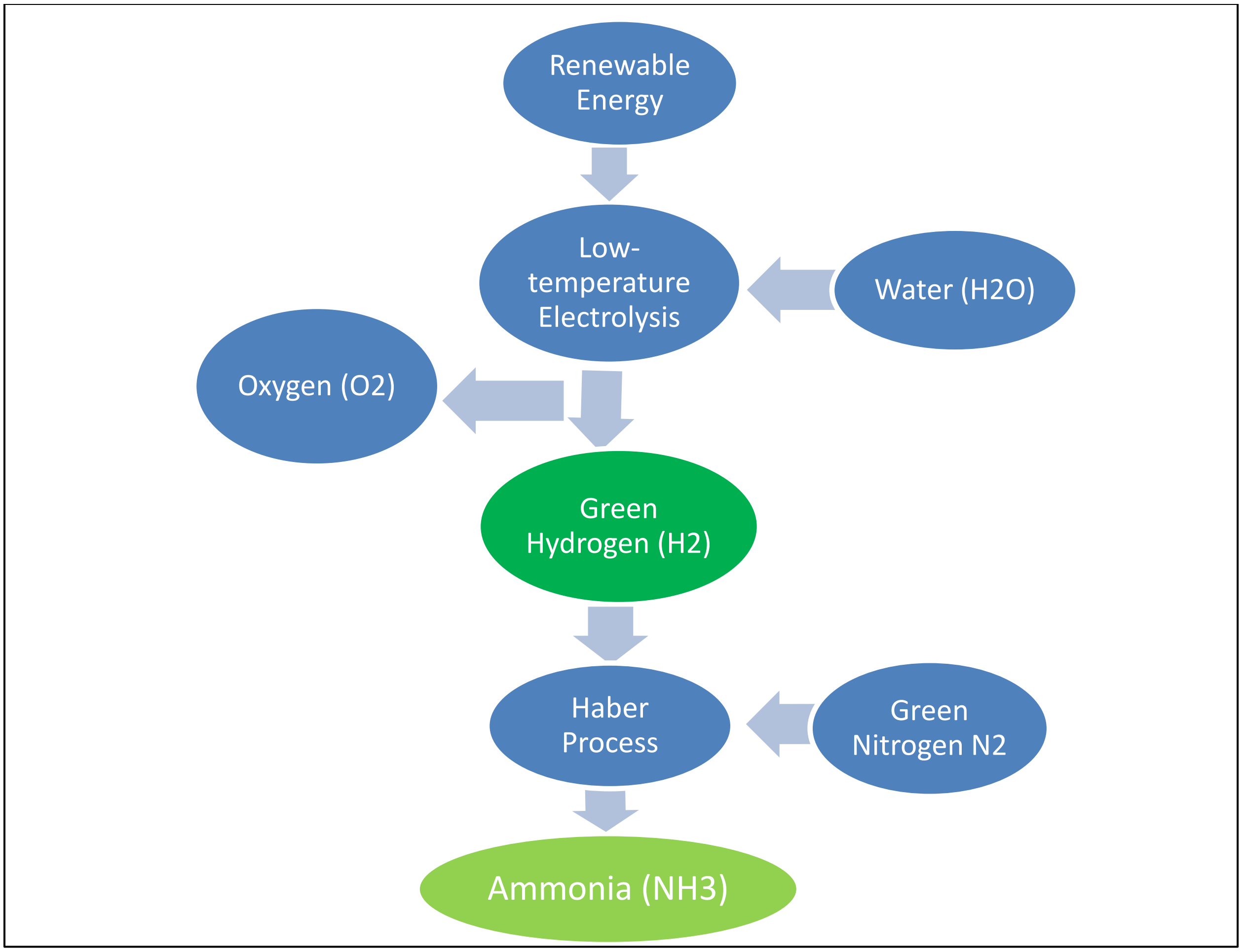


Figure 15: Green ammonia process map (Research, 2022).

4.3.1 Haldor Topsoe

A combination of solid oxide electrolysis cell (SOEC) and Haber Bosch process is another technique of producing hydrogen, being developed by Haldor Topsoe, Figure 16. When compared to today's typical alkaline or PEM electrolyzers, Topsoe's unique SOEC electrolyzers provide higher performance in electrolysis of water into hydrogen with efficiencies exceeding 90 % (Frøhlke, 2021). The SOEC removes the oxygen from the air/ steam blend, eliminating the need for an air separation unit. Electricity to ammonia conversion efficiency is predicted to be around 71 percent. The energy required for the Haber Bosch synthesis is estimated to be only 6% of the total energy consumed by the entire process (DNV, 2020), (John Bøgild Hansen, 2019). Haldor Topsoe has recently announced the start of the SOC4NH3 project (Solid Oxide Electrolysis Cell based production and use of ammonia), which will utilize this unique technological combination, with commercial availability expected in 2030.

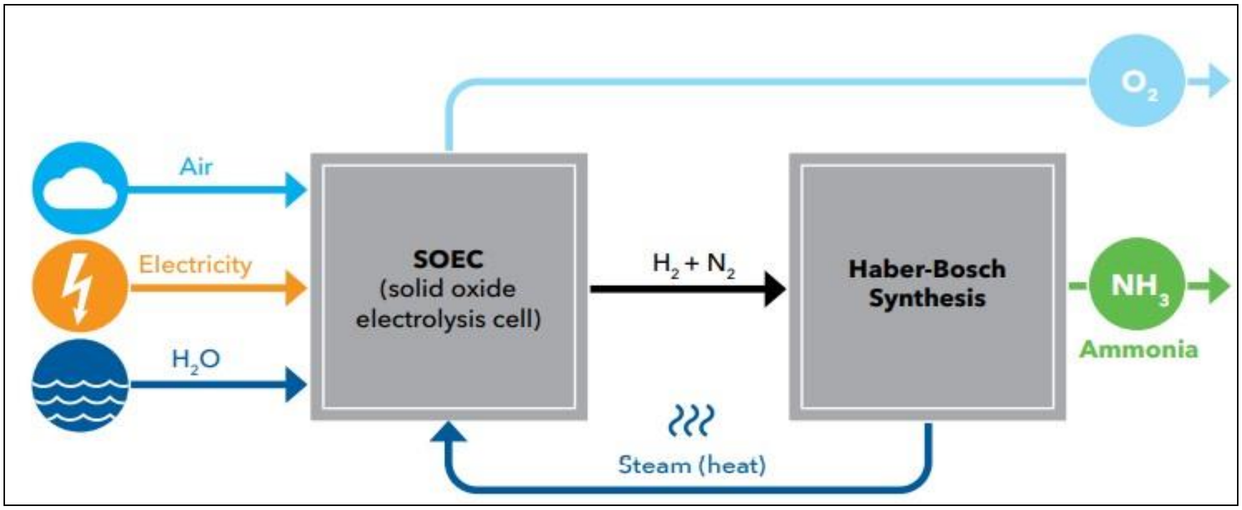


Figure 16: The SOEC concept for ammonia production by Haldor Topsoe (DNV, 2020).

4.3.2 Another methods for green ammonia production

Other recognized techniques of green ammonia manufacturing exist in addition to the Haber – Bosch process. All are currently in the early stages of research:

- Ammonia is created naturally by bacteria that include an enzyme catalyst named nitrogenase, which synthesizes ammonia from water and nitrogen at ambient temperature and pressure. Since Biological Nitrogen Fixation (BNF) is an excellent source of green ammonia, additional study and development is needed before large scale industrial production is addressed (Society, 2020).
- Electrochemical production is a method that uses electricity to produce green ammonia directly from water and nitrogen. There is no separate phase in the hydrogen generation process. This method would be appropriate for distributed small scale generation and would be more tolerant of intermittent power supplies. In laboratory investigations, however, only low rates of ammonia generation have been established. New electrolytes, electrocatalysts and systems should be invented so that ammonia can be produced instead of hydrogen at competitive rates (Society, 2020).
- Chemical looping methods entail a succession of chemical/ electrochemical reactions that produce ammonia as a by- product, while recycling and avoiding the loss of the core reaction ingredients. Some of these cycles, for example, bypass the requirement for a separate hydrogen generation stage by reacting straight with water (Society, 2020).

4.4 Uses of ammonia

Ammonia compounds are already imported and exported through more than 120 ports, with some even providing storage facilities. Such infrastructure might be a valuable resource for ensuring the supply of ammonia as a marine fuel. It is used in a variety of industries and handling practices and safety training have been widely disseminated. As a result, for those who are familiar with it, utilizing it for ships should not be an issue (KR, 2021). Although production is theoretically possible in any nations and according to U.S. Geological Survey in 2018, China produces around 31% of global total ammonia, followed by Russia (8.7%), India (7.3%) and the United States (7%). Canada, Indonesia, Saudi Arabia are other major suppliers (7%). In the Sustainable Development Scenario, the total tonnage of ammonia used as shipping fuel – which does not exist on a commercial scale- seems to be comparable to more than half of the volume used for conventional agricultural and industrial use and 110 % in the Net Zero Emissions by 2050 Scenario.

4.4.1 Fertilizer

The majority of ammonia is used as a fertilizer in agriculture. According to the Centre for European Policy Studies, fertilizer accounts for around 80 % of worldwide ammonia output, with 88 % in the United States. The most commonly used fertilizer is urea or ammonium nitrate of different grades, which is made from ammonia and carbon dioxide (DNV, 2020). The agricultural industry uses pressurized tanks to store, transport and handle anhydrous ammonia as a liquid. Manual procedures such as connecting and disconnecting pressurized vessels, as well as transporting pressurized tank equipment are all part of the equipment handling process (Laval et al., 2020).

4.4.2 Refrigerant

Ammonia, along with Freon gas, has excellent thermodynamic properties, making it an efficient refrigerant. This method uses over 360,000 metric tons of ammonia each year in North America. It is also worth noting that ammonia in maritime industry is commonly handled as cargo and used as a refrigerant onboard. All of the required methods for safe ammonia handling onboard, including operational and safety measures are already well known in the maritime industry and recognized by crew and operators (Laval et al., 2020).

4.4.3 Industrial

NH_3 is often used to make household cleaning products, nitric acid, that can be used to make dyes, plastics and fibers, explosives like ammonium nitrate, trinitrotoluene (TNT) and nitro-glycerin and cyanides that are being used to produce synthetic polymers like nylon and acrylics, as well as obtain gold from ore bodies (Afif et al., 2016).

4.5 Nitrogen cycle

The usage of ammonia has its drawbacks. Human disruption of the global nitrogen cycle, mostly through the use of ammonia based fertilizers, contributes to worldwide biodiversity reductions, widespread air quality issues and global greenhouse gas emissions. New applications of ammonia, such as storage, its direct use as a fuel and the use of renewable energy, must be decoupled from environmental impact, with a focus on avoiding and successfully reducing nitrogen oxide and ammonia emissions. Ultimately, we may see the ‘’ammonia economy’’ as a totally circular and sustainable cycle, Figure 17.

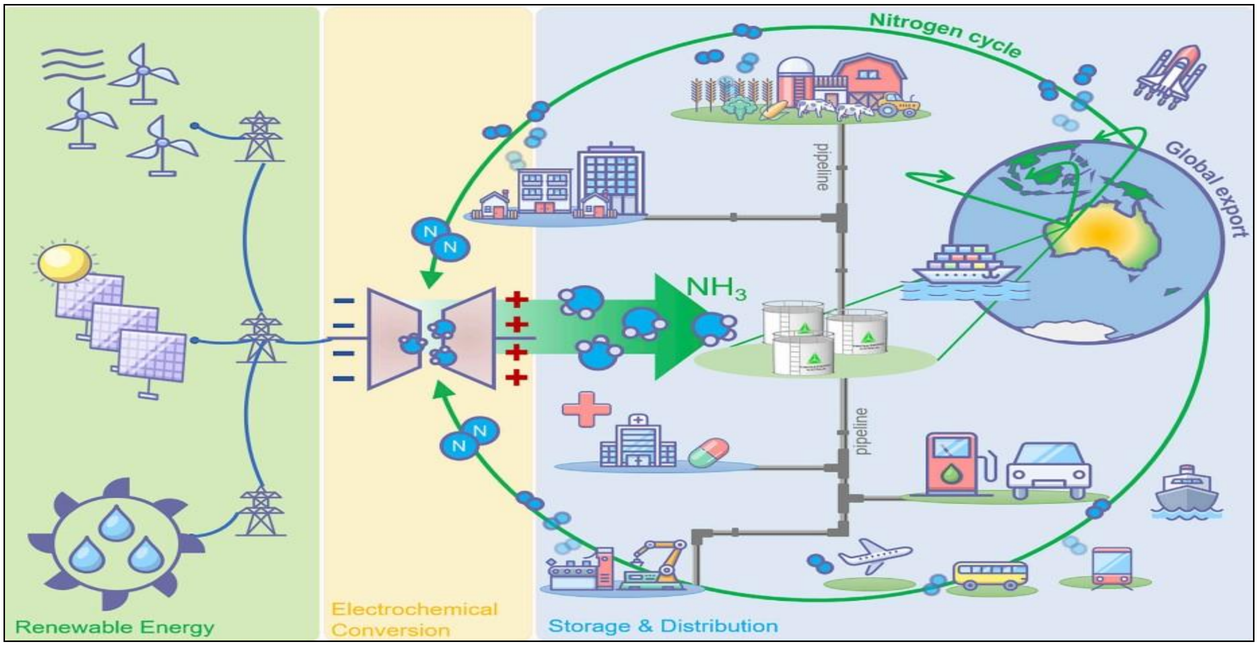


Figure 17: Vision of the ‘’Ammonia Economy’’ in which the Energy Sources and Uses are all based on Ammonia (MacFarlane et al., 2020).

A significant move from a fossil carbon based economy to an economy based on ammonia necessitates thorough consideration of the environment consequences of the new fuel’s production and usage. Similarly to how the global carbon cycle is made up of a complicated web of biogeochemical processes, the global nitrogen cycle is complex and poorly understood. It is apparent that humanity cannot avert one catastrophe involving CO_2 emissions by causing a second crisis concerning NH_3 and NO_x emissions.

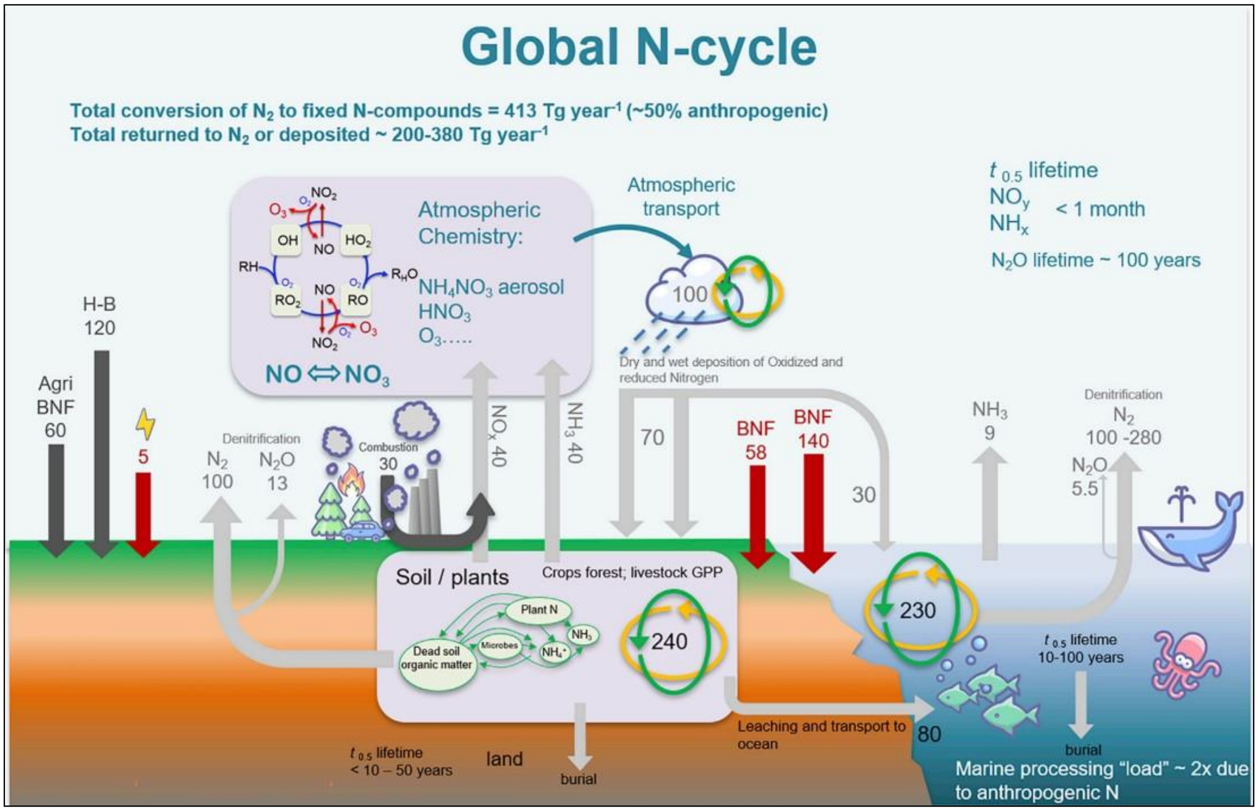


Figure 18: The Planetary Nitrogen Cycle (MacFarlane et al., 2020).

Figure 18 depicts a worldwide nitrogen cycle overview, as reported by Fowler et al. in Philosophical Transactions in 2013 (Fowler et al., 2013), to demonstrate the relative relevance of current anthropogenic ammonia generation. This graphic illustrates the major atmospheric, marine cycles and land-based that exchange N_2 for several key types of manufactured nitrogen such as, any forms of inorganic, organic or biological nitrogen other than N_2. The descending arrows represent nitrogen fixation by natural mechanisms, like plant based biochemical nitrogen fixation (BNF). On the left, the Haber-Bosch process and other anthropogenic loads are depicted. The upwards arrows depict several processes that result in re-emissions to the atmosphere.

Among the most significant signals conveyed by this graphic is that the anthropogenic fixation already produces a quantity of fixed nitrogen compounds each year that is about similar to that produced by natural processes. Because the Earth's cycle and re-emission systems will eventually have to deal with this extra fixed nitrogen, it is critical to remember that the overall demand on these natural processes has already doubled in the previous 100 years when Haber Bosch technology became widely used. Given that a considerable share of the fixed nitrogen is converted to nitrate, which travels via aquatic systems to the oceans and that there are marine Nitrogen cycles with extremely long durations (half–life, $t_{0,5}$ ~ 100 years), one would be obliged to conclude that there are unknown consequences. In other terms, the destiny of the anthropogenic caused doubling of fixed nitrogen inside the Nitrogen cycles has yet to be fully compensated for or understood. The impact of rising nitrate concentrations on marine ecosystems, in particular, is an issue that requires further consideration (MacFarlane et al., 2020).

Even though the ammonia economy is meticulously and rigorously aimed toward the $N_2 \rightarrow NH_3 \rightarrow N_2$ cycle depicted in Figure 17, there will be unavoidable losses and inefficiencies, resulting in extra NH_3 and NO_x emissions, which will add additional load to the Figure 18 cycles. The additional monitoring, analysis and understanding of these cycles is an important component of progressing toward an ammonia economy (MacFarlane et al., 2020) .

Identifying economical and effective answers to all of these issues, as well as establishing technological feasibility, adopting suitable legislation and putting in place safety measures, will be critical in allowing more flexible paths to a low carbon energy future on a global scale. NH_3 has the potential to provide a huge influence in the future decades by allowing us to move away from our worldwide reliance on fossil fuels and contribute significantly to the reduction of GHG emissions (MacFarlane et al., 2020).

5 Ammonia as a marine fuel

5.1 Barriers

IMO has set regulations and limits in order the goals of the Paris Agreement to be achieved. The use of an alternative fuel than a conventional fuel like ammonia seems to be the driver for a sustainable shipping sector. Shipowners are concerned about the choice of an alternative fuel and they should focus on the aspects of the fuel in order to comply with the legislation. Engine suitability, infrastructure, maturity, prices, health and environmental hazards, handling and storage of the fuel are some vital aspects that have the power to help shipowners to take the suitable choice.

Ammonia (NH_3) is thought to be a great green marine fuel that may be utilized in energy generating and transportation systems due to its high hydrogen density and existing infrastructure. It has been identified as a potential fuel for internal combustion engines (ICEs), for fuel cells and gas turbines.

5.2 Internal combustion engines

Internal combustion engines (ICEs) are a well - known technology that has been utilized for over 100 years in automotive, off-road and marine industries (GL, 2019a). Marine engines are usually divided into three categories:

a) Slow - speed engines, which operate at a maximum of 300 RPM but commonly 80-140 RPM. These are two – stroke engines that are used to propel huge ships.
b) Medium- speed engines, which operate in the range of 300 to 900 RPM. They are usually four – stroke engines that may be employed for both propulsion and auxiliary power generation on a wide range of ships.
c) High – speed engines with a rotational speed of more than 900 RPM. They are four - stroke engines that are utilized for propulsion and auxiliary functions in smaller ships.

In a combustion chamber, an ICE burns fuel with an oxidizer (typically air). The expansion of the high - temperature and the high - pressure gases produced by combustion, acts directly on the pistons of an ICE. This pressure propels the piston forward, converting chemical energy into mechanical energy. In ICE, ammonia or ammonia hydrogen mixtures can be used. Compression ignition (CI) engines, which often use diesel fuel and spark ignition (SI) engines, which typically use gasoline fuel, are the two principal engine technologies. SI gasoline engines are mostly seen in light–duty trucks. CI diesel engines are used in the vast of medium and heavy duty vehicles (de Vries, 2019). Because of the high temperatures and pressures involved in the combustion of ammonia in compression ignition engines, considerable levels of NO_x are produced. Nitrous oxide (N_2O) is a powerful greenhouse gas with a greenhouse warming potential 298 times that of CO_2 over a 100 year period (ABS, 2020b). A Selective Catalytic Reduction (SCR) system, which reduces NO_x emissions, is already utilized to treat emissions and control unburnt ammonia in IC engines.

NH_3 has been used as a fuel for internal combustion engines, rocket engines and fuel cells. It cannot be used straight in conventional ICEs due to its high auto–ignition temperature, high heat of vaporization and relatively low flame speed. Partially to decomposing ammonia to hydrogen and nitrogen is one technique to make it viable fuel for ordinary ICEs. The presence of hydrogen in the fuel blend, which enhances the combustion process, is closely attached to the improved combustibility of partly cracked ammonia. Combining ammonia with a robust fuel that works as a combustion booster is another practical approach to make it work in ICEs (Nozari and Karabeyoğlu, 2015).

5.2.1 Compression ignition engines

A Cooperative Fuel Research (CFR) engine with a compression ignition method and liquid ammonia pumped directly into the cylinder was successfully tested in 1967. The compression ratio of the engine has to be 35:1 with jacket and intake air temperatures of 150 °C in order to accomplish effective ammonia auto ignition (Gray Jr et al., 1967). Other recent studies showed that for all start main injection timing conditions, using compression ratios up to 30:1 yielded in less than 90% combustion efficiency. Under specific situations, NO emissions can be decreased by 25%. Nonetheless, a significant quantity of ammonia was lost because of the decrease and as a result, it was determined that the commencement of pilot fuel injection should be carefully controlled to avoid significant amounts of ammonia slip and to limit NO emissions(Lee, 2018).

With a compression ratio of 16:1, consistent combustion in a Homogeneous Charge Compression Ignition (HCCI) may be obtained up to 70% volume of ammonia and 30% volume of hydrogen. It was discovered that when using ammonia hydrogen blends, a trade- off must be made between a high compression ratio to encourage ammonia combustion and a low compression ratio to avoid hydrogen ringing. Whenever the combustion energy is to great level in HCCI engines, a local auto- ignition causes a gas expansion at the speed of sound that oscillates inside the cylinder and this phenomenon is called ringing (de Vries, 2019).

5.2.2 Spark ignition engines

The internal combustion engine's versatility makes it desirable for NH_3 fuel use, especially when a spark is used to help promote ignition. Because to the high octane number of ammonia, spark ignition engines (SI) typically run at high compression ratios (CR) without risking engine knock. Early investigations showed that single-cylinder and multi-cylinder SI engines could be affectively run on pure ammonia fuel.

In an experiment an engine that used is a four-cylinder four-stroke SI engine that has been converted to a single-cylinder by only fuelling one cylinder. Because of its piston bowl tuned for gasoline direct injection, this engine has increased aerodynamics, with a tumble ratio of roughly 2.4. An electric motor forces the engine to run a constant speed of 1500rpm. With little or minor design changes, NH_3 has been verified as a highly good SI engine furl for current engines. Low and moderate hydrogen addition, with slightly fuel- rich and slightly fuel- lean circumstances, respectively, had the highest estimated efficiency and pressure. Lean mixes with a high hydrogen concentration, on the other hand, performed well (Lhuillier et al., 2020).

5.3 Fuel cells

The fuel cell (FC) turns electrochemical energy directly into electric power by converting the chemical energy of particular molecules into electricity without the use of combustion. As a result, it releases both electrical and thermal energy in the process with high efficiency and zero emissions, compared to internal combustion engines. Electrical efficiency of 50-60 % is projected, which is somewhat greater than marine diesel generators, depending on fuel cell type. The efficiency may be increased to 80% using heat recovery. Although noise and vibrations are minor and fuel cells are predicted to demand less operational service than traditional combustion engines and turbines. On the other hand, fuel cells have a lower life expectancy than internal combustion engines and fuel cell stack replacement is required numerous times throughout the lifespan of a vessel, resulting in additional capital expenses (Dnv, 2019), (GL, 2019a).

The operating temperature, efficiency, applications, prices and electrolyte materials of fuel cells are all classified. The electrolyte classifications of fuel cells are divided into six primary systems (Afif et al., 2016):

- Phosphoric acid fuel cells (PAFCs).
- Alkaline fuel cells (AFCs).
- Solid oxide fuel cells (SOFCs)
- Molten carbonate fuel cells (MCFCs).
- Direct methanol fuel cells (DMFCs).
- Proton exchange membrane fuel cells (PEMFCs).

PEMFC is available from a variety of manufacturers and has been utilized in a wide range of transportation modalities such as buses, vehicles and trains. Ammonia is not suitable for PEMFCs; because it can has bad effects on the conventional membrane. The advantage of using ammonia as a hydrogen carrier is that it is easier to transport and store and takes up less space than hydrogen. Because a PEMFC can only use pure hydrogen as a fuel, breaking and purifying of ammonia are necessary when using ammonia as a feedstock (Aziz et al., 2020). However, hydrogen cracking lowers the system's efficiency and raises the cost size of the propulsion system.

SOFCs have a significant advantage over the other types of fuel cells in terms of combining ecofriendly power generation with fuel flexibility. NH_3 technology has a rather infrastructure, which has sparked interest in employing ammonia in SOFCs. It can be used directly in fuel cells, reducing any pretreatment requirement or divided into H_2 and N_2 at high temperatures, usually between 500 and 1000 degrees, with the H2 being utilized in the FC (Afif et al., 2016), (Jeerh et al., 2021). Since there are no experiments with ammonia SOFC in maritime applications and SOFCs have mostly been investigated for land based power production, the technical readiness level (TRL) of SOFC is lower than PEMFC. On the other hand, because of the direct usage of ammonia in SOFCs, they are a possible future fuel contender. The emissions will be substantially lower than those projected from ICE. Since the SOFC operates at a greater temperature than a PEMFC, NO_x emissions are more possible, but there are ways to avoid them. According to KR (2020), the SOFC might be in conjunction with PEMFC or batteries to generate a suitable energy output for the primary and auxiliary engines (Cames et al., 2021).

Ammonia is a perfect energy carrier since it is a mass- produced, low cost and carbon free molecule. Extent research has explored various forms of ammonia – fuelled fuel cells utilizing certain electrolytes and electrodes at different temperatures in order to determine the optimal performance and use for every type. However, its progress has not yet reaches the point of commercialization, which means that there is no application in shipping industry (Afif et al., 2016).

5.4 Gas turbines

A compressor is used in a gas turbine to increase the pressure of atmospheric air flows. The energy is then added by spraying fuel into the air and lighting it, resulting in a high temperature flow from the combustion and the hot gas expands to atmospheric pressure in turbine. The turbine generates enough energy to power the compressor and a load. When the power required by the compressor is below the power provided by the turbine, the system as a whole produces a shaft work output in the process (de Vries, 2019), (Klein Woud and Stapersma, 2003).

Ammonia has been considered as a potential fuel for gas turbines. In comparison to hydrocarbon fuels, pure ammonia combustion in a gas turbine with liquid injection has numerous restrictions. Ammonia burned at half air-flow velocity of carbon fuels in flame stability tests and the variety of comparable ratios for stable flame was very narrow compared with hydrocarbon fuels (Valera-Medina et al., 2021).

In a previous study of liquid ammonia injection in a gas turbine, partly dissociated ammonia was used. It was determined that NH_3 with a partial dissociation of 28 percent may be employed as a replacement fuel in gas turbine combustion systems designed for hydrocarbon fuels. The lowest ignition energy and flame stability were almost identical to those of methane (Valera-Medina et al., 2021).

Ammonia – hydrogen mixtures have also been explored in a gas turbine burner. A 50 percent ammonia and 50 percent hydrogen combination was employed to achieve stable flames and similar laminar burning flame velocities as methane. The use of ammonia- hydrogen mixtures enhances the stability and the efficiency of the system, as well as its capacity to reduce NOx emissions and improve power loading situations (Valera-Medina et al., 2021). One option to attain burning rate more close to hydrocarbons would be to crack some of the ammonia back to hydrogen and ignite the unseparated mix of NH_3, N_2 and H_2.

GHG emissions in power production applications might be minimized from the use of ammonia or ammonia blends with other fuels as a gas turbine fuel. On the other hand, those systems are rare in maritime industry, as gas turbines are not widely employed due to their high fuel costs and low efficiency. For this reason, it is also being researched the ability to send liquid ammonia straight to the gas turbine without evaporation, which would result in cost savings and increased efficiency. NH_3 co- firing has a low level of technology readiness, but gas turbine manufacturers have announced plans to produce large scale NH_3 fired gas turbines around 2025. For example, Mitsubishi Heavy Industries has revealed intentions to commercialize a 40 MW gas turbine that burns 100 % ammonia directly by 2025. End of pipe technology may and must be used to control NO_x and N_2O emissions such as scrubbers.

5.5 Aspects of ammonia

There are various practical elements to consider while analyzing the possible operation of ammonia as a maritime fuel, including storage and handling of fuel, safety and technological suitability.

5.5.1 Storage and handling of ammonia

Ammonia is a superb hydrogen carrier and a good energy storage medium. In ships with a limited amount of capacity, the ability to store future energy is a critical consideration. Depending on tank capacity, ammonia can be compressed and stored as liquid in either atmospheric or pressurized tanks. However in order for this arrangement to be dependable, backup mechanisms must be in place to guarantee that the tank maintains a constant low temperature and pressure (DNV, 2020). The tank pressure is approaching atmosphere and the temperature is -33.3 when kept in huge quantities over 10,000 tons. The tank pressure is a few bars in amounts between 100 and 1,000 tons, while the temperature is still about 0°C. It is commonly stored at ambient temperature and up to 20 bar in tanks with capacities less than 100 tons. The tank volume must be estimated in order to ensure complete ammonia availability for ship propulsion. As a result, the total installed power, the predicted market potential in the ports where the ship is docked and the ammonia energy density all play a role. Because of its high energy density, ammonias net storage volume should be around 70 % larger than LNG and almost three times that of distillate (Laval et al., 2020).

It has also been recognized as a carbon-free fuel that can serve as a good energy storage medium. It has a 12.7 MJ/l energy density which is half of the energy density of HFO and the size of the storage tank is about three times that of regular conventional fuels (Laval et al., 2020), (Agency, 2021). The main advantage of NH_3 is that it is easier to store than hydrogen and the tank and fuel line installation restrictions are expected to be equivalent to the DNV GL criteria for propane (LPG) fuel at low pressure in ambient settings, as temperature and pressure are very similar. The above involves a shortest variance from the ship’s sides and bottom to prevent tank destruction in the event of a crash and grounding. The tank should be kept away from engine rooms and other high fire risk regions, as well as crane operations and other high fire risk regions as well as crane procedures and many other mechanical damage prone places. As a result, the cost of storage per unit energy is substantially lower than the cost of hydrogen and electricity stored in batteries or LNG (DNV, 2020).

5.5.1.1 Type C tank

A tank C pressurized tank appears to be the most cost effective solution for storing ammonia aboard ships with restricted routes and installed power. This tank can keep the product at a room temperature, eliminating the need for a reliquefaction mechanism. Moreover, the type C tank can be installed on the deck and can be fitted into a commercial ship’s overall design. The type C tank’s intended application limit is 2000 m^3 (Laval et al., 2020).

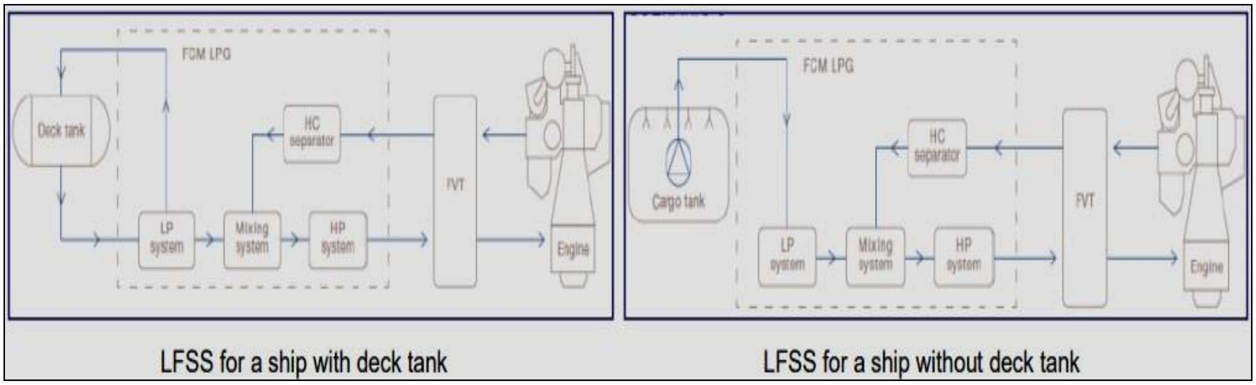
5.5.1.2 Liquid fuel supply system

The instance of a ship carrying ammonia as a cargo is the most straightforward. Based on recent experience with LNG, methanol and LPG, it is expected that these ships would be the first to burn it as an alternative fuel. The ship’s modifications will most likely be confirmed to the installation of a specialized NH_3 liquid fuel supply system (LFSS) and the requisite engine upgrades. In this scenario, special care should be given to prevent any unnecessary degradation of the cargo as a result of pollutants released by the engine. As a consequence, the LFSS architecture should be capable of insuring this feature (Laval et al., 2020).

The LFSS is the technology that supplies ammonia to the engine when it is needed. The LFSS can be mounted on the deck and linked to the engine through double walled pipe to reduce the potential of ammonia leakage in the engine room. Deployment in the engine room (ER) is also conceivable, although with considerations such as the placement of an airlock system to avoid ammonia dispersion. Several functions are performed by LFSS system as we can see below (Laval et al., 2020):

a) regardless of storage situations, it delivers fuel to the engine at the proper pressure and temperature
b) it separates the fuel from the payload, protecting the latter from pollutants generated by the engine
c) it has the ability to do purging when necessary
d) it can manage product recovery after purging, while minimizing emission into environment under safe conditions

The LFSS have a variety of designs depending on the engine technology. It may be comparable to low pressure LNG delivery systems for engines receiving secondary fuel as a gas at low pressure. The system being used for LPG on LGIP engines may be implemented with relatively few modifications to engines receiving secondary fuel at high pressure in liquid phase. A block schematic for a ship with or without a specific fuel tank is shown below, Figure 19 (Laval et al., 2020).



LFSS for a ship with deck tank

LFSS for a ship without deck tank

Figure 19: Alternative block diagrams for the Ammonia LFSS (Laval et al., 2020).

5.5.1.3 Selective catalytic reduction technology

Ammonia burning in internal combustion engines may produce NO_x and N_2O, both of which are potent greenhouse gases. If ammonia is to be a feasible zero emission fuel, existing SCR technology is expected to be capable of addressing the NO_x problem from unburnt ammonia (ammonia slip) and engine makers will need to discover methods to manage N_20 (Laval et al., 2020).

MAN ES engines, for instance, are fitted with modern SCR technology to minimize nitrogen oxide emissions (NOXs) and to meet regionally varying emission laws. In the 1990s, four bulk carriers were equipped with an ammonia based SCR system. Depending on the results of the first engine tests, an increase in SCR capacity and ammonia usage may be required to attain Tier III compliance.

The SCR system is an after treatment method that uses catalytic decrease to capture NO_x generated by combustion from the exhaust flow. Typically, the needed ammonia is supplied to the exhaust gas by inserting a urea solvent or it can be used instead of urea as the catalytic agent. One advantage is that an ammonia fuelled ship has already ammonia on board. In comparison to ammonia fuel use, the SCR system will consume extremely little ammonia (Solutions, 2020). In the catalytic reaction, NH_3 and NO_x are converted to nitrogen (N_2) and water (H_2O), as Figure 20 shows. The ammonia based SCR technique can eliminate more than 90% of NOx generated by a stationary source. From the standpoint of price competitiveness and stability, it has been marketed as the best NO_x control technology.

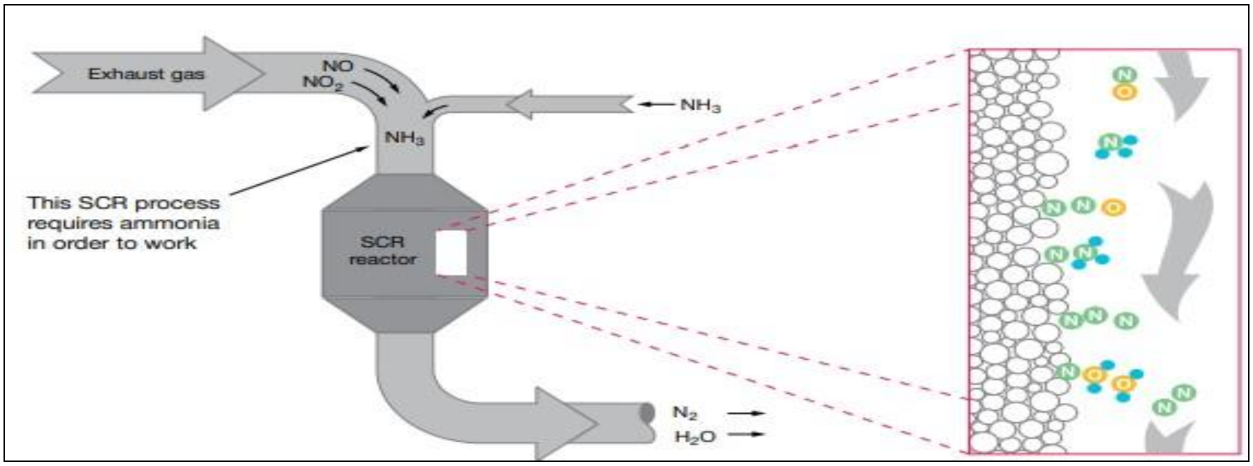


Figure 20 : The selective catalytic reduction process (Solutions, 2020).

5.5.1.4 Exhaust gas recirculation

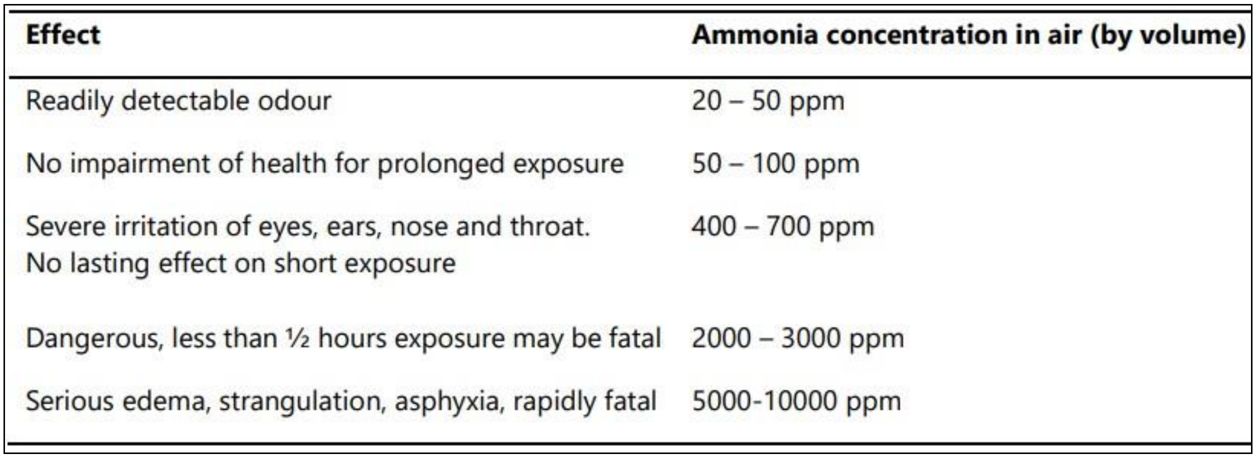
The exhaust gas recirculation (EGR) is also one of the effective strategies used to minimize NO_x emissions. The EGR decreases the partial pressure of oxygen in the atmosphere, slowing the combustion process and lowering maximum temperatures and NO_x generation. EGR is a particularly efficient method for decreasing NOx, with around 20% of the exhaust gas recirculated reducing NO_x by up to 50% (Henningsen, 1998).

5.5.2 Health risk

When considering the potential use of ammonia as a maritime fuel, a number of challenges may arise. The usage of ammonia as a fuel will lead to an increase in the volume of NH_3 handled in public places on a daily basis. As a result, the hazards of its unintentional release and exposure must be carefully examined and minimized. The usage of ammonia as a renewable and sustainable energy source fuel will certainly cause some societal concern from a safety standpoint.

The primary worries are with ammonia’s toxicity and safety. Ammonia is a poisonous, caustic and combustible gas with a strong distinctive odor. Ammonia has an odor threshold ranging from 5 to 50 parts per million (ppm) of air, which means that humans can smell it at low amounts that do not pose a health danger. It does not remain in the body and does not produce long term effects. Also, it has not been linked to the development of cancer and does not classed as a carcinogen like gasoline, which is known to contain carcinogenic substances (ABS, 2020b).

Legislation establishes acceptable human occupational exposure to ammonia, which are often a function of concentration and exposure duration. The limit is established at 25 – 50 ppm, with quantities beyond 300 ppm posing a serious health risk. Figure 21 shows some examples of exposure guidance (GL, 2020). The health hazards of gasoline, liquefied petroleum gas (LPG), natural gas (NG), methanol are 1 and the health hazard of ammonia is 3, which means that it is dangerous as Figure 22 shows.

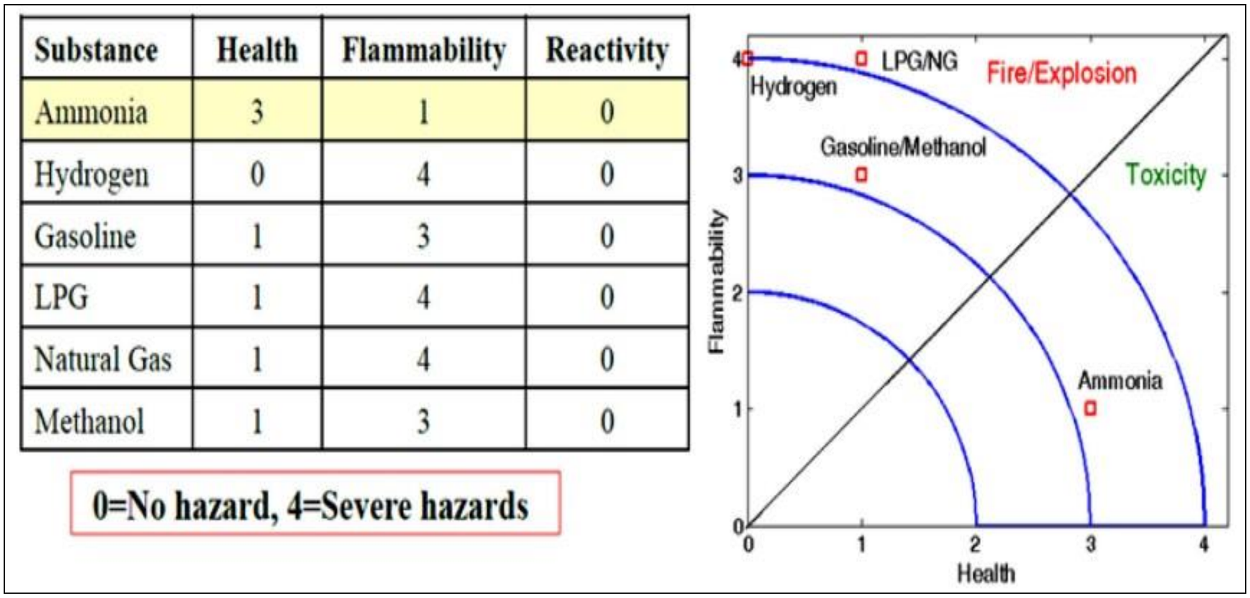


Effect	Ammonia concentration in air (by volume)
Readily detectable odour	20 – 50 ppm
No impairment of health for prolonged exposure	50 – 100 ppm
Severe irritation of eyes, ears, nose and throat. No lasting effect on short exposure	400 – 700 ppm
Dangerous, less than ½ hours exposure may be fatal	2000 – 3000 ppm
Serious edema, strangulation, asphyxia, rapidly fatal	5000-10000 ppm

Figure 21: Exposure guidance (GL, 2020).

5.5.2 Flammability, corrosivity and toxicity

NH_3 is a flammable gas with a limited spectrum of flammability. Flammability is the ability of a chemical to burn or ignite, causing fire or combustion. In dry air, it has a flammable range of 15.15% to 27.35% and temperature of 651°C for auto ignition. Because of its limited flammability range, comparatively high ignition energy and low laminar burning rate, it poses a reduced danger of fire than other fuels (ABS, 2020b), as we can see in Figure 22. NH_3 has the minimum ignition energy of 8 MJ, which is 29 times higher than methane (0.28 MJ) and 727 times higher than hydrogen (0.011) (KR, 2021). In addition, NH_3 is incompatible with a number of substances and it interacts with and corrodes brass, copper, zinc and other alloys in the presence of moisture. Acids, halogens and oxidizing agents react with ammonia, which is an alkaline reducing agent.



Substance	Health	Flammability	Reactivity
Ammonia	3	1	0
Hydrogen	0	4	0
Gasoline	1	3	0
LPG	1	4	0
Natural Gas	1	4	0
Methanol	1	3	0

0=No hazard, 4=Severe hazards

Figure 22 : Toxicity and Fire/ Explosion comparison of different fuels (Karabeyoglu and Evans, 2012),(Valera-Medina et al., 2018).

Double walled tubes must be utilized as supplementary protection if tubes are inside confined areas, such as under the deck line, due to its toxicity and flammability. When tubes are installed in open air, double walled pipelines can be useful for detecting leaks quickly and keeping dangerous zones to a minimum. Sniffers will identify any leaks and trap the fuel in the secondary containment even before it affects humans or ignite generators.

In comparison to other gaseous fuels, the concern of ammonia toxicity requires careful attention and novel methods for dealing with gas emissions are mandatory. DNV GL has conducted HAZIDs (HAZard Identification) in collaboration with a variety of partners, including engine manufacturers, ship owners and fuel delivery system makers, in order to examine safety and especially toxicity. The HAZIDs addressed NH3 transmission from freight to storage tanks, ammonia’s transport to engines, engine operation and secure ammonia’s management in the engine room and on the deck (DNV, 2020). According the EU Classification, Labeling elements and Packaging of substances (CLP) regulation (EC) No. 1272/2008, ammonia is categorized as below in Table 8 (Ammonia, 2012).

H221	Flammable gases, Category 2	Physical hazards	
H280	Contains gas under pressure; may explode if heated	Physical hazards	
H331	Toxic if inhaled, Category 3	Health hazards	
H314	Causes severe skin burns and eye damage, Category 1B	Health hazards	
H410	Very toxic to aquatic life with long lasting effects, Category 1	Environmental hazards	

Table 8 : Hazard statements (CLP) and Hazard pictograms (CLP) (Ammonia, 2012).

5.5.3 Safety and technological suitability

Undoubtedly, social acceptability of NH_3 as a large scale fuel is a critical issue that will necessitate further research, the creation of guidelines and requirements and intergovernmental, policy- level work. However, it seems to be no fundamental fault in this regard, that would put the ammonia's economy in jeopardy. It is noteworthy that the Ammonia Safety Training Institute's work as a non- profit organization and provides guidance in the continued development of safe handling techniques.

In accordance with hazards, a lot of information and regulations are under the table in order ammonia to be handled. Ammonia poses a safety risk primarily in pressure storage, which means that if leaks occur then a harmful air concentration increases. Because NH_3 has a distinct stench, it is immediately detected, allowing personnel to get away from the leak and take proper actions. This has been ammonia's most significant benefit in terms of safety. The most important is that automated ammonia gas detection at the ppm level, as well as automated actions like alarms, improved ventilation and line shut down are commonly employed devices that help ammonia handling systems to operate safely. As referred above, NH_3 is a corrosive element. So, for ammonia tanks, fittings and pipelines, only iron and steel, as well as non-ferrous alloys resistant to ammonia should be used.

5.6 Regulatory framework for low flashpoints fuels

The International Maritime organization (IMO) restricts the use of fuels under the International Convention for the Safety of Life at Sea (SOLAS). Conventional fuel oil standards are restrictive and established on years of expertise. To avoid tank accidents and fires, using fuels with a flashpoint below 60°C, commonly named Low Flashpoint Fuels, is normally forbidden. The SOLAS Convention was updated in 2015 to enable ships that conform to the International Code of Safety for Ships Using Gases or other Low Flashpoint Fuels (IGF Code) to utilize low flashpoint fuels (GL, 2020). In other words, it is an International Maritime Organization regulation that is applicable to all gaseous and other low flashpoint fuels in transportation, as well as all gas powered ships, apart from gas carriers. The International Code for the Construction and Equipment of Ships Carrying Liquefied Gases in Bulk (IMO IGC Code) covers the use of low flashpoint fuels in gas carriers(Dnv, 2019).

5.6.1 The IGF code

The IMO accepted the IGF Code in June 2015 and it went into effect on 1 January, 2017. It is required for all ships that use gas fuel or other low flashpoint fuels and it presently includes specific clauses for natural gas in liquid or compressed form. The IGF Code comprises necessary regulations for the design, implementation, management and monitoring of low flashpoint fuel using apparatus, equipment and systems for the ship in order to eliminate the risk to the crew, vessel and environment. The IGF Code demands that the systems' safety, efficiency and dependability be similar to those of new and comparable traditional oil fueled main and auxiliary gear (GL, 2020).

The Code is based on best standard operating procedures, including good naval architecture and interior concepts, as well as the greatest knowledge and information of current operational experience, field data, research and development. According to the quickly changing modern fuels technology, the IMO shall evaluate the Code on a regular basis, taking into consideration both experience and technological advances. This Code was purposefully developed for LNG, but it will include specifications for ammonia, ethanol and methanol as well (ITF, 2019). So, the goal of the IGF Code is to establish the safe and environmentally sustainable design, construction and operation of ships loaded with propulsion engines and other engine parts that use low flashpoint fuels.

5.6.2 The IGC code

The International Gas Carrier Code (IGC) of the International Maritime Organization (IMO) forbids the use of hazardous and toxic cargoes as ship fuel. The IGC Code has a distinct chapter on the use of cargo as fuel, but does not allow the use of dangerous cargoes such as ammonia for this reason. However, if ammonia carriers are expected to be the first ships towards using NH3 as a fuel, the IGC will need to be change.

The International Code for the Construction and Equipment of Ships Carrying Liquefied Gas in Bulk (IGC Code) specifies precautions for staff engaged onboard ammonia carrying gas carriers, as listed below (Laval et al., 2020).

- Respiratory and eye protection devices for emergency escape purposes shall be provided for every person onboard, with some minimum requirements (no filter-type; self-contained breathing apparatus 15 minutes minimum duration)

- Protective clothing to be gas-tight

- One or more suitably marked decontamination showers shall be available on deck, depending on the size of the ship, and shall be able to operate under all ambient conditions

In addition, in the example of ammonia, the IGC Code defines the following specific standards for cargo tanks and accompanying pipes, fittings, adapters and certain other items of equipment that are generally in close interaction with the cargo fluid or vapour (Laval et al., 2020).

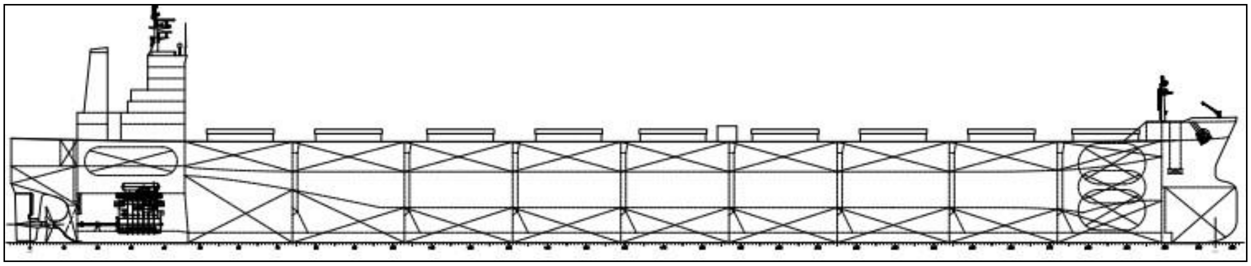
- Mercury, copper and copper-bearing alloys, and zinc shall not be used for cargo handling ammonia and for equipment normally in contact with ammonia liquid or vapour
- The ammonia shall contain not less than 0.1% w/w water
- Maximum nickel content in steel is 5%
- Minimum requirements for steel yield strength and post-welding treatment are indicated in IGC Code chapter 17.12

5.6.3 The IBC code

The International Code for the Construction and Equipment of Ships Carrying Dangerous Chemicals in Bulk (IBC), Amended by Resolution MEPC.225 (Jeerh et al., 2021), is to provide an international standard for the safe carriage in bulk by sea of dangerous chemicals and noxious liquid substances listed in chapter 17 of the Code. The Code establishes design and construction criteria for ships and the equipment they should carry, taking into account the nature of the items involved, in order to reduce the hazards to ships, their crews, and the environment (I.M.O., 2019b).

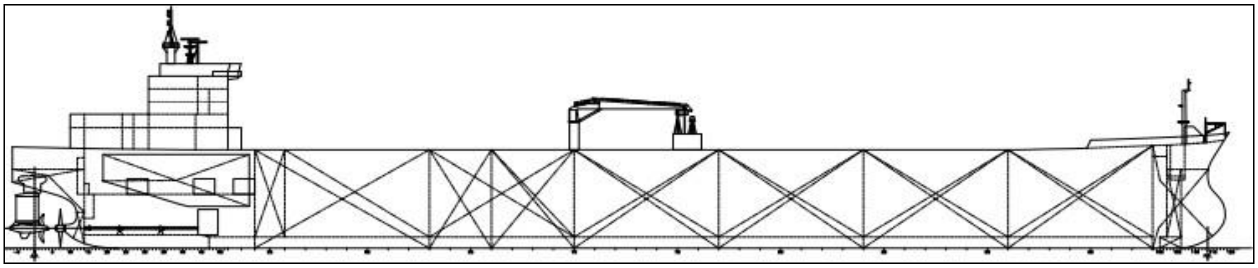
5.7 The future ammonia ships

The NH_3 ICE bulk carrier



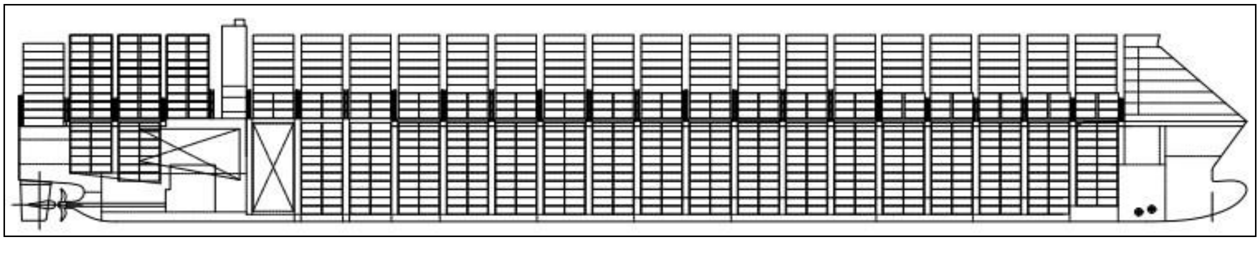
The engine room layout is quite comparable to that of a standard ship. Because ammonia has a lower heating value and density than HFO, it needs a much higher fuel capacity than HFO. In contrast to the tanker, where deck space is available for Type C tanks, fuel is carried below the deck in the engine room and Hold One, reducing the cargo volume by around 5% from 255,000 m^3 to 241,000 m^3 (ABS, 2020a).

The NH_3 SOFC TANKER



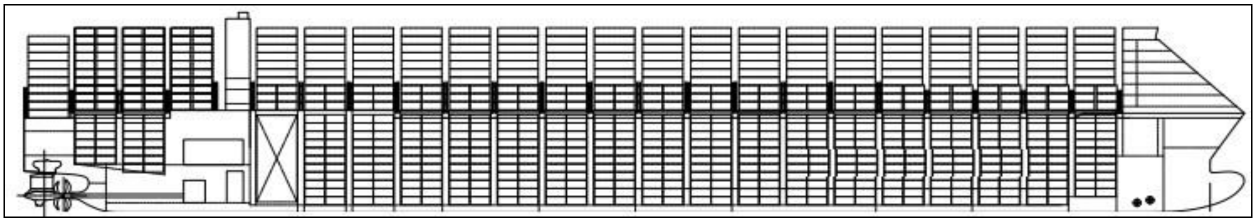
This model contains technology that is much beyond the state of the art right now. The power generation and propulsion system is planned to be entirely electric, with all of the energy coming from SOFCs powered by ammonia. The overall propulsive efficiency was considered to be 60 %. The fuel cells are sized for auxiliaries with a maximum power capacity of 1.0 MW and propulsion with a maximum power capacity of 13.9 MW. Two contra-rotating propellers supply propulsion power: one is a standard shaft propeller powered by an 8.5 MW electric motor and the other is a 5.4 MW steerable pod. A minimum of 169 MWh of installed battery capacity is utilized for power conditioning, hybrid processes and dynamic stability. The ammonia is kept in two prismatic Type B tanks in the engine room or it may be transported in Type C deck tanks (ABS, 2020a).

THE NH_3 ICE CONTAINERSHIP



This ship's general design is nearly identical to the current generation of modern panamax 14,000 TEU carriers. It comes with a single direct-connected ICE and standard auxiliaries. By assessing the importance of optimized hull design and a bigger slower turning, optimized propeller design based on a de-rated main engine, with moderate aerodynamic fairing, an overall 5 % to 6 % gain in hull efficiency is estimated when compared to the baseline ship. Ammonia is stored in a single Type B membrane tank in front of the engine room and two identical tanks on either side. The ship's design of 21.5 knots ate the design draft is one knot slower than the present generation of ultra-large container ships and its total propulsion power is less than 80 % of the base line design (ABS, 2020a).

THE NH_3 SOFC CONTAINERSHIP



The design of this ship is extremely similar to that of the hydrogen fuel cell ship considered and detailed in ABS 2019 Outlook and it contains sophisticated technology, some of which are well beyond present state of the art. The ship will be entirely electric, with all power coming from an ammonia-fueled SOFC. The fuel cells are sized to provide 15 MW of auxiliary power and 43 MW of propulsion power. Two contra-rotating propellers, one a conventional shaft propeller driven by a 26 MW electric motor and the other a 17 MW steerable pod, provide propulsion. A single Type B membrane tank stores fuel. However, alternate fuel tanks might be of the Type B prismatic kind. For the 12,000 nm endurance, 11,500 m^3 of stored ammonia is required (ABS, 2020a).

5.7.1 MAN and Wärtsilä

Ammonia fueled internal combustion engines are being developed by two of the world's largest maritime engine manufacturers MAN and Wärtsilä and are expected to be commercially available by 2024. According to MAN, an ammonia retrofit package will be commercially available by 2025, making it easier to convert a fossil fuelled vessel to a low emission one. The term ''ammonia- ready'' is becoming widely used to describe vessels that are built to run on ammonia in the future. Ammonia fueled marine vessels begin to be deployed in the mid- 2020s under the Sustainable Development Scenario and the Net Zero Emissions by 2050 Scenario. Container shipping would be the first market to see ammonia powered vessels joins the fleet, because the itineraries these ships sail are largely centralized and the increased expense can be distributed among many clients. Tankers transporting energy commodities, which already have the storage capacity and operating knowledge to handle fuels, are also anticipated to be early movers. In addition, MAN Energy Solutions is pursuing flag state clearance to utilize ammonia as a marine fuel under the IGC Code.

Wärtsilä, like MAN Energy Solutions, acknowledges ammonia as a ship fuel and is taking steps to address it. In November 2018, it inked a memorandum of understanding (MOU) with LUT University of Technology and Nebraska Public Power District to use alternative fuels such ammonia, methanol and dimethyl ether (DME) to power generator engines. It acknowledges the technological challenges, such as hydrogen's poor energy density and extremely low storage temperature, but maintains that ammonia, which can be manufactured using hydrogen, is a potential ship fuel. It created a coalition with five firms for Zero Emission Energy Distribution at Sea (ZEEDS) in June 2019 and is leading the effort to build an ecosystem for ammonia as a ship fuel. Table 9 shows an overview of ammonia related projects in the maritime sector.

Name of project/ initiative/ vessel	Project partners	Propulsion	Other details
NoGAPS(Nordic Green Ammonia Powered Ship)	Global Maritime Forum, engine manufacturers (MAN ES, Wärtsilä), classification societies, finance stakeholders	ICE	Ammonia-fuelled deep sea vessel by 2025
MAN ammonia engine	MAN ES	ICE 2-stroke	Engine development by 2024
CASTOR	MAN ES, Yara, MISC, Samsung Heavy Industries, Lloyds Register	ICE	System perspective / infrastructure around port
Wärtsilä ammonia engine	Wärtsilä	ICE 4-stroke	Engine development
ZEEDs	Wärtislä, Grieg Maritime Group	ICE	Ammonia-fuelled tanker by 2024
Colour Fantasy	16-party consortium incl. Color Line, ABB, Wärtsilä, DNV GL	unknown	Passenger vessel / Ro-Ro cruise liner, retrofit
Japanese consortium	MLIT Japan, MAN ES, Imabari, ClassNK and others	ICE	Ammonia-fuelled ship incl. Supply infrastructure
Dutch consortium	C-Job Naval Architects, Proton Ventures, Enviu	ICE / FC	Ammonia tanker fuelled by its own cargo

Campfire	Big consortium incl. Yara, Carnival, Sunfire	ICE / FC	Whole value chain of ammonia supply to a ship
Maersk Mc-Kinney Moller Center for Zero Carbon Shipping	Maersk Mc-Kinney Moller Center for Zero Carbon Shipping, Maersk, Yara and others	-	Supply-chain in port of Singapore
ShipFC	14-party consortium incl. Yara, Wärtsilä, Equinor	SOFC	EU funded retrofit of vessel Viking Energy by 2024

Table 9: Overview of ammonia projects in the maritime sector (Cames et al., 2021).

5.8 Conclusion

In conclusion, advantages and disadvantages of the use of ammonia as a potential fuel are listed below:

ADVANTAGES

- Zero carbon fuel
- No SO_x emissions
- Existing infrastructure
- Low flammability risk
- Handling and storage experience
- High energy density compared to H_2
- Application in ICE and in fuel cells

DISADVANTAGES

- Toxicity
- Corrosive to some materials
- Lack of engine technology
- NO_x emissions
- Missing regulations to be used as fuel

In the long run, ammonia is seen as the ‘’destination fuel’’ for ocean going vessel, accounting for roughly a quarter of total final consumption in national and international maritime shipping in 2050 in the Sustainable Development Scenario and around 45 % in the Net Zero Emissions by 2050 Scenario.

6 Production

6.1 Production of ammonia

The manufacturing of ammonia is already a well- established and mature integrated system. Up to 90 percent of the world's ammonia production is based on steam reforming of natural gas via a very well Haber-Bosch process, as referred in chapter 4. HB process may ne rapid and efficient when supplied by fossil fuels, but it generates 1.4 percent of the world's CO_2 emissions. This is an extremely energy intensive method, needing 8 MWh of energy per ton of ammonia, with the creation of hydrogen being the most harmful environmental stage, accounting for the majority of power consumption and almost 90% of total carbon emissions (Cardoso et al., 2021).

The catalytic reaction of hydrogen (H_2) and nitrogen (N_2) is the underlying idea of underpinning ammonia production via water electrolysis. Water electrolysis is the act of transferring electrons through water to divide water molecules into oxygen (O_2) and hydrogen (H_2) in order to produce sustainable hydrogen (H_2). Nitrogen is extracted directly from the air using an air separation unit (ASU), which contributes to 2 – 3% of the total energy consumed in the process. Cryogenic distillation is the most widely used air separation unit, accounting for more than 90% of nitrogen production. It uses the boiling points temperatures of nitrogen and oxygen to separate air into them. The Haber – Bosch process and the steam reforming both have high technical readiness levels (TRL) and energy efficiencies of 73% – 80% and 70%, respectively (Cames et al., 2021). The HB process produces no direct CO_2 emissions and zero-emission ammonia synthesis is conceivable if the power utilizes is practically carbon free.

The HB process, which can be driven by renewable energy, is used to manufacture green ammonia. By using renewable electricity, the standard HB process may be improved while still playing a significant role in the manufacturing process. Figure 23 shows the carbon- free ammonia production roadmap and its various end and use (Cardoso et al., 2021).

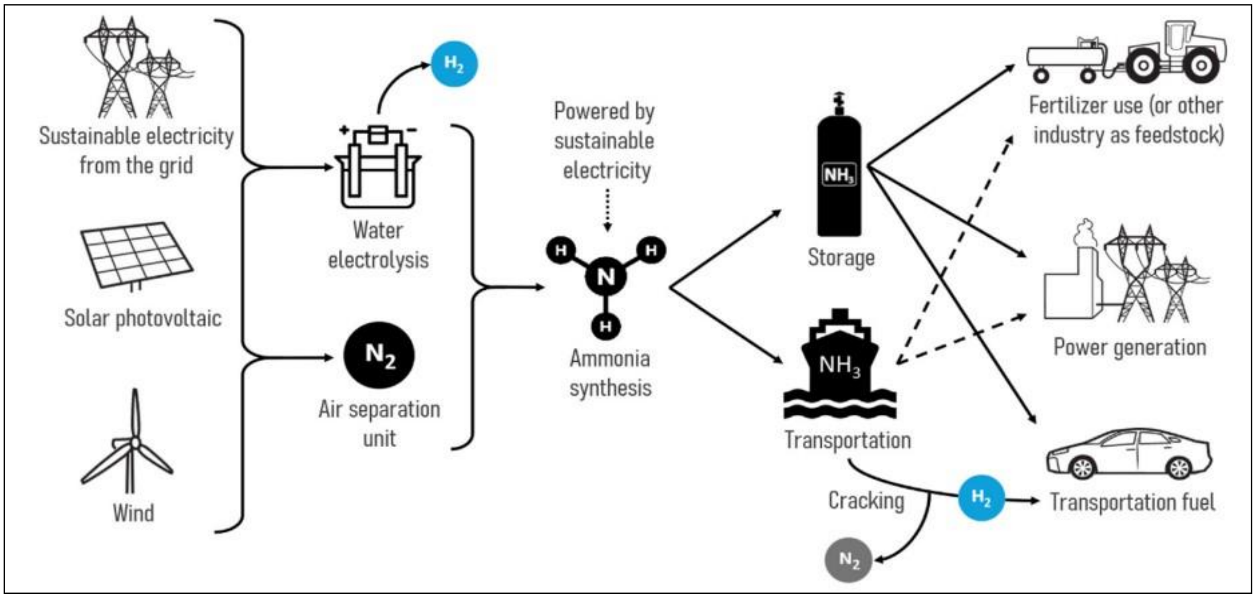


Figure 23 : Carbon- free ammonia production roadmap and its various end and use (Cardoso et al., 2021), (Sánchez et al., 2019) .

Almost all electric power was produced in big central combustion based units that burned vast volumes of cheap fossil fuels. Despite the fact that fossil fuels are still cheap, factors such as tough competition, industrialization and optimization throughout the renewable energy, the value chain have pushed the cost of renewable energy below that of conventional fuels in most power markets. The continuing cost reductions justify considering expanding the use of renewable energy outside the traditional power industry by electrifying nearby energy industries directly and indirectly. With ammonia as the major energy carrier marine fuel is one of the clearest industries to electrify indirectly via electrolysis.

Ammonia production from renewable energies, whether from using it as a marine fuel, energy store or for fertilizing, is no longer a science fiction topic being addressed in scholarly communities. Instead, as evidenced by the numerous large-scale commercial initiatives presently being built throughout the world to decarbonize the electrical grid, green ammonia is a reality. Whereas this huge growth in green ammonia projects is exciting because it comes closer to the Paris Climate Change Agreement's targets and it is clear that this innovation will not be accessible in the short term for the developing world due to the high investment threshold in these major energy developments (Faria, 2021).

The large volume of marine fuel utilized by the world's shipping fleet necessitates a significant but achievable growth of renewable energy producing capability. The present usage of a marine fuel is estimated to be about 250 million tons. Ammonia is predicted to replace 25-50 percent of current fuel usage by 2050. When taking into consideration ammonia's lower energy density, delivering 30% of current maritime fuel usage as renewable ammonia would need the production of 150 million tons of ammonia. With current electrolysis and synthesis technologies, the necessary electrical power would be around 10 MWh/ tNH_3, implying that supplying 30 % of the fuel requirement would require 1500 TWh of renewable energy (Laval et al., 2020).

6.2 Water electrolysis for hydrogen production

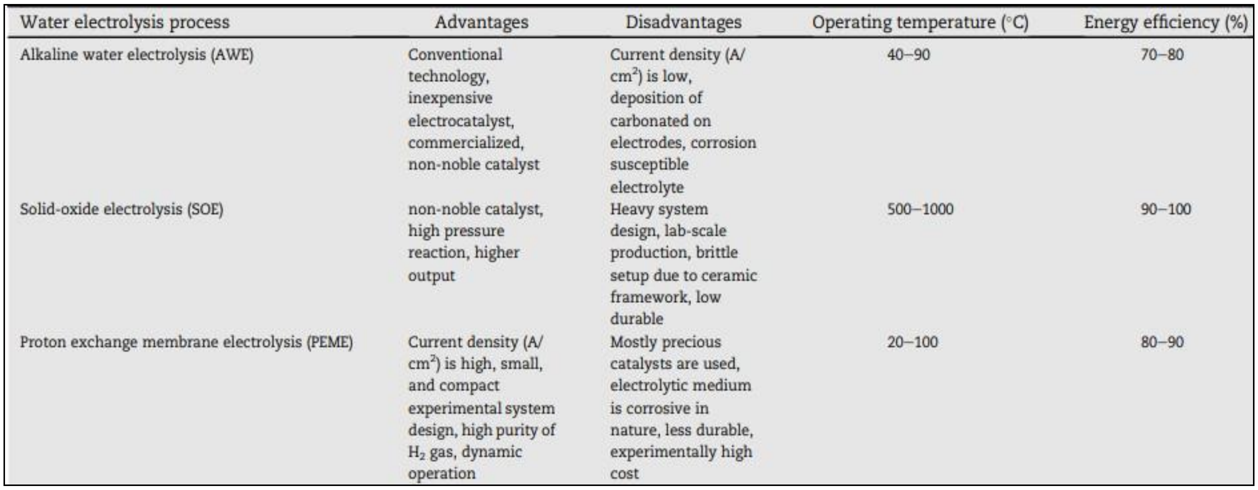
The growing tendency to replace fossil fuels as a source of energy, fuels and chemicals, as well as the ongoing reduction in the cost of renewable power, has reignited interest in converting electricity to hydrogen using water electrolysis. Because it has no carbon impact, electrochemical water splitting is one of the most environmentally benign methods for producing hydrogen and there are three different types of water electrolysis methods.

- Alkaline water electrolysis (AWE)
- Solid- oxide electrolysis (SOEC)
- Proton exchange membrane electrolysis (PEME)

Alkaline water electrolysis was created by Troostwijk and Diemann in 1789 and generated megawatts of high rank hydrogen internationally, is by far the most developed and usual process for producing hydrogen energy from water. The operational temperature range for these units is typically 40 to 90 °C (Table 10), with an efficiency range of 70 to 80%. AWE has several advantages, including the ability to produce pure hydrogen energy with non- precious electrocatalysts and the fact that it is a cutting edge technology. The AWE cells are extremely stacking, allowing the region to use approaches that are very scalable. On the other hand, alkaline water electrolysis has certain drawbacks, such as limited current densities and low working pressure and temperature, which can result in low energy efficiency. Overall consumption of water was approximately 11.5 times that of hydrogen production. The biggest AWE plant currently in service is NEL hydrogen's 25 MW, 5500 Nm^3/ h hydrogen plant in Malaysia. However, additional huge projects are being developed at rapid pace(Anwar et al., 2021), (Laval et al., 2020).

Solid- oxide electrolysis (SOEC) has gained a lot of interest, because it converts electrical energy into chemical ones and produces ultra – pure hydrogen with great efficiency. SOEC works at a high temperature of 500 to 1000 °C. This method has the potential to be industrialized and utilized in continues hydrogen production since it can work at high pressures of up to 3 MPa. Because of the cooling need, water consumption is approximately 83.3 times higher than hydrogen production. Low temperature innovation, like AWE, has a higher degree of technical readiness than high temperature SOEC technology, which is currently under development. Because a portion of the energy required for hydrogen generation may be given as a high temperature heat, when combined with a heat- generating chemical process like ammonia synthesis, the total energy efficiency becomes even more appealing. Moreover, the SOEC requires no precious metals and the future cost potential is compelling and comparable to AWE. The SOEC approach has certain limitation, such as electrode deterioration and the usage of ceramic electrolytes at temperatures exceeding 1000 °C. This demonstrated a lack of strength and stability (Anwar et al., 2021), (Laval et al., 2020).

Proton exchange membrane electrolysis (PEME) is a potential technology for producing pure hydrogen gas from renewable energy sources. The PEME also known as polymer electrolyte membrane electrolysis was initially developed to solve the drawbacks of alkaline water electrolysis and achieves higher current densities enabling for substantially more compact water electrolysis plants. It turns liquid water into hydrogen and oxygen in a low temperature range of 20 to 100 °C typically run at high pressures up to 40 MPa, which reduces the energy requirement by compressing. The PEME's membrane permits the proton, a charger carrier, to flow through while prohibiting other gases from moving. One of the most significant disadvantages and problems is certainly production costs due to the precious metals and lower energy efficiencies. PEME has a high power density and like alkaline water electrolysis, consumes roughly 11.5 times the total quantity of hydrogen generated and it requires the least amount of cooling. PEME is now being rapidly commercialized foe a variety of uses, including local hydrogen generation at refueling stations for fuel cell vehicles (Anwar et al., 2021). Air Liquide, debuted the world's largest PEM electrolyzer in early 2021, with a capacity of 20 MW and the potential to produce 8.2 tonnes of hydrogen per day.



Water electrolysis process	Advantages	Disadvantages	Operating temperature (°C)	Energy efficiency (%)
Alkaline water electrolysis (AWE)	Conventional technology, inexpensive electrocatalyst, commercialized, non-noble catalyst	Current density (A/ cm^2) is low, deposition of carbonated on electrodes, corrosion susceptible electrolyte	40–90	70–80
Solid-oxide electrolysis (SOE)	non-noble catalyst, high pressure reaction, higher output	Heavy system design, lab-scale production, brittle setup due to ceramic framework, low durable	500–1000	90–100
Proton exchange membrane electrolysis (PEME)	Current density (A/ cm^2) is high, small, and compact experimental system design, high purity of H_2 gas, dynamic operation	Mostly precious catalysts are used, electrolytic medium is corrosive in nature, less durable, experimentally high cost	20–100	80–90

Table 10 : Three types of water electrolysis technologies including advantages and disadvantages, energy efficiency and operating temperature (Anwar et al., 2021).

It is crucial to highlight how electrolyzer costs and energy efficiency evolve in the future. With the continuous production expansion, NEL expects to achieve 420 USD/ kW and 320 USD/kW in

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future major operations. These values are used to forecast green ammonia prices in 2025, 2030 and 2040, appropriately. According to more optimistic cost predictions, future green ammonia costs might be as low as 100 – 150 USD/ kW, making the costs of green ammonia plausible, though not cautious. Based on low heating value (LHV) of hydrogen, the energy efficiency of an alkaline electrolysis system at full load is already 63 % and is predicted to rise up to 65 % in the near future. In the long run, more optimistic AWE projections promise efficiencies of up to 70 %. Because of the precious metal component, PEME is predicted to remain considerably more costly. Nonetheless, it will achieve comparable energy savings and will remain the solution with the highest potential for responding to rapid electrical demand changes. When combined with ammonia synthesis, SOECs are predicted to attain comparable cost levels as alkaline water electrolysis while preserving the energy efficiency benefit of 90 % of total energy efficiency, indicating that SOEC could become the long term innovation victor (Laval et al., 2020).

6.3 Market

Ammonia is a crucial chemical product that serves as a component to all synthesized nitrogenous fertilizers. With 185 Mt of output in 2020, it was the highest produced basic chemical, with 75% coming from natural gas, 23% from coal gasification, roughly 2% from oil products and a fraction of a percent point from electrolysis. The worldwide ammonia industry was estimated to be worth USD 55 billion each year in the previous decade, due to market pricing of USD 300 per metric tonne (USD/t). Currently, 120 ports throughout the world have capabilities for importing and exporting ammonia as we can see in Figure 24. For the rapid development of ammonia availability, ship to ship bunkering, where ammonia is delivered by another ship or barge anchored alongside the receiving vessel and enhanced bunker hose handling will be necessary. Loading and unloading from port facilities to ammonia carrying ships is currently done safely with specific training and safety is thought to be enhanced by utilizing a bunkering ship as an intermediary between the terminal and the ammonia fueling ship. A bunkering ship would be the preferable method for deep sea ships with considerable volumes of fuel to be bunkered. When bunkering in heavily populated regions, extra caution is advised. This method is also applicable to LNG and has as a result to reduce facility expenditure while allowing the fuel to be delivered where and when it is needed (DNV, 2020).

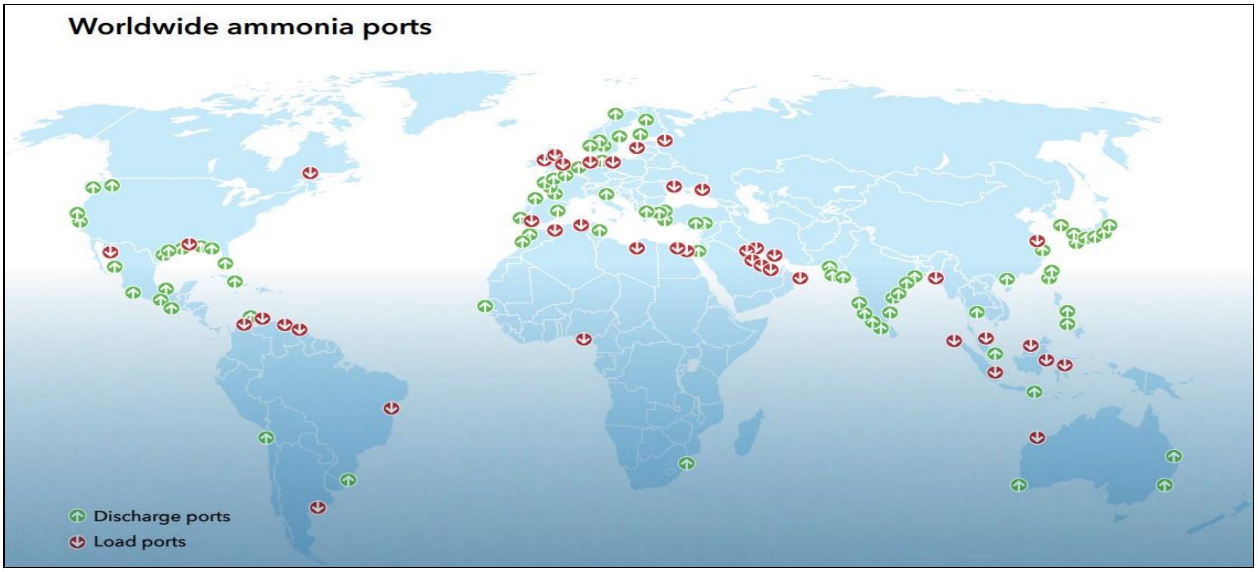


Figure 24: Worldwide ammonia ports. Source: Navigator Gas (DNV, 2020).

According to International Energy Agency (IEA, 2021) global commerce of ammonia was over 20 Mt, accounting for around 10% of total output. Russia, Trinidad and Tobago and the Middle East were the top trading nations and areas, accounting for 24% (Russia), 23% (Trinidad and Tobago) and 15 % (Middle East) of worldwide NH_3 exports, respectively. The European Union (EU), India and the United States (US) are the three largest importing zones, accounting for 24% (EU), 14% (India) and 13% (US) of world imports, correspondingly. Figure 25 shows the percentages of the top ammonia exporting regions and countries and Figure 26 shows the percentages of the top ammonia importing regions and countries in 2019.

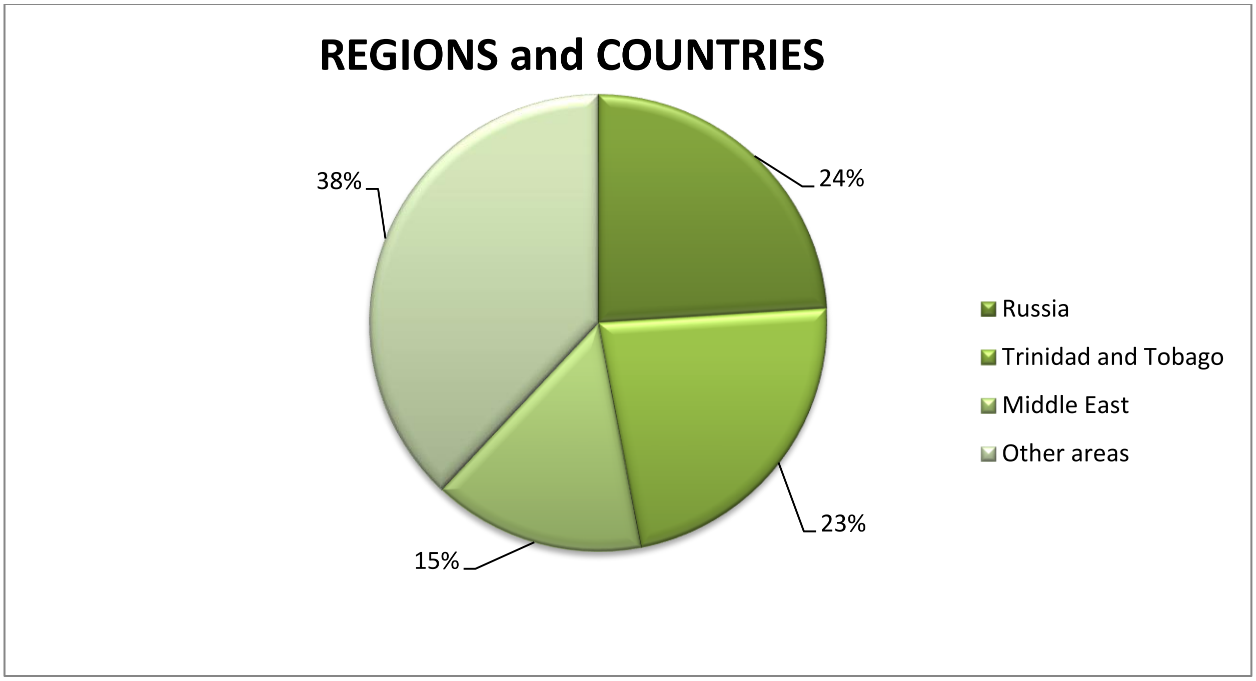


Figure 25 : Top exporting regions and Countries in 2019 (IEA, 2021).

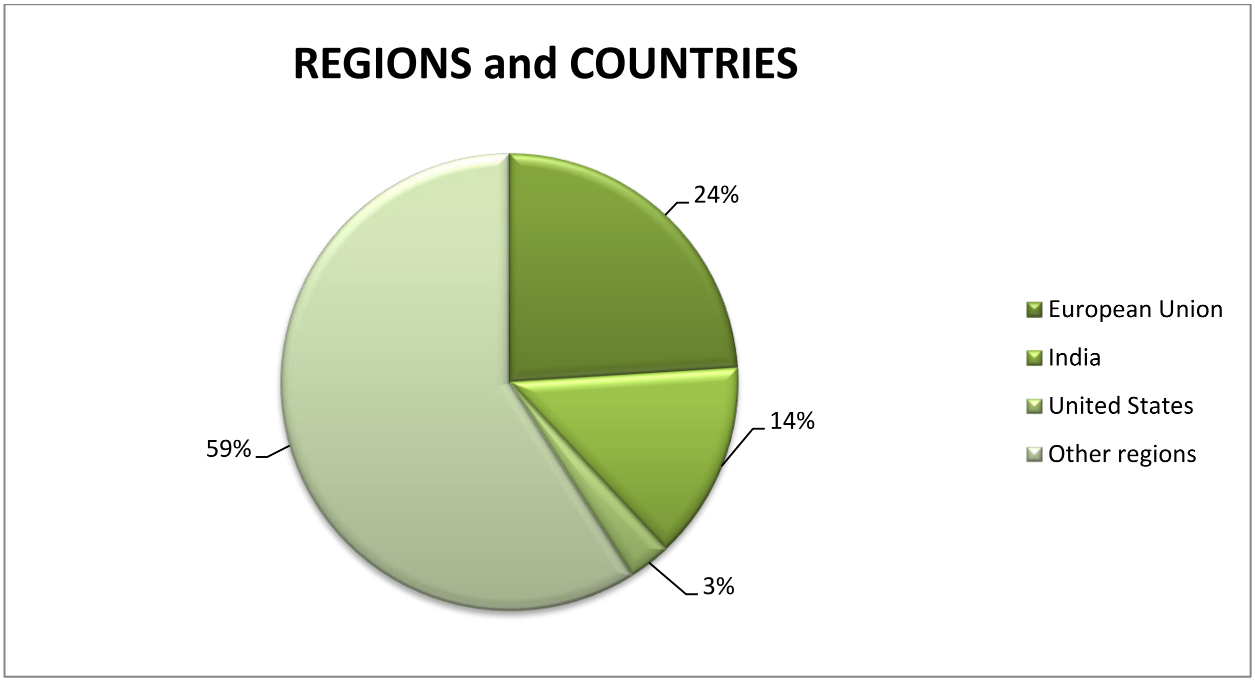


Figure 26 : Top importing regions and countries in 2019 (IEA, 2021).

Ammonia might become the preferred fuel for marine shipping and a major manufacturer estimates that it will be able to supply ship engines that run on 95 % ammonia in only few years, along with the conversion on around one-third of existing ships. As a result, the production of green ammonia is imperative. Furthermore, due to the dramatic fall in the cost of green hydrogen, the market did not consider green ammonia as a financially attractive option until recently. The cost of renewable electricity, which comes from wind and PV solar, has decreased, allowing for the global scalability of renewable power units and together with advancements in the cost and energy efficiency of electrolyzers have paved the way for green hydrogen. The use of renewable power to generate hydrogen from water electrolysis might lower the carbon footprint of ammonia synthesis from 1.6 to 0.1 tCO_2/ tNH_3, with the potential to reduce it to practically zero emissions in the term. Also, converting hydrogen to ammonia has become a critical step in lowering the ultimate cost of highly volatile renewable energy (Faria, 2021).

Green ammonia must become more financially viable against conventional ammonia in order to become profitable, as 90% of production still relies on fossil fuels. While the cost of creating green ammonia in the United States is nearly twice as expensive as natural gas based ammonia under ideal conditions, the cost of solar, wind and hydro power in places with ample resources may be as low as USD 0.03 per kilowatt hour. Some examples of these places as IEA stated are Australia, Northern Chile, North and South Africa, Southern Peru, and Patagonia, as well as numerous Chinese provinces.

Low power prices may make it possible to produce sustainable fuels like ammonia that are competitive with coal gasification and natural gas reforming. More cautious analyses, on the other hand, express worries that worldwide renewable energy surpluses may not be adequate to meet future fuel demand. The development of these energy sources would need a large increase in investment. So, if vast quantities of fuels, such as hydrogen and NH_3 are consumed by 2035, it will be necessary to guarantee that manufacturing plants are based on sustainable power generation. Consequently, there is no certainty of a reduction in CO_2 emissions when opposed to regular HFO (IEA, 2019b).

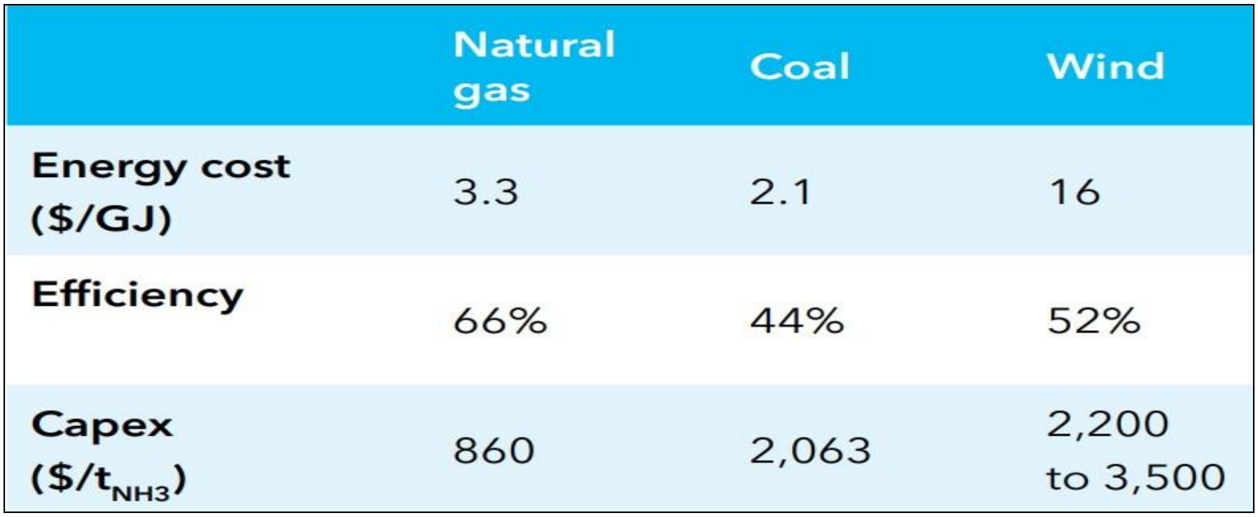
6.4 Prices for ammonia

Capital Expenditures (CAPEX) are funds used by a company to acquire, upgrade and maintain physical assets such as property, plants, buildings, technology and equipment.

Operating Expenses (OPEX) is shorter- terms expenses required to meet the ongoing operational costs of running a business.

According to DNV, ammonia costs fluctuate a lot over time and are not the same everywhere. In the recent decade, prices as low as 200 \$/t and as high as 700 \$/t have indeed been recorded. Due to market considerations for natural gas and ammonia supply, the value has been below 400 \$/t since 2016 and is regularly 200 – 300 \$/t. From 2008 through 2017, the average price per tonne was around $400. Depending on the natural gas pricing, natural gas provides 70 % to 85 % of the ammonia manufacturing cost in the United States. Several areas display similar outcomes as well. As a result, the cost of natural gas will be mostly determines by the local price, that has already been estimated to range from $100 per tonne in the Middle East to more than $400 per tonne in Western Europe as of 2013 (DNV, 2020).

Table 11 shows the typical efficiencies and capital expenditures along with typical US energy prices. Ammonia produced from coal will be more expensive than ammonia produced from natural gas due to lower efficiency and more Capital expenditures (CAPEX). Renewable ammonia, such as that produced by wind turbines, would be more costly than natural gas feedstock. This will be mostly determined by the cost of power, as well as developments in technology. The cost is projected to range between $ 2,200 and $ 3,500 per tonne of yearly production capacity, depending on the equipment scaling for the electrolyzer stacks. Based on a price of 1,000 $/ kW, the electrolyzers are estimated to contribute roughly 77 % of the CAPEX before scaling (DNV, 2020).



	Natural gas	Coal	Wind
Energy cost ($/GJ)	3.3	2.1	16
Efficiency	66%	44%	52%
Capex ($/$t_{NH3}$)	860	2,063	2,200 to 3,500

Table 11: Energy costs, efficiency and capital expenditure per tonne annual production capacity for various feedstocks for the production of ammonia (DNV, 2020).

The electrolyzer price is approximately half as much as it was before scaling and electrolyzers account for 65 % of the CAPEX as Figure 27 shows. At this lower price point, greater electrolyzers have also been noted to be available. Renewable energy is on the verge of being competitive with coal based ammonia.

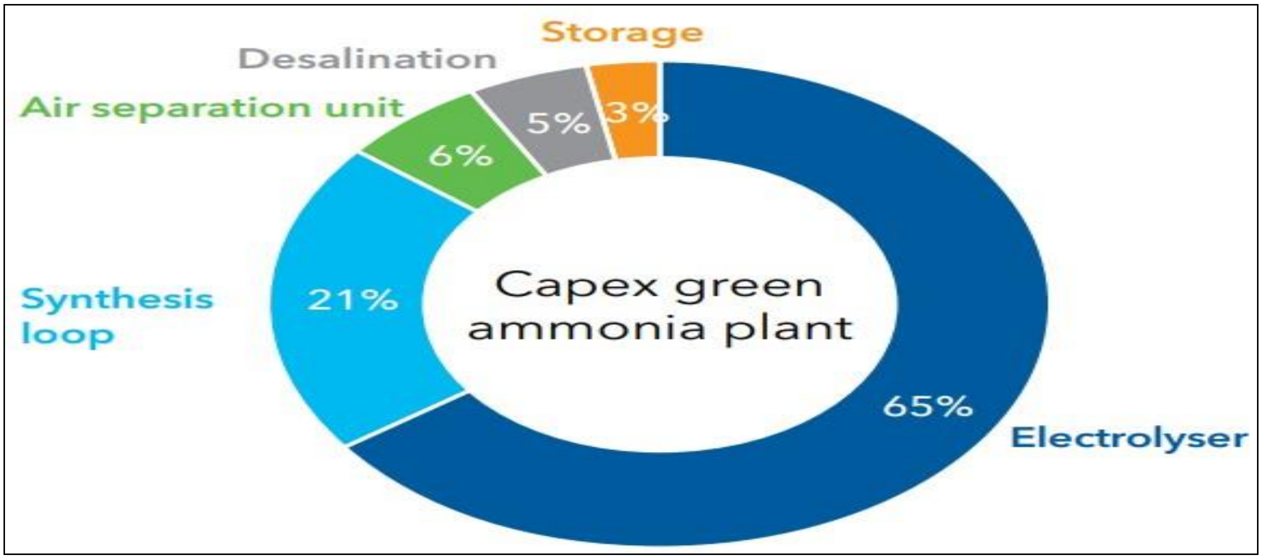


Figure 27: CAPEX breakdown of a 300 t/day green ammonia plant with electrolyzer scaling (DNV, 2020).

The cost of producing renewable ammonia will be primarily determined by two important factors:

I. Electricity prices
II. CAPEX

For a factory that produces ammonia from electricity, (DNV, 2020) estimated a potential ammonia production price as Figure 28 shows. This is evaluated as a function of electricity prices for multiple CAPEX values and is based on a project's internal rate of return of 10 % over 20 years, with 52 % efficiency, a 5 % discount rate and yearly operating costs of 2.5% of the CAPEX. The cost of on-shore wind generation is mostly influenced by the CAPEX and capacity factor in favorable areas and it has been estimated at 0.04 to 0.05 $/kWh. According to the International Renewable Agency (IRENA), the global weighted average cost of on- shore wind power was 0.045 $/ kWh in 2020, while the PV solar cost was 0.048 $/kWh. The current renewable ammonia pricing, based on these numbers, would be between 650 and 850 $/t, however power costs for renewable energy from wind and solar will be significantly site specific. Furthermore, it fairly predicted that the cost of renewable energy will fall over time and that the cost of electrolysis will fall as well (DNV, 2020).

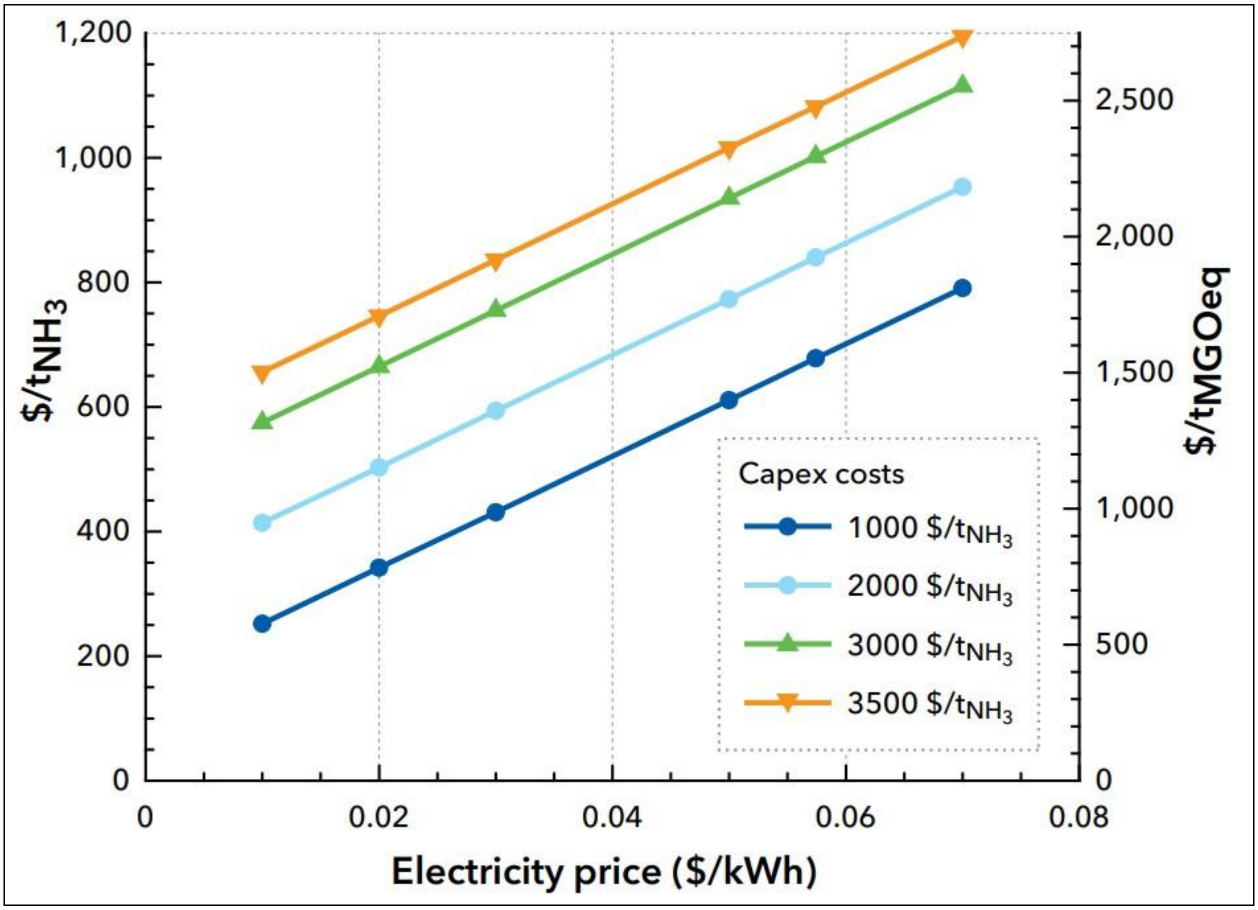
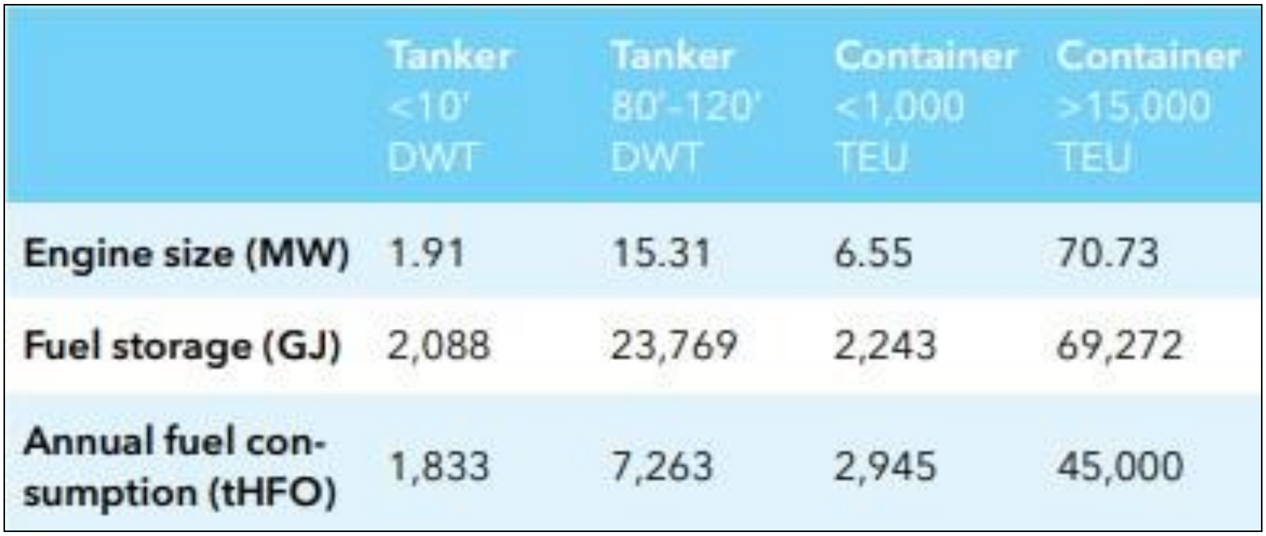


Figure 28: Estimated production cost of renewable ammonia as a function of the electricity cost at various capital expenditures (per tonne annual production capacity) (DNV, 2020).

6.5 Suitability from a financial point of view

The capital cost for an ammonia two stroke internal combustion engine and fuel supply system is estimated to be comparable to the cost of an LPG engine. Earlier studies from DNV GL and MAN Diesel & Turbo looked at a number of scenarios for different variants of an LR1 tanker to examined which fuel type would be the most cost effective to plan for. One of several findings was that LPG was financially viable, despite of its higher investment cost; LPG's lower fuel prices were more than offset when compared to extremely low sulfur fuel oil (VLSFO) (DNV, 2020).

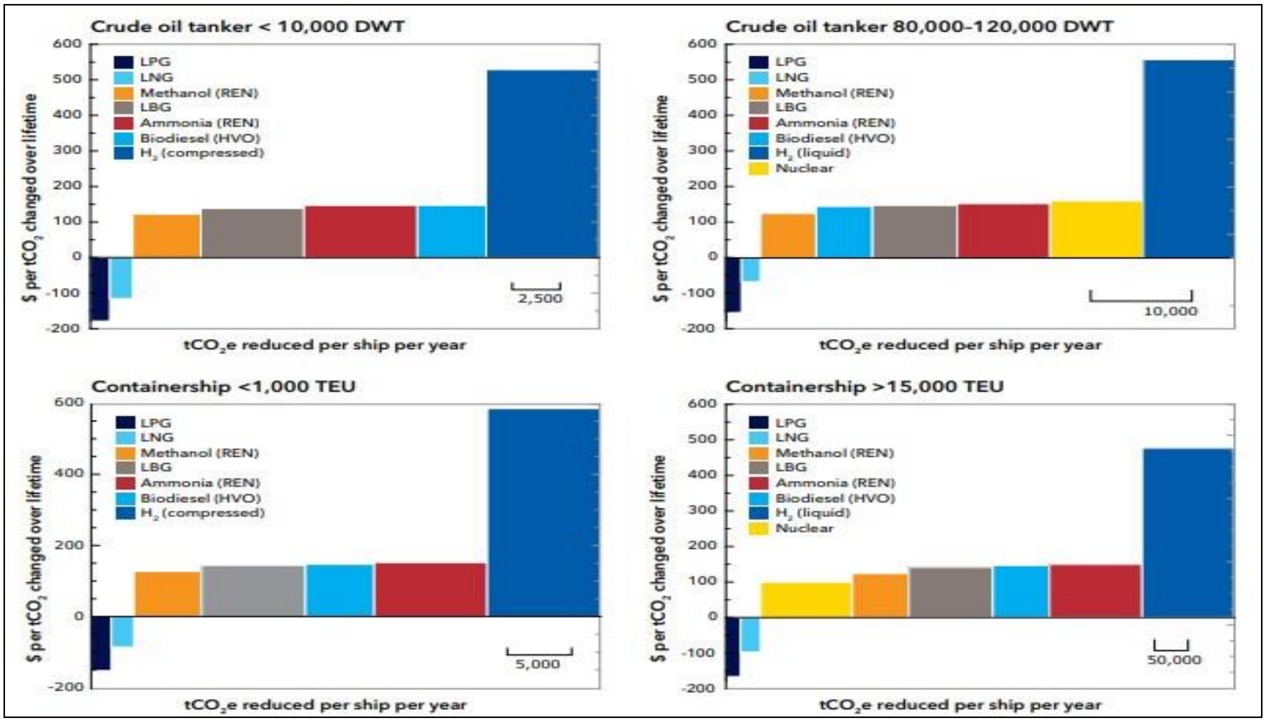
In order alternative fuels to be compared, the metric GHG abatement cost $/tCO$_2$ over lifetime of 25 years was used. The cost of lowering one tonne of CO$_2$ emissions (on a well to wake basis) is the GHG abatement cost, which is computed over the life of the mitigation project. Based on technical information from the HIS Fairplay database and the speed and trade pattern form AIS data, this was done for numerous portions. Depending on fuel use and the amount of port calls, the fuel storage required has been estimated, and from the technical data, the average engine size was estimated, too, Table 12 (DNV, 2020).



	Tanker <10' DWT	Tanker 80'-120' DWT	Container <1,000 TEU	Container >15,000 TEU
Engine size (MW)	1.91	15.31	6.55	70.73
Fuel storage (GJ)	2,088	23,769	2,243	69,272
Annual fuel consumption (tHFO)	1,833	7,263	2,945	45,000

Table 12: Engine size, annual fuel consumption and storage capacity assumed in the calculations of the GHG Abatement Cost Curve in Figure 27 (DNV, 2020).

According to LR1 analysis, capital expenditure per installed capacity for newbuild was employed. The discount rate set at 5% and 15% of the fuel usage was classified as being in an SECA. The fuel prices are based on end of year 2019 and the calculations assume no cargo capacity decrease (DNV, 2020).



Crude oil tanker < 10,000 DWT

Crude oil tanker 80,000-120,000 DWT

Containership <1,000 TEU

Containership >15,000 TEU

Figure 29: GHG abatement cost curves for alternative fuel for an average ship in terms of technical data and operations (DNV, 2020).

Considering on the fuel prices utilized in Figure 29, the GHG abatement costs for LPG and LNG are negative, making them more financially advantageous for newbuilds over the lifetime of the vessel than using oil-based fuel. Compressed and liquefied hydrogen offers a greater potential for reducing emissions, but it is more expensive due to the high cost of storage and fuel cells. It is also worth noting, as referred in chapter 3, that hydrogen and particularly the compressed one, takes up a lot of space, which could mean a smaller payload or a shorter range and more frequent bunkering. There are four fuels with a marginal abatement cost of around 150 $/tCO_2$ in the middle area, in addition to nuclear propulsion for large ships. Renewable biodiesel (HVO) and renewable methanol are thought to have a lower potential for lowering emissions. Liquefied biogas has a significant reduction potential, but it is only available in restricted quantities. Ammonia has a similar abatement cost, a substantial emission reduction potential and the ability to be scaled up.

Fuel prices will fluctuate and abatement costs will be linked to them. For example, given the low oil prices as of March 2020, new green technologies will struggle to compete unless governmental or market based initiatives are implemented that drastically alter this situation (DNV, 2020).

6.6 Scalability

Because green ammonia synthesis requires only renewable energy, water and air, it can theoretically be scaled up to supply the whole marine sector with fuel. However, the expenses of supplying ammonia from renewable energy to all ships would be enormous, as new capacity for green ammonia or ammonia from natural gas with CCS would need to be created. The current fuel use of 300 million tonnes of oil equates to 650 million tonnes of ammonia, requiring approximately 6,500 TWh of renewable electricity. This amount of electricity is equal to China's total electricity generation. New production capacity of this size is required in order for ammonia to be deemed emission free (DNV, 2020).

A typical expenditure for an on shore wind farm would be 0.5 million USD per GWh annual production capacity based on global weighted average of 1497 USD/ kW and capacity factor of 34 %, implying a CAPEX of 3.2 trillion USD for the electricity required (DNV, 2020). Considering an annual production capacity of at least 2,000 USD per tonne through electrolysis of water, 650 million tonnes of NH_3 would result in 1.3 trillion USD in ammonia plant investments. Before considering the effect economies of scale that would lower investment costs, total investments for fuel would need to be 4.5 trillion USD. Nevertheless, this estimate excludes capital investments for fuel delivery and bunkering, as well as investments in ships themselves. At today's rates, costs for renewable power capacity are much larger than costs in ammonia plants, and prices for electrolyzers are anticipated to fall considerably if many units are built.

A research (Ash and Scarbrough, 2019) has been released that proposes installing ammonia facilities as well as local solar and wind power plants to run all container and dry bulk ships that sail through Moroccan ports. The annual electricity demand was expected to be over 100 TWh, with investment expenses of around 100 billion dollars, resulting in an ammonia price of 830 USD per tonne. Although the investment expenditures are high, the electricity required to produce the 10 million tonnes of ammonia is said to be less than 1 % of the country's theoretical wind and solar potential (DNV, 2020).

The extra renewable electricity required to create ammonia would compete with other decarbonization efforts, particularly in the power sector. If renewable energy can be used to replace coal power plants, for example, it will reduce emissions more than utilizing renewable electric energy to produce ammonia to replace oil-based marine fuel which has lower emissions per energy unit than coal. In some nations, however, ammonia production may be utilized to stabilize the grid and allow for a higher percentage of intermittent renewable energy than would otherwise be possible. Furthermore, the method enables the transfer of renewable resources from areas where electricity demand is insufficient (DNV, 2020).

7 Results

Diesel engines running on marine fuel oils power the majority of the world's fleet and the current engines are not able to burn ammonia as a fuel. The first ammonia dual-fueled ships would join the fleet in the near future. While the internal combustion engines are preferable for shipowners as an energy converter, marine fuel cells are projected to be scaled up into power systems in the next years, giving improved efficiency and thus lower fuel usage.

One impediment is the restrictions that must be followed by ships that use ammonia as a fuel. Without guidelines in place, shipping companies run the danger of establishing a system that is subsequently found to be incompatible with the regulations and this has a result companies to be hesitant to convert to ammonia. Because the demand for ammonia is in a minimum level and the regulatory agencies are not considered it an urgent concern, the implementations of the rules will be delayed. This reciprocity has the potential to slow down the entire process. Also, another concern about ammonia is the safe handling of it because of its low flammability and toxicity. However, it is estimated that the extent knowledge from other gas fuels like LNG, LPG and since ammonia has already used in shipping sector, it would easily be complied with the rules.

The availability of ammonia in ports will also influence whether or not shipowners switch to ammonia. Because ammonia used as a fertilizer and is shipped globally, the framework for delivering ammonia through ports is already in place. Ammonia storage facilities are provided at ports along the most typical routes and many of these ports are found in ammonia plants along the sea or river's canals. Loading and unloading from port facilities to ammonia carrying ships is currently done safely with specific training and safety is thought to be enhanced by utilizing a bunkering ship as an intermediary between the terminal and the ammonia fueling ship. A bunkering ship would be the preferable method for deep sea ships with considerable volumes of fuel to be bunkered.

Ammonia production contributes for about 1.9% of total global carbon dioxide emissions, when 185 million tonnes produced each year. To fulfill net zero goals it is important the decarbonization of ammonia production by using renewable energy and not fossil fuels ones. The most effective and commercially process to produce ammonia in large scale is water electrolysis via the Haber- Bosch system and larger plants must be built in order ammonia's demands to be covered. The electrolysis of water to produce "green ammonia" provides a path to zero-carbon ammonia synthesis, but it requires low-cost sustainable electricity and ongoing electrolyzer cost reductions.

A clear picture about ammonia and other alternative fuels and each barrier are depicted in chapter 3. In order to determine whether ammonia will be used in the shipping sector a great comparison between the aspects of alternatives fuels must be conducted and shipowners must come to a conclusion and decide which option is better for them.

8 Discussion

Due to the climate change and the global warming, authorities are enacting increasingly harsh rules on the amount of GHG emissions. Through shipping industry, the world is getting increasingly globalized and industrialized nowadays. Shipping sector has been considered as a large generator of emissions because of its overdependence on fossil fuels, which means that by strengthening emission targets, engine manufacturers are obliged to conduct research to find modern, sustainable and greener ways to produce engines that are compliant with changing laws. The use of an alternative fuel which is zero carbon such as ammonia can play a significant role in the transition from coal to ′′cleaner′′ energy production.

Ammonia has been utilized as a compound for over a century, but for purposes other than fuel. Today, the ammonia produced from fossil fuels via the Haber- Bosch process around the world is used mainly as a fertilizer, refrigerator or for industry purposes. Among the most compelling arguments for using ammonia as an alternative marine fuel is that it is a zero carbon molecule with the possibility for zero GHG emissions at the exhaust. However, the used ammonia must be manufactured from renewable sources in order to obtain minimal GHG emissions across the life cycle.

Because NOx emissions are regulated by the IMO, NO_x emissions from ammonia combustion are a significant issue. To reduce NO_x emissions and ammonia slip, an exhaust gas recirculation (EGR) or selective catalytic reduction (SCR) system can be utilized as an after treatment system.

One issue with ammonia as a fuel in engines is safety. When inhaled, ammonia is extremely hazardous to humans and aquatic life. Because of ammonia's toxicity, this thesis made it clear about its utilization as a fuel in internal combustion engines; that has the same level of hazards as other fuels. Toxicity must be addressed while developing the fuel handling system for both bulk storage and operation. The lack of rules governing the potential use of ammonia as a marine fuel is a hurdle to its adoption and there is a scarcity of research and real world projects. However, despite toxicity, ammonia has been used effectively in other industry sectors.

Presently, the price of ammonia based on its energy content is significantly greater than that of LNG. Nonetheless, when comparing future cost predictions for alternative maritime fuels, ammonia is predicted to cost nearly as much as hydrogen.

In the future, ammonia could be one of the marine alternative fuels. It has an advantage due to its carbon free and sulphur free structure. The major marine engine manufacturers recognize ammonia's potential qualities and have focused their research on it. Engine manufacturers have influenced decisions about which fuels will be utilized globally in the future and it appears that ammonia will be one of them.

9 Conclusion

Ammonia is a carbon free fuel that has the ability to assist deep sea vessels on reducing their carbon footprint when renewably sourced. To verify the practicality of ammonia as a marine fuel, a number of additional hurdles must be overcome. First and foremost, the greatest potential disadvantage is the issue of the safety such as corrosion, toxicity and low flammability. Conversely, because ammonia has been used as a refrigerant and liquefied cargo and an SCR lowering agent in ships, the methods taken to address these issues could pave the way for ammonia to become a safe fuel. Despite the fact that ammonia is poisonous and has a lower energy density than conventional fuels, it also requires less energy for renewable synthetic production than them. It is a better option than hydrogen for future use in cargo carrying vessels with modifications in internal combustion engines and low pressure fuel tank and as for the price of ammonia, estimations shows that is almost in the same range as hydrogen.

Moreover, LNG has the benefit of getting been utilized in the shipping industry and of being combined with a proven propulsion technology that can significantly reduce emissions when compared to conventional fuels. But its biggest issue is how possible is to meet the future climate targets. While the LBG, a renewable alternative to LNG, has the potential to satisfy climate targets during the fuel life cycle, the limited production and high fuel price could not cover shipping industry's needs.

To ensure that the sustainable potential of ammonia can be realized, present ammonia production capacity must be significantly increased, and production with renewables or CCS technology is required. Previous research has found that some manufacturing systems are well established, while others are still in the early stages of development. It is fairly affordable, safe mode of transportation, easily liquefied and has a large manufacturing and delivery infrastructure. Ammonia can be manufactured using both conventional and revolutionary processes from hydrocarbon fuels and green energy sources. The Haber – Bosch method remains the most prominent pathway for ammonia production, despite the fact that it is energy demanding and has the biggest carbon footprint.

In addition, green ammonia has the chance to be a critical component of the IMO's decarbonization strategy, allowing it to fulfill and perhaps exceed its goal. The marine industry demand might help to unlock the investment in the supply network for zero carbon fuels like ammonia and this could also assist to unlock more investment in low carbon sector and renewable energy. This is a once in a lifetime chance for a long term green economic growth and dissemination of bunkering infrastructure.

Today, there are over 200 gas tankers capable of carrying ammonia as cargo, with approximately 40 of them stationed with ammonia freight at any given time. Because they already carry the fuel as cargo and seem to having been expertise in handling ammonia, such as tankers will be natural contenders for the first ammonia fueled engines. About engines, from previous studies, using ammonia in fuel cells seems to perform better than ammonia in internal combustion engines because of the increased efficiency of the fuel cells and their improved results in terms of potential environmental and health effects. On the other hand, fuel suppliers and shipowners prefer to burn ammonia in ICEs over similar FC choices.

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Acknowledgements

This master thesis was performed at MSc program ‘’Sustainability and Quality in marine industry’’ of the University of Piraeus. I would like to thank my supervisor Ernestos Tzannatos for his guidance and support throughout this thesis, his positive attitude and competence has inspired me. I would also thank Professor and Director of the MSc program Fani Sakellariadou for her advices and the other Professors for their effort to passing on their extent knowledge.

Finally, I could not have achieved to complete this thesis without the support and the grateful power that my family, my friends and Ioanna have given me.

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