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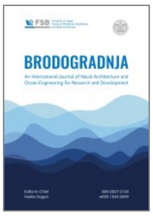

The decarbonisation of the maritime sector: Horizon 2050

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ABSTRACT

The decarbonisation of the maritime sector is one of the world's priorities to reduce the volume of polluting emissions. The basis of this decarbonisation is the adaptation of existing ships to emission control regulations by means of transformations, installation of new equipment, development of new low-emission fuels and development of the infrastructure that makes the supply of this new generation of fuels feasible. In addition, hydrogen is the energy vector for all these new technologies, and its role over the next 30 years needs to be addressed. In a changing global situation such as the one we are currently experiencing; this article has the objective of making a review paper on the different fuels currently being used in the maritime sector and the existing alternatives. It also discusses the situation and the impact the current environmental situation has on the world ship order book, both in terms of legislation and economics. As a conclusion, the Liquefied Natural Gas (LNG) will have a very important role to play as a bridge between the current situation and the development of hydrogen technology. Hydrogen is an energy vector that can achieve the decarbonisation objectives by 2050. Storage problems, lack of infrastructures to supply it and the development of technology and regulations are the major challenges it will have to face. Biofuels also present a serious proposal for the decarbonisation of the sector, and the role of hydrogen in their composition, is essential to achieve green fuel generation.

1. Introduction

In the maritime sector, hydrogen is gaining traction as a prospective solution to pressing environmental and energy-related issues. The pursuit of cleaner shipping alternatives has prompted a surge in interest around hydrogen as a potential fuel source.

Studies and pilot initiatives are actively examining hydrogen's feasibility for ship propulsion. Its high energy density and potential for zero-emission operation make it an attractive candidate for reducing both air pollutants and carbon emissions in the shipping industry.

However, notable challenges remain. Efficient storage of hydrogen onboard vessels, large-scale sustainable production, and the establishment of robust distribution networks are complex issues that necessitate careful consideration. Moreover, the upfront costs of adopting hydrogen-based systems and the requirement for tailored regulations present additional aspects to address.

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Advanced renewable energy technologies, such as solar, wind, tidal and wave, as well as alternative fuels, are available and their application in ports and ships to reduce CO2 emissions is assessed by different researchers, as well as the importance of electrification, hybridisation, and alternative fuels to achieve port decarbonisation. Energy efficiency is highlighted as a key measure to reduce greenhouse gas (GHG) emissions while generating economic benefits [1].

The life cycle of a ship includes design, construction, operation, and scrapping, with the operational phase being the main contributor to GHG emissions, about the 96%. Although regulations exist for the design, operation and scrapping phases, the lack of comprehensive regulations for ship construction highlights a gap in the overall reduction of emissions. The transition to zero-carbon fuels in shipping, such as electricity, sail, and solar energy, highlights the need to consider shipyard operations in the life cycle of a ship. Research shows that the operational cycle of fossil fuel-powered ships makes up most of their lifecycle emissions, but as more sustainable energy sources are adopted, the fraction of shipyard operations will become more significant [2].

Diesel engines, the main drivers of ships, are also significant sources of air pollution, generating global concern. Many studies focus to enrich technological knowledge to select energy equipment that meets emissions standards throughout the lifetime of ships. Factors that affect the formation of NOx or SOx in exhaust gases are identified, pointing out that the reduction of these emissions must consider the composition of the mixture and the combustion temperature [3,4].

The aim of this article is to provide a comprehensive review of the various fuels presently employed within the maritime industry, along with exploring available alternatives. About this, the analysis of this situation is dealt with in four sections. The first one reviews all the existing fuels in the marine sector, and the open research avenues, in terms of their evolution.

The second section covers the regulations passed in recent years and their impact on the sector. It also addresses the limitations on emissions in force and the implementation of legislation on environmental protection and the control of pollutant emissions.

The third section is comprised of three transcendental points for the maritime sector towards the year 2050. First, it analyses the situation of the ship order book and where the shipbuilding market is heading. Second, the position of the new fuel markets, such as biofuels, electrofuels, blue fuels or nuclear fusion and fission energy. Finally, it tackles the necessity of transforming existing ships and adapt them to the current regulations and are the existing mechanisms to do so. Finally, as a conclusion, an overall assessment is presented.

2. State of the art of marine fuels

The combustion of a fuel such as fuel oil generates pollutant gases such as sulphur oxides (SO_x), nitrogen oxides (NO_x) and carbon oxides (CO_x), as well as particulate matter [5].

In addition to these regulatory measures, there is a growing interest in the use of alternative fuels, the improvement of energy efficiency in shipping, as well as the development of technologies that reduce fuel consumption [6].

The International Maritime Organisation (IMO) has set ambitious targets for reducing nitrogen oxide and particulate matter emissions and has also set limits for carbon dioxide emissions from 2023 which have been set out in Annex VI of the MARPOL Convention. Furthermore, emission reductions of 40% compared to 2008 and 70% by 2050 have been set [7].

Globally, shipping emitted around 2.9% of global greenhouse gas emissions in 2018 [8], the 15% of global NO_x and 6% SO_x emissions [9].

In 1997, the International Maritime Organisation (IMO) adopted the agreement approving ANNEX VI of the MARPOL (Marine Pollution) Convention: Regulations for the Prevention of Air Pollution from Ships, which came into force on 19 May 2005, regulating NO_x and SO_x emission limits, as well as prohibiting emissions of ozone-depleting substances and the delimitation of particularly sensitive areas for this type of emissions. In the case of sulphides, it set its maximum in marine fuel at 4.5% [10].

In 2008, the IMO announced the chronology by which the reduction of sulphur emissions will be required through the reduction of the concentration of sulphur in marine fuels, and in 2010 the limit of 1% of sulphur content in the fuels of ships sailing in Emission Control Areas (ECAs) came into force.

Furthermore, in July 2011, the IMO approved the obligation to adopt measures to improve energy efficiency on board ships [11], and in 2012 the maximum sulphur content of marine fuels outside ECA areas was set at 3.5%.

In 2015, the rule that within ECA areas is reduced from 1% in 2010 to 0.1% sulphur content in marine fuels came into force.

Following the gradual application of the different environmental regulations over the years, as well as the different grades of MARPOL ANNEX VI, on 1 January 2020 the latest and most restrictive limitation on the sulphur content of marine fuels came into force, contained in regulation 14.1, limiting the sulphur content of the fuel to 0. 5% of its percentage by mass outside ECA areas [10], which has led to a multitude of alternatives being investigated over the last few decades, such as improvements in fuels, in the design of the hydrodynamics of the ship's hull, and in propulsion systems, among others, with the intention of minimising consumption and emissions of pollutant gases into the atmosphere [12].

Likewise, in accordance with the IMO's emissions reduction strategy, three scenarios have been taken into account in the short, medium and long term for the application of energy efficiency measures in ships through the Energy Efficiency Design Index (EEDI), which has been mandatory for all newly built ships since 2013 and the Ship Energy Efficiency Management Plan (SEEMP), which has been mandatory for all ships in MEPC 62 since July 2021 [13].

At the beginning of 2023, the mandatory measurement of the Energy Efficiency Index applied to existing ships (EEXI) and Carbon Intensity Indicators (CII) has also entered into force [13]. This aims to achieve a reduction of carbon dioxide emissions, based on the EEDI ship classification of 40% in 2030 according to Figure 1.

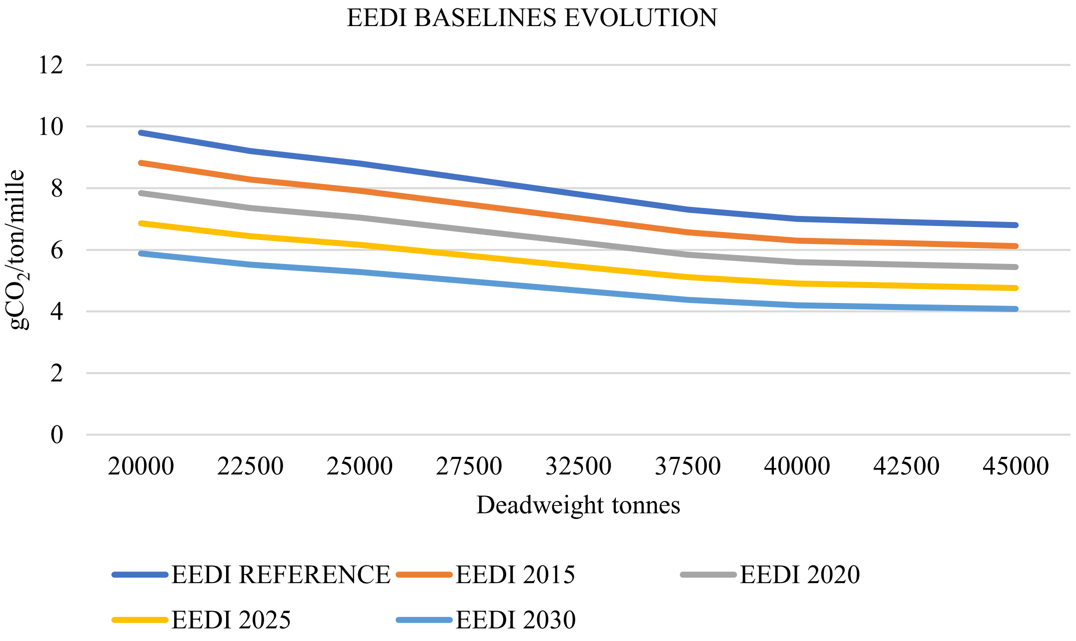


Fig. 1 Evolution of EEDI emission baselines

In this context of the need to reduce polluting gas emissions and particulate matter, in the case of the maritime sector, conventional renewable energies have been displaced due to two aspects: the low impact they have on the high energy demands on board a ship, and their complexity of installation on board does not make them viable for maritime transport. Only 3-15% of the required auxiliary power could be obtained from wind energy, 1-3% from wave energy and about 1% from solar energy, to cite a few examples [14].

In addition, the instability of the meteorological phenomena used to produce clean energy such as wind or solar power is highly fluctuating over time and has long periods of intermittency [15].

As an alternative to renewable energies to reduce polluting emissions, it has been shown that synthetic fuels, ammonia, methanol, the development of processes for obtaining hydrogen and the use of Liquefied Natural Gas (LNG), would allow an energy transition within the sector towards a zero emissions scenario with the aim of displacing the use of marine diesel in favour of these fuels [16].

Of these alternatives, the European Commission, in July 2020, published a document in which it established that green hydrogen will be the key energy vector for the ecological and energy transition towards zero emissions by 2050 by EU countries [17], and focuses its use in the maritime sector within the scope of short sea shipping. It should also be borne in mind that the decarbonisation process not only affects emissions, but also the number of tanker or gas tanker charters carrying fuels to be used in industrial processes or energy production, to cite two examples [14].

According to Figure 2, the types of marine fuels currently in existence or under development can be summarised in six types: fossil fuels, synthetic fuels, electro-fuels, blue fuels, hydrogen, and nuclear energy.

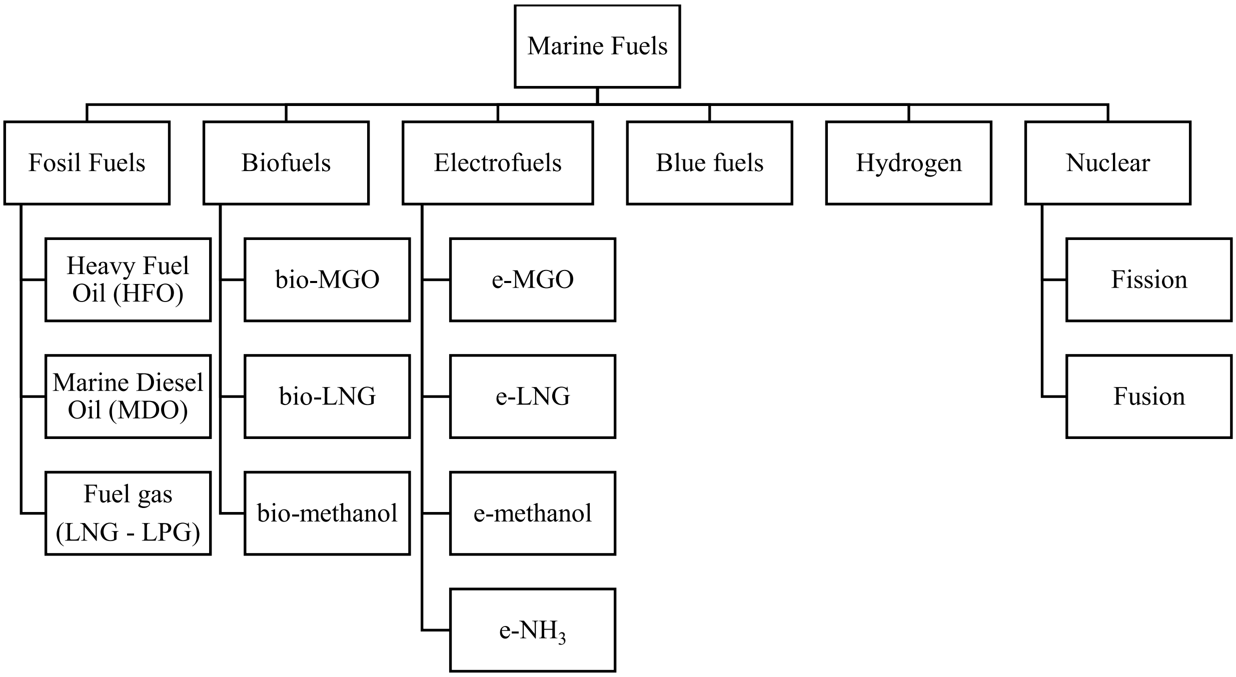


Fig. 2 Fuels used in the maritime sector

2.1 Fosil Fuels.

A fossil fuel is one that has been generated from organic matter transformed by the action of pressure and the passage of time. This type of fuel includes coal, oil or natural gas, and this type of fuel is the main cause of the increase in pollutant emissions. By fractional distillation of oil, different types of fuels and lubricants are obtained depending on the different boiling points, as shown in Table 1.

Of these petroleum derivatives and as far as Fuel Oil type marine fuels are concerned, the international standard ISO 8217/2017 - Fuel Standard for marine distillate fuels, differentiates marine fuels into two classes: distillate and residual [18].

The fuel category is composed of the letters D or R depending on whether they are distillate or residual, followed by the letter M which corresponds to the term of application, which in this case is Marine, and followed by the letter X, A, Z, B, D, E, G or K, which indicates the properties depending on the product specification.

- Residual fuels: These are heavy fuels or fuel oils, and are divided into the categories: RMA, RMB, RMD, RME, RMG and RMK.

- Distillate fuels: These are fuels known as DMX, DMA, DFA, DMZ, DFZ, DMB and DFB. In this case the letter F corresponds to FAME, being the nomenclature for biofuels.

Table 1. Fractional distillation of crude oil

Product	Temperature
LPG	< 25ºC
Gasoline	25-60 ºC
Naphtha	60-180 º C
Paraffins	180-220 ºC
Diesel	220-250 ºC
Fuel oil	250-300 ºC
Lubricants	300-350 ºC
Bituminous	> 350ºC

2.1.1 Heavy fuel oil

Heavy Fuel Oil (HFO) is defined in the MARPOL Convention as a fuel with a density of more than 900 kg/m^3 at 15 °C or, alternatively, a kinematic viscosity of more than 180 mm^2/s at 50 °C [10].

HFO is mostly used as a marine fuel, being one of the most widely used fuels to date on long voyages and is obtained from the fractional distillation of petroleum. According to ISO 8217, the main distinguishing feature between light and heavy fuel oil is the sulphur concentration. On this basis it is stated:

- High Sulphur Fuel Oil (HSFO): HSFOs are fuel oils with a maximum sulphur content of 3.5% as stipulated in ISO 8217.
- Low Sulphur Fuel Oil (LSFO): These are fuel oils that have a low sulphur content, specifically below 1%. It was the fuel type used in ECA areas until 1 January 2015.
- Very Low Sulphur Fuel Oil (VLSFO): With the entry into force of the 0.1% sulphur restriction on marine fuels in ECA areas, this type of fuel has been developed to comply with the sulphur concentration restrictions. Generally, because desulphurisation of heavy fuel oils is too costly to obtain such a low percentage, this term is used for marine gas oils.

2.1.2 Marine diesel oil and Marine gas oil

Marine Diesel Oil (MDO) is understood as a mixture of various distillates, including heavy fuel oil. It should be noted that within the MDO, after adding fuel oil to the mixture, this fuel is called Intermediate Fuel Oil (IFO) and has a darker colour than the MGO type due to the presence of HFO. Marine Gas Oil (MGO), on the other hand, consists of a blend of various distillates without the presence of fuel oil.

According to ISO 8217/2017 [14], those fuels of the RME, RMG and RMK type that are qualified as IFO, have a sufficiently high viscosity that it is necessary to heat it to pump it [19].

Because marine diesel fuels are obtained in a wide variety of forms and can guarantee, depending on their composition, a sulphur concentration below the limits set in MARPOL Annex IV, they can also operate with a wide variety of engines and auxiliary equipment from different manufacturers, which makes it possible to have efficient and compliant fuel available in different ports around the world.

In fact, one of the main functions of marine diesel fuel on board ships is related to their manoeuvring at berth or in port areas. Annex VI prohibits the use of HFOs in these waters, and auxiliary engines are changed before docking to comply with emissions regulations.

2.1.3 Gases from fuel oil

Within the different gases that can be extracted from oil, two types must be differentiated: Those extracted from oil fields (natural gas) and those obtained in the last stage of distillation.

In both cases, both the natural gas and the gas distilled from oil are transported in their liquefied form, obtaining the well-known names of Liquefied Natural Gas (LNG) and Liquefied Petrol Gas (LPG) respectively.

Of these two types, LNG is the one that has the greatest impact on the maritime sector, both in terms of freight and fuel on board.

In fact, LNG is the energy transition fuel in the maritime sector with a view to an absolute decarbonisation target.

However, despite being a fuel that has a lower pollution rate than other types of fuel, it is necessary to address the problems associated with the combustion of LNG because of unburned gases.

Recent studies on the climate implications of LNG as a fuel have compared the emissions generated during the production and distribution of LNG, MGO, VLSFO and HFO fuels, with the addition of Methane Slip (MS) in the case of LNG [20].

MS is defined as the unburned methane resulting from its combustion [21].

Comparisons have been carried out on 2-stroke high-pressure injection dual fuel (HPDF), 2-stroke low-pressure injection dual-fuel (LPDF) and 4-stroke low-pressure injection dual-fuel (LPDF) engines, with different types of fuels, obtaining the data in Figure 3.

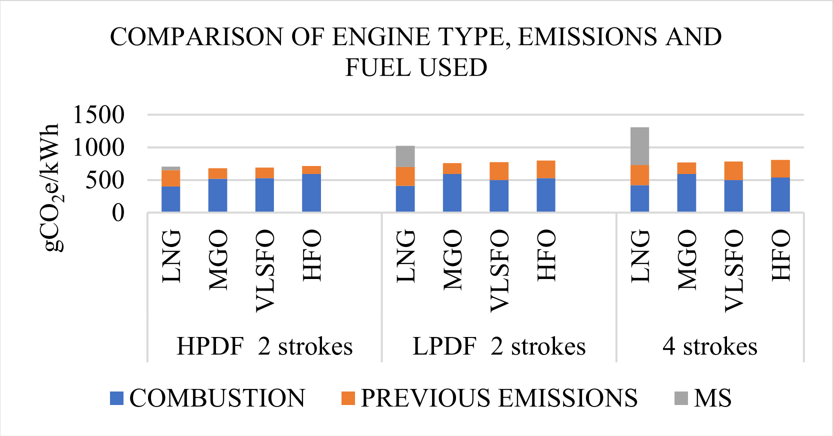


Fig. 3 Diagram of predominant fuels in the maritime sector

If the MS is omitted, there is an emission saving over the life cycle of the engine, but when this unburned methane gas component is added, the emissions far exceed any other fuel type in LPDF type engines and are at an acceptable level in HPDF type engines. There are cases where the MS is as high as 15% at low engine load.

Of the three engine types, only the HPDF type has the lowest pollutant emissions, with the 2-stroke LPDF emitting 1% more emissions and the 4-stroke 8% more emissions than using MGO as fuel [20].

It should be noted that at lower engine loads, there is a higher MS. In fact, in the wake of the financial crisis, many ships have decided to slow down during voyages, which forced them to operate at very low engine loads, causing their emissions to be much higher than those estimated in recent studies [20].

2.2 Biofuels

Biofuels are those extracted from biomass and forest residues, and can be of three types: biogas, liquid biofuel, or solid biofuel [22].

Within biofuels in the maritime sector, the combination of fossil fuels with other environmentally friendly mixtures of organic origin is being advocated, obtaining fuels such as bio-MGO, bio-methane or bio-methanol, the latter being one of the fuels with the greatest projection in the coming years. Methane derivatives are called synthesis gas or synthetic gases and are commonly referred to as SYNGAS [14].

In April 2015, the shipping company Stena Lines commissioned the world's first ship to run on a dual MGO and methanol engine, achieving reductions of 99% in sulphur emissions, 60% in nitrogen oxides and 25% in CO_2 [23].

This type of fuel, which a few years ago seemed to be overtaken by LNG as the fuel par excellence to lead the energy transition in the maritime sector, has re-emerged due to the rise in gas prices, geopolitical tensions derived from the Ukraine war conflict and changes in alliances between exporting countries. Proof of this is that Alphaliner, with the year 2022 still to close, has already noted a 28% increase over 2021 in dual methanol-gasoil engine vessels [24].

Despite these good numbers, there is also a clear reality, and that is the lack of infrastructure needed today to be able to have a network of ships that use methanol as fuel due to the current price of methanol because of its low demand.

2.3 Electrofuels

Electrofuel is a type of synthetic fuel that guarantees zero carbon emissions, obtained from hydrogen combined with CO_2. The process is carried out by means of electrolysis using electrical energy of renewable origin, achieving fuels like those already existing and which have been christened e-MGO, e-LNG, e-methanol and e-NH3, given that this type of technology is used to obtain the hydrogen to be used to obtain the fuel.

The main problem with this type of fuel is the need for an important infrastructure of electrical energy supplies, as well as a profound development of the electrolysis technology that also goes hand in hand with obtaining green hydrogen by the same route [14, 25].

The existing scenarios for the evolution of the price of these fuels according to their demand up to 2050 are shown in Figure 4 [25].

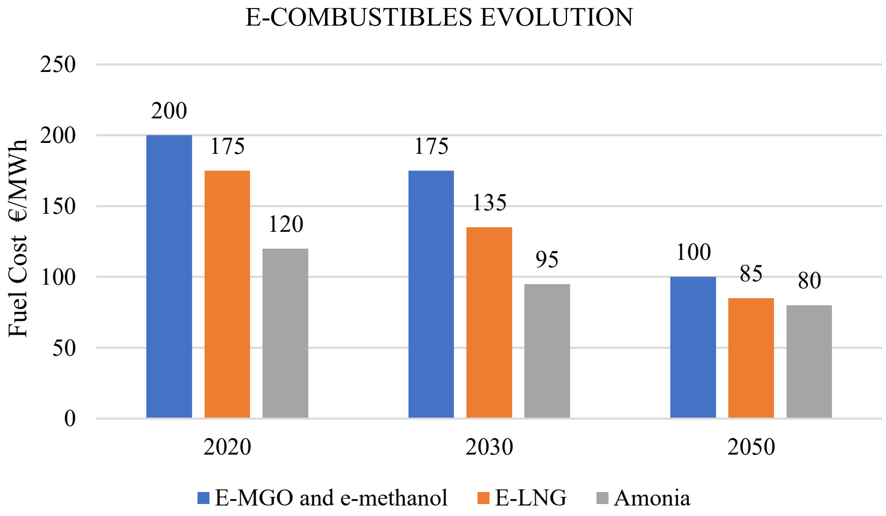


Fig. 4 Comparison of the evolution of the cost of e-fuels

Despite the decrease in the cost of fuel up to 2050, ammonia is the one that is always lower than the rest of the e-fuels, mainly due to the ease with which it can be obtained from water (from which hydrogen is extracted) and air (from which nitrogen is extracted).

About the use of ammonia, there is also a tendency to obtain it from processes that generate CO or CO_2, which would be called blue ammonia. In these cases, the existing infrastructures are valid, and their adaptation would be quick for the implementation of the process.

2.4 Blue fuels

Blue fuels are all those obtained from the treatment of carbon-containing gases such as CO or CO_2.

Among the Greenhouse Gas emissions (GHGs), CO_2 is the most emitted gas and the main cause of global warming. One of the options that was considered as a measure to reduce emissions was to confine and store CO_2, although recently there has been a change of scenario in which its use is also being studied to obtain carbon as a raw material, and even as a component for fuels with zero net emissions [26].

There are three ways in which CO_2 capture can be achieved:

- Post-combustion capture: which involves the treatment of post-combustion gases (nitrogen oxides, water vapour and CO_2).
- Removal of carbon from the fuel prior to the combustion process by oxidation of the fuel [21].
- Oxy combustion, using pure oxygen for combustion to obtain water vapour and CO_2 [21].

At this point it is worth highlighting the hydrogenation process, which consists of a chemical reaction in which the result is the addition of hydrogen, and which is produced with the support of a catalyst [26], which allows the capture of CO_2 from any source, obtaining methanol and its derivatives [27].

Recent R&D trends are focusing on taking advantage of this CO_2 capture technology and the use of hydrogen from renewable sources (green hydrogen) as a green methanol production system to obtain a decrease in GHG emissions on the one hand, and to obtain a fuel that can be used in the sector on the other [28].

Methanol can be obtained from CO_2 in a one- or two-step process. In the one-step case, direct hydrogenation of carbon dioxide to methanol takes place (equation 1), while in the two-step process it is first converted to CO by the reverse water gas shift reaction, which is then hydrogenated to methanol (equation 2) [28].

- Direct hydrogenation:

$$CO_2+3\ H_2 \leftrightarrow CH_3OH+ H_2O \qquad (1)$$

- Water gas shift reverse reaction:

$$CO_2+H_2 \leftrightarrow CO+H_2O \qquad (2)$$

In the scheme of the CO_2 capture process shown as Figure 5, it starts with the capture of flue gases from a certain plant, which are sent to a compressor unit after treatment. At the same time, green hydrogen is obtained in the same plant with another process that is also compressed. Once the compressed hydrogen and CO_2 are obtained, they are fed into what is called the methanol reactor, which is where methanol generation takes place through hydrogenation [29].

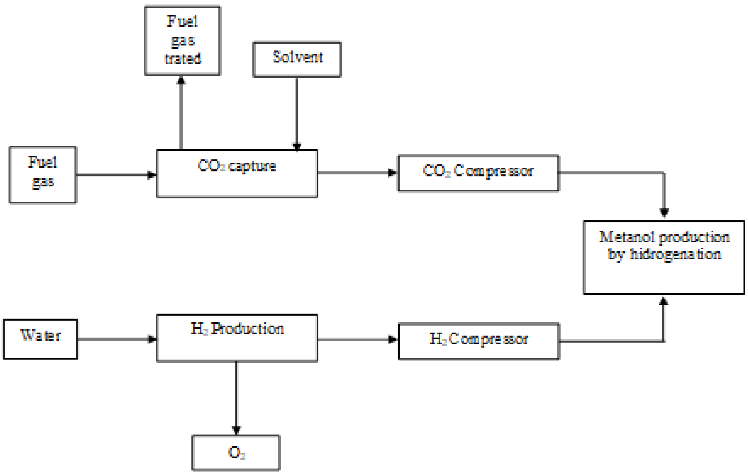


Fig. 5 Operating diagram of a hydrogenation methanol plant

In this case, methanol would not be considered green, as the same amount of CO_2 is emitted in the combustion process as in the fuel gas. Biomass combustion would allow methanol to be obtained with net zero CO_2 emissions.

2.5 Hydrogen

Hydrogen is one of the most abundant resources in nature [30], but it is not found alone, it is found with other elements and therefore, to obtain it, it is necessary to separate it by means of chemical processes [31].

There are four most important types of hydrogen according to the type of technology used to obtain it, as shown in Figure 6 [32-34].

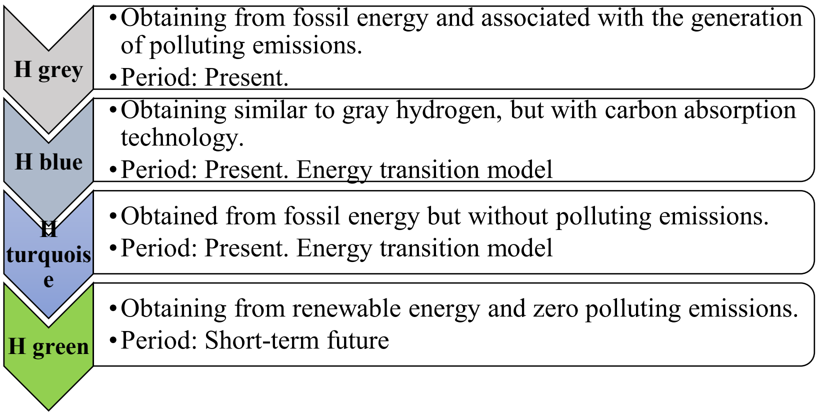


Fig. 6 Summary of most important hydrogen types and methods of production

There are 5 sources from which hydrogen can be extracted by means of 13 different processes: either from fossil resources (natural gas, carbon, and oil) or from renewable resources (water and biomass), as shown in Figure 7.

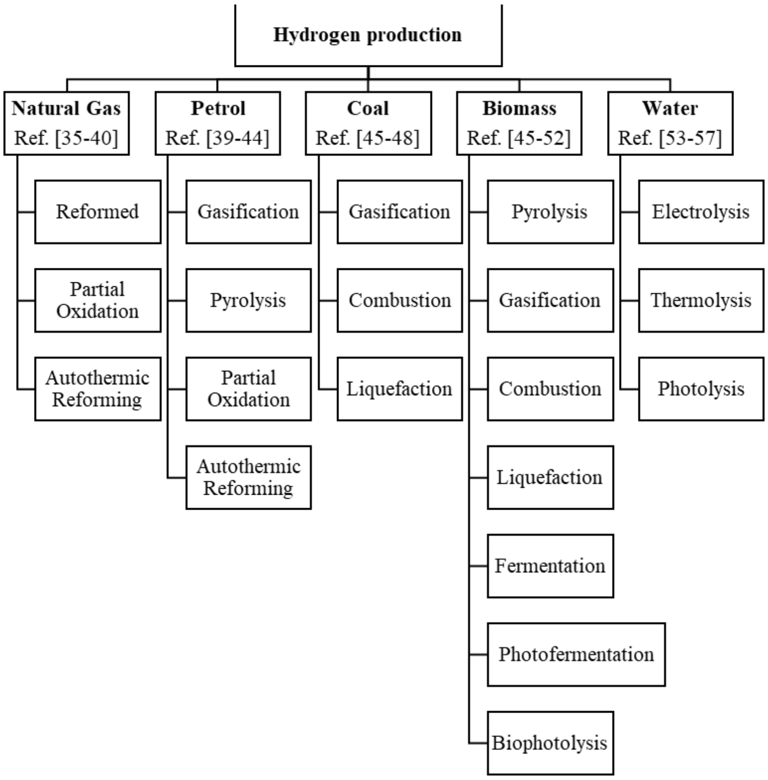


Fig. 7 Methods of obtaining hydrogen according to type of resource.

Hydrogen can be used as a fuel either in combustion engines by injecting it for combustion in pure form or mixed with other types of fuel to create synthetic fuels, or in electrochemical cells, which are integrated into shipboard processes [59-62].

In contrast to the main environmental advantage of green hydrogen as a zero-emission fuel, there are many limitations to H_2 production by water electrolysis, mainly due to the need for a high-power supply.

At ambient temperature and pressure, 1.23 V is needed to obtain hydrogen from water after decomposition, which corresponds to an electrical energy consumption of 3.54 kWh/Nm3 H2 [62]. The kinetics of the reaction (equation 3) between oxygen at the anode (equation 4) and hydrogen at the cathode (equation 5) is slow, a high potential is required to obtain an acceptable hydrogen generation, which implies an electrical energy demand of 4.3-5.7 kWh/Nm^3 H_2 [63].

- Reaction:

$$C + 4\ Fe_3^+ + 2H_2O \rightarrow CO_2 + 4\ Fe_2^+ + 4H^+ \tag{3}$$

- Anode:

$$Fe_2^+ \rightarrow Fe_3^+ + e^- \tag{4}$$

- Cathode:

$$2H^+ + 2e - \rightarrow H_2 \tag{5}$$

The consequence of this is that green hydrogen is two to three times more expensive than hydrogen produced from fossil fuels due in part to the rising cost of electricity [63].

2.6 Nuclear energy

The nuclear energy can be divided in two types: nuclear fission energy and nuclear fusion energy. Nuclear fusion energy consists of a heavy atom capturing an incident neutron, causing it to split into two or more nuclei of light atoms, releasing a large amount of energy [64]. This energy is harnessed to heat water to drive a turbine coupled to a generator.

In the maritime field, nuclear propulsion has mainly been used for ships such as icebreakers or military vessels, especially submarines or aircraft carriers, belonging to the navies of Russia, the United States, the United Kingdom, China, or France. In fact, in 2019, Russia commissioned the first floating nuclear power plant known as "Akademik Lomonosov", which was installed in Pevek with an output of 35 MW and two reactors [65].

This type of nuclear energy has a strong public opinion against it due to the waste that is difficult to manage, but it is undoubtedly one of the types of energy generation that currently has the greatest capacity, as the units that have nuclear fission reactor systems are recharged once throughout their useful life, allowing for the amortisation of the installation and a high level of independence from a fuel supply network for ships [14].

It is important to note here the Molten Salt Reactor (MRS). There are currently none in operation, but there are several prototypes that, if installed on board ships, would allow them to have fuel throughout their useful life, with the considerable reduction in emissions that this would entail.

The reactors designed contain fluoride salt in a solid state until it reaches 500 degrees Celsius, then it melts inside the reactor and dissolves the uranium with it, acting as a protective barrier. If the reactor were to explode, as the uranium is solidified with the fluoride salt, there would not be the radioactive cloud characteristic of such accidents. Furthermore, the fluoride salt does not dissolve in water, so there would be no danger of contamination if the ship were to sink [66]. As an example of this type of reactor, the Danish company Seaborg is developing ships containing such reactors capable of supplying from 200 MWe to 800 MWe.

In this regard, in 2022, the US Department of Energy awarded the classification society American Bureau of Shipping (ABS) a contract for regulatory drafting and research on legislation for nuclear-powered commercial vessels of the MRS type [67].

There is another type of nuclear energy that is currently under investigation and has extensive international collaboration. Fusion energy consists of a reaction where two nucleoli of light atoms, usually hydrogen and its isotopes (deuterium and tritium), fuse together to generate a helium nucleus and particles in the process, which enable the chain reaction [68].

The largest known project to date, in which the United States, Russia, India, Korea, the United Kingdom, Switzerland, China and the European Union are collaborating, is known as ITER (International Thermonuclear Experimental Reactor), located in southern France.

The main problem with this type of technology, which has been in the experimental phase for decades, is the need for very high temperatures, of the order of 100 million degrees Celsius, to overcome the forces of the Coulomb barrier which prevent deuterium and tritium from fusing, with all that this entails (research into materials, new fuel supply systems, reactor design, sizing of the lasers responsible for bombarding the particles, etc.).

It should be noted that, according to the latest information announced by the US Government, at the Lawrence Livermore National Laboratory in California, using the inertial confinement technique, 2.5 MJ of energy were produced compared to the 2.1 MJ supplied by the laser, which is the first time in history that a net energy gain has been achieved [69]. At the time of writing, these data are still under analysis and are not yet published.

2.7 Advantages and disadvantages of marine fuels

Table 2. Summary of the main advantages and disadvantages of marine fuels

FUEL	ADVANTAGES	DISADVANTAGES
HFO	• Has a globalized fuel supply network • Relatively inexpensive compared to less polluting and modern fuels • Mature technology	• Pollutant • Strong dependence on exporting countries
MDO/MGO	• Less polluting than HFO • Has an important global supply network • Easy to transport on board • Mature technology	• Pollutant • Strong dependence on exporting countries
LNG	• The least polluting of the fossil fuels • Growing market as a transition fuel • High demand in the maritime sector	• Market unpredictability • Load management problems due to its temperature • Pollutant • Methane slippage
BIO-FUELS	• Reduction in pollutant emissions compared to HFO, MDO and LNG	• Production capacity • Impact on the increase in the price of necessities. • High prices at present
E-FUELS	• Zero net pollutant emissions	• Green electrolysis technology is still in the final stages of development.
BLUE-FUELS	• Zero net pollutant emissions • Use of CO_2 as fuel	• Green electrolysis technology is still in the final stages of development.
HYDROGEN	• Water vapor as the only emission in the combustion process. • Abundant in nature	• Storage and security problems • Lack of infrastructure • Low demand in the maritime sector • Technology not mature enough
NUCLEAR	• Zero CO_2 emissions • Low refuelling frequency	• Low social acceptance • Waste management and safe storage capacity (fission) • Clean nuclear energy (fusion) still under development.

Having analysed the advantages and disadvantages of fuels it should be noted that fossil fuels have an established infrastructure for their distribution, while cleaner options are still under development, still lacking a sufficiently extensive infrastructure to guarantee fuel supply to ships operating with them.

The main advantages and disadvantages of marine fuels are summarised in Table 2 [20-30,64,68].

2.8 The importance of electrolysis in the generation of new fuels

There are 3 types of technology for hydrogen production depending on the electrolyte applied in the electrolysis: Alkaline Electrolysis (AEL), Proton Exchange Membrane Electrolysis (PEMEL) and Solid Oxide Electrolysis (SOEL).

Direct Electrolysis of Seawater (DES) could be added for the remarkable impact it has from the use of seawater, producing hydrogen and dioxygen with 100% Faradaic efficiency without chloride oxidation under proper operating conditions [32] [70-71].

The main characteristic of alkaline water electrolysis (AEL) is that its electrolyte is a 25-35% aqueous solution of KOH [72], which has a working temperature of 70-90°C and a pressure below 3.2 MPa. The efficiency of these systems allows a specific energy consumption of between 4.5-5.5 kWh/Nm3 and a lifetime of more than 30 years. Moreover, as it is a well-studied technology with relatively low development and deployment costs, it is classified as the most appropriate technology for large-scale green hydrogen production compared to other types of electrolysis [73].

In the case of PEMEL technology, the main problem for implementation is the cost of both catalysts and membranes, which makes large-scale development very complicated [74], while SOEL technology, due to its chemical complexity, is developed in small-scale modules, below 1 MW [75].

Table 3 shows a comparison of the main characteristics of each of the four types of electrolysis explained above, showing the costs involved, their useful life and the danger of integrating these systems.

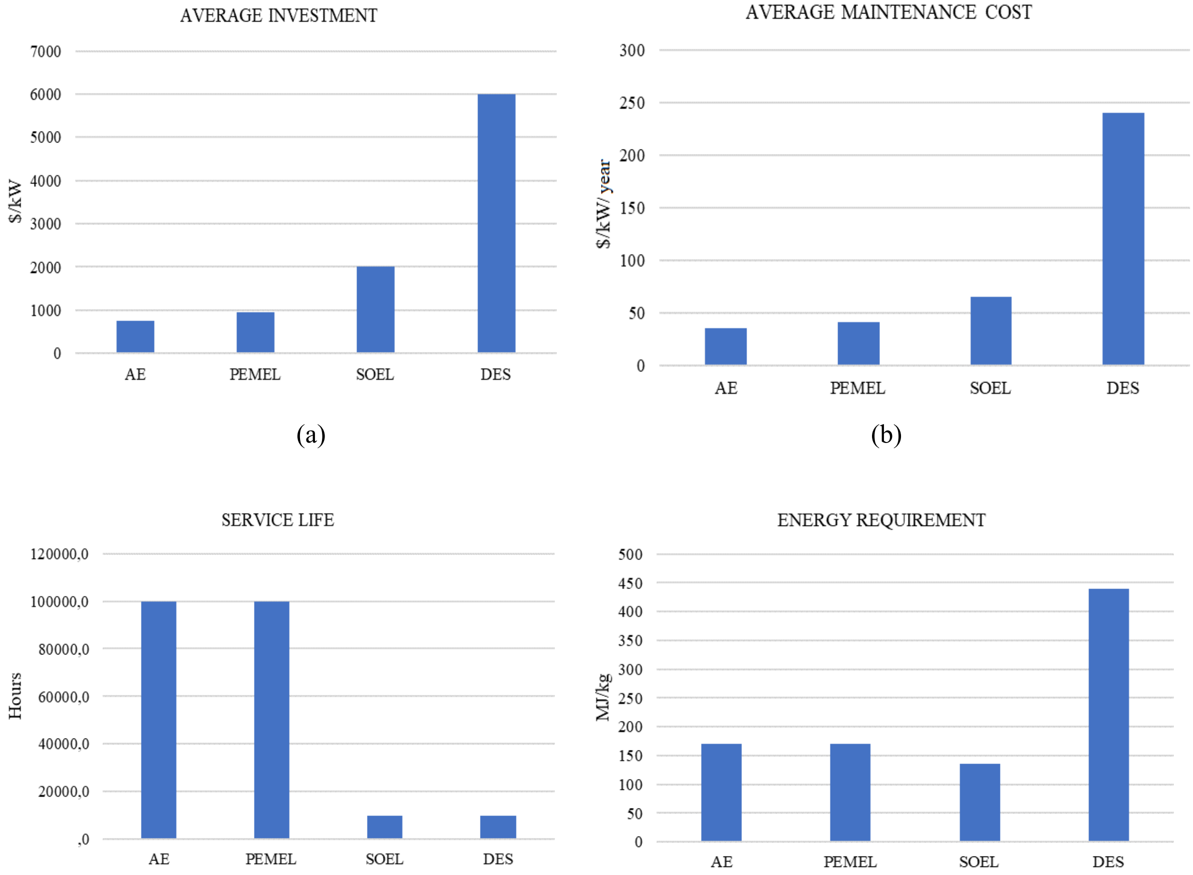
Table 3. Summary of the main characteristics of the types of electrolysis

Features	AE	PEMEL	SOEL	DES
Investment ($/kW)	500-1000	600-1300	>2000	>6000
Average investment ($/kW)	750	950	2000	6000
Maintenance cost ($/kW/year)	10 - 60	18 - 65	> 65	> 240
Average maintenance cost ($/kW/year)	35	42	65	240
Service life (hours)	100.000	100.000	10.000	10.000
Energy requirement (MJ/kg)	170	170	135	440
Danger	Half	Very low	Half	Very high

It should be noted that despite the different types of production that exist, and governmental constraints, hydrogen production is far from being considered green today. In fact, it is highly dependent on the reforming of natural gas (76% of the world total) and coal (23%), resulting in an estimated generation of 830 Mt/year of CO_2 emissions [76].

Of the two renewable sources of hydrogen (biomass and water), electrolysis is the predominant one. It requires on average about 53 kWh to generate 1 kg of hydrogen, which corresponds to an average efficiency of 74.5% based on the gross calorific value of hydrogen (142 MJ/kg) and 63% based on the lower calorific value of hydrogen (120 MJ/kg) [77]. These data, among others, underpin the decision that hydrogen generation by electrolysis is one of the most prevalent today.

As can be seen in Figure 8, within electrolysis, AEL has the lowest average investment and maintenance costs. In addition, it has one of the longest useful lives, together with the PEMEL system, and although it does not have as low an energy requirement as the SOEL system, it is just behind it. Coupled with the fact that the hazard of this system is moderate, AEL technology is the most cost-effective and safest method of green hydrogen production to date [73, 78].



(a) (b)

(c) (d)

Fig. 8 Average investment cost for each electrolysis process (a), Average maintenance cost for each electrolysis process (b), Average investment cost for each electrolysis process (c), Energy requirement of each electrolysis process (d)

2.9 Role of hydrogen in the maritime sector

As far as the role of hydrogen in the marine sector is concerned, it has a large potential to complement the new generation of fuels in its production, but its role as a fuel per se is not promising.

At this point, it is necessary to compare methane with hydrogen to assess the viability of one versus the other [79]. Two elements are key: the flammability range of hydrogen is 4-74% by volume, well below that of methane, which is 5-15%, and hydrogen has a lower ignition energy of 0.02 MJ compared to 0.28 MJ for methane [80].

If this is added to the movements of the cargo inside the tanks of a ship, such as a container ship on a route between Europe and South America, the agitation of hydrogen can generate electrostatic charges that could cause ignition [81]. Furthermore, according to laboratory experiments, the flame propagation speed of hydrogen has been found to be much higher than that of methane; in fact, this increase in speed has been quantified to be 10 times faster than that of any other hydrocarbon [82]. This comparison can be summarised in the data provided in Table 4.

In terms of storage, there are currently four forms of hydrogen storage: chemical hydrides, as solid-state material, compressed or liquid.

Of these four forms, chemical hydrides or as solid material are the least used at present. In its hydride form, hydrogen is obtained by combining chemicals with water and turning the hydride into a hydroxide, and as a solid form it is obtained through the form of composite metal hydrides (materials that are used to absorb hydrogen in a reversible way) or through carbon nanostructures (carbon nanofiber structures that absorb hydrogen).

Table 4. Comparison of LNG and Hydrogen

Feature	LNG	Hydrogen
Flammability range (% volume)	5-15%	4-74%
Ignition Energy	0,28 MJ	0,02 MJ
Flame propagation speed	x1	x10

Of the other two forms of storage, either compressed or liquefied, as in the case of natural gas, the liquefied form predominates, as it allows for greater transport and storage volume, which also translates into greater commercial profitability of the product.

Depending on the hydrogen molecule, the way in which its storage is evaluated also changes. A hydrogen spin isomer with antiparallel spins forming a singlet is called a parahydrogen [83], and an orthohydrogen is one with parallel spins, as shown in Figure 9.

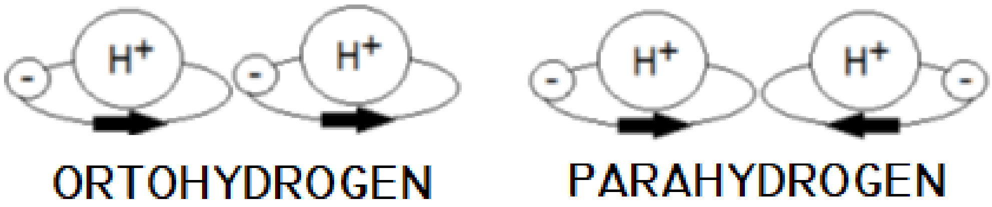


Fig. 9 Orthohydrogen and parahydrogen representation

At a temperature of 20K, almost all the hydrogen present is in the parahydrogen form, but at room temperature or above, the equilibrium shifts towards a concentration of 25% parahydrogen and 75% orthohydrogen [84].

Thus, the temperature of liquefied hydrogen at atmospheric pressure is 90 °C lower than that of LNG [85]. This means that the fuel service system will be subject to strong thermal variations, even greater than those of an LNG system, reaching variations of around 270 ºC, when in an LNG system it is around 180ºC [79]. Likewise, the low storage temperatures of hydrogen in its liquefied state give rise to specific storage materials, with the consequent higher investment [86].

Another fact to take into account in the hydrogen storage chain is that hydrogen is only liquid between -240ºC and -253ºC, which will require highly advanced systems to avoid heating of the charge both through heat transfer during storage and during loading/unloading operations, if these have to be carried out, as well as for the type of molecule it is in (ortho or parahydrogen) [79], and during loading/unloading operations if these have to be carried out, as well as for the type of molecule in which it is found (ortho or parahydrogen) [79], which would cause problems in the management of the boil-off gas (BOG) generated during storage in the tanks.

Regarding the energy density of hydrogen, it is one of the elements with the highest energy density per unit mass with a value of 39.5 kWh/kg, however, its main disadvantage is its low energy density per unit volume of 2.2 kWh/m3. This means that a 60-litre tank under normal conditions has an energy capacity of 0.2 kWh, while the same tank filled with fuel oil has an energy capacity of 629 kWh [87].

All these points have been considered without assessing the imperative need for all seafarers operating hydrogen-fuelled ships to be highly trained and qualified due to the high safety standards that such equipment would require. It should also be noted that although liquefied hydrogen has been used as rocket fuel in the space industry for decades [16], there are currently no ships that make long-distance hydrogen-fuelled voyages, thus lacking the necessary know-how for the development of such ships to overcome all the above problems, among others.

The availability of hydrogen is very limited, in addition to the problems involved in its implementation as an alternative in the maritime sector. It should also be stressed that water-based electrolysis technology will not be available until 2030 at the earliest.

In addition, it would have to contend with the need for an extensive supply network, which is currently practically non-existent and which, today, as a fuel, cannot compete with LNG, which has numerous regasification plants on the coasts and more than 180 bunkering vessels [79]. Therefore, the role of hydrogen during this energy transition until 2050 in the marine sector would be to support synthetic fuels, such as SYNGAS, and its use in short sea shipping, but never in large commercial routes.

3. Emissions regulations for ships

The TIER Regulations are named after the implementation of ANNEX VI of the MARPOL Convention, which establishes emission limits for NO_x and SO_x from ships, as well as controls on emissions of ozone-depleting substances.

This applies to ships with a gross tonnage of more than 400 tonnes and voyages to ports annexed to the ratification of the annex to the convention [10].

TIER I was adopted in 1997 and entered into force in 2005, applying to ships with an installed power of more than 130 kW built on or after 1 January 2000.

The TIER II and TIER III regulations, which came into force in 2011 and 2016 respectively, set, among other things, NO_x emission standards for new and existing engines, and established marine fuel quality characteristics [10].

In addition, NO_x and SO_x Atmospheric Emission Control Areas (ECAs) were established according to Table 5.

Table 5. ECA's' relation [10]

	SO_x		**NO_x**	
Area	*Agreement year*	*Effective*	*Agreement year*	*Effective*
Baltic	1997	2005	2016	2021
North Sea	2005	2006	2016	2021
USA and Canada	2010	2012	2010	2012
Caribbean	2011	2014	2011	2014
Mediterranean	2022	2025	-	-

NO_x emissions, which are included in regulation 13 of Annex VI, have 3 application modalities depending on the date of construction of the ship, as well as the inclusion of emission control areas for nitrogen oxides. In accordance with this regulation, the emission levels for ships are as shown in Figure 10.

About SO_x emissions, which are regulated in accordance with regulation 14 of ANNEX VI, maximum limits are established for sulphur content in fuel, thereby achieving a dual objective: limiting SO_x emissions and at the same time limiting emissions of suspended particles.

In accordance with the entry into force of the regulation restricting the percentage of sulphur in fuels, the limits shown in Figure 11 generated from it have been set over the years for the ECA areas and at a global level.

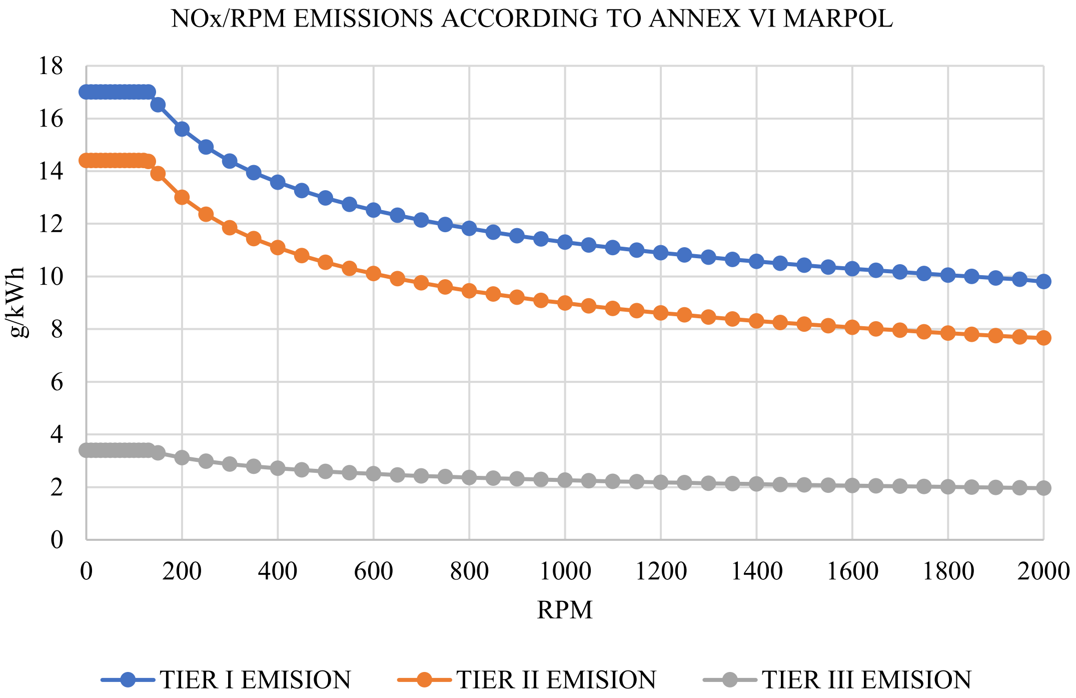


Fig. 10 NO_x emission curves as a function of RPM according to Regulation 13 of MARPOL Annex VI

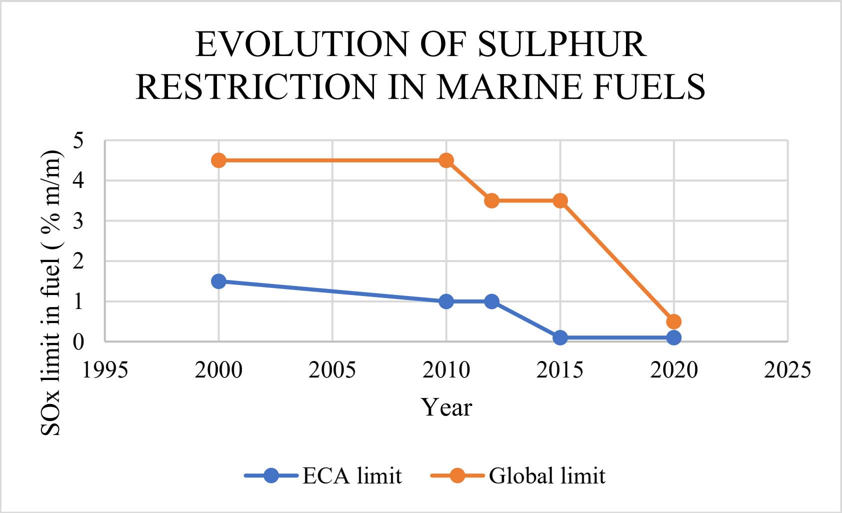


Fig. 11 Evolution of the fuel sulphur percentage restriction in ECA areas and globally according to Regulation 14 of MARPOL Annex VI

It is important to note that the use of HFO is permitted, if it complies with the sulphur limits set out in this regulation [10]. In addition, the ship must comply with the anti-pollution regulations established by MARPOL, and therefore, when heavy fuels are used, they usually integrate an exhaust gas cleaning system to limit sulphur dioxide emissions to below 6 g/kWh.

As far as GHGs control is concerned, Chapter IV of MARPOL Annex VI regulates the EEDI (Energy Efficiency Design Index) and SEEMP (Ship Energy Efficiency Management Plan) mechanisms to minimise emissions, which have been mandatory since 1 January 2013 for all ships of 400 tonnage and above.

On 1 November 2022, the rules came into force with the aim of measuring the carbon intensity of ships in order to comply with the reduction of GHG emissions, and which, as of 1 January 2023, make it mandatory for all ships to measure their energy efficiency index applied to existing ships (EEXI) and to report their carbon intensity indicator (CII), thus reaching the end of the timeline of actions carried out by the IMO in terms of emissions control in accordance with Figure 12.

The EEXI is defined as the energy indicator of a ship compared to a baseline. According to IMO, "Ships achieving the EEXI will then be compared to a required energy efficiency index applicable to existing ships, based on an applicable reduction factor expressed as a percentage in relation to the baseline EEDI." [88]

As regards the CII, this is an indicator that "determines the annual reduction required to ensure continuous improvement of a ship's operational carbon intensity within a particular classification level." [88]

These new ratings will be measured according to a standard that goes from the letter A (most efficient category) down to the letter E (the most energy deficient category).

According to regulation 28 of Annex VI, administrations, port authorities and other interested parties, as appropriate, are authorised to provide fiscal incentives to ships classified as A or B, as well as to set limitations on ships that do not comply with environmental legislation, with both incentives and penalties falling within the competence of the Member State.

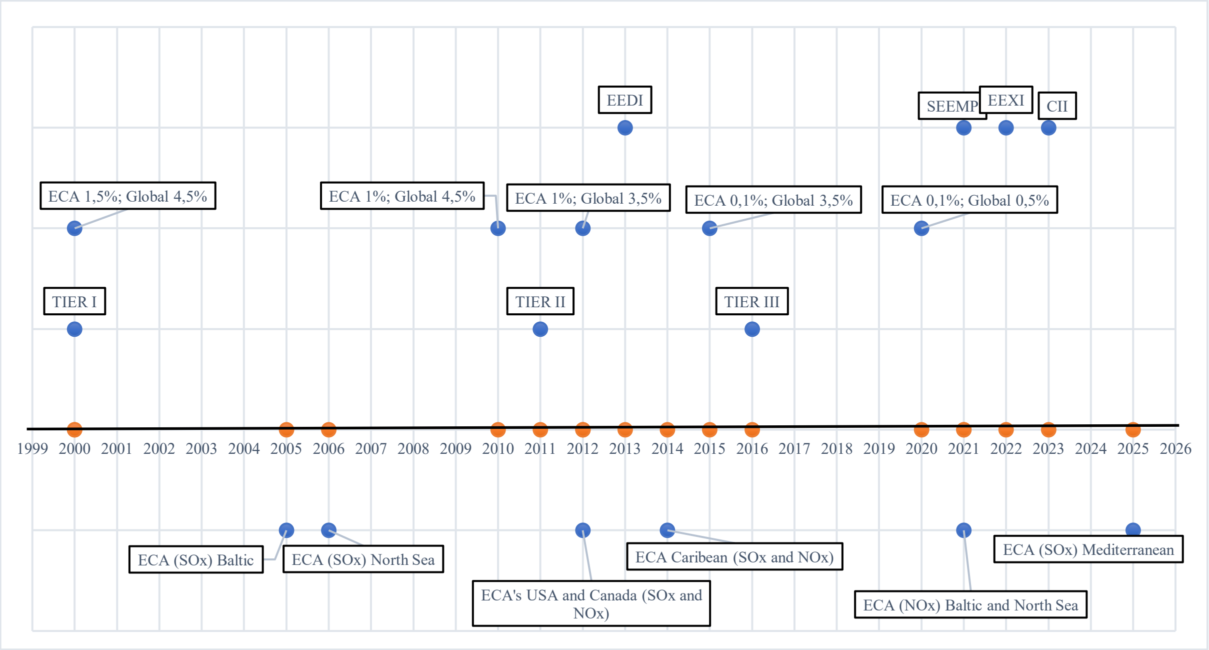


Fig. 12 Timeline of the entry into force of IMO regulations and ECA's

There are other specific regulations to ships for certain regions, as is the case in Europe with the new taxonomy, the Fuel-EU regulation or the European Emission Trading System. For this review, only IMO regulations have been taken into account.

4. Future and forecasting

4.1 About order books and vessel types

Recent studies have shown that there is still a long way to go to meet zero emission targets in the next 30 years [14]. 98.8% of the world fleet currently uses conventional fuel oil as its main propulsion fuel, although this has been reduced to 78.9% for the new order book [14], as shown in Table 6.

As far as LNG fuel is concerned, there are currently 923 ships with this type of propulsion, to which must be added 534 in the order book. As far as LPG is concerned, there are 19 vessels with this type of fuel and 57 in the order book. As far as methanol is concerned, there are currently 11 vessels with methanol as the main fuel, to which must be added 35 vessels under construction. There are only 3 vessels on order with hydrogen as propulsion.

Table 6. List of existing vessels and new orders; unit and %

Fuel	Existing Vessels		New Vessels	
Hydrogen	0	0.00%	3	0.06%
Fuel oil	112500	98.82%	3912	78.90%
Methanol	11	0.01%	35	0.71%
LPG	19	0.02%	57	1.15%
LNG	923	0.81%	534	10.77%
Fuel Cell/ Hybrid	396	0.35%	417	8.41%
TOTAL	113849	100.00%	4958	100.00%

Although it is true that the sector is moving towards decarbonisation, more than 75% of the demand for new ships continues to be met by propulsion systems that consume fossil fuels, specifically fuel oil. Moreover, with the gradual increase in the number of ships with LNG-based propulsion, LNG has become the most demanded option over any other type of alternative fuel and can be considered as a more than possible transition fuel to zero emissions, as can be seen in the comparison in Figure 13.

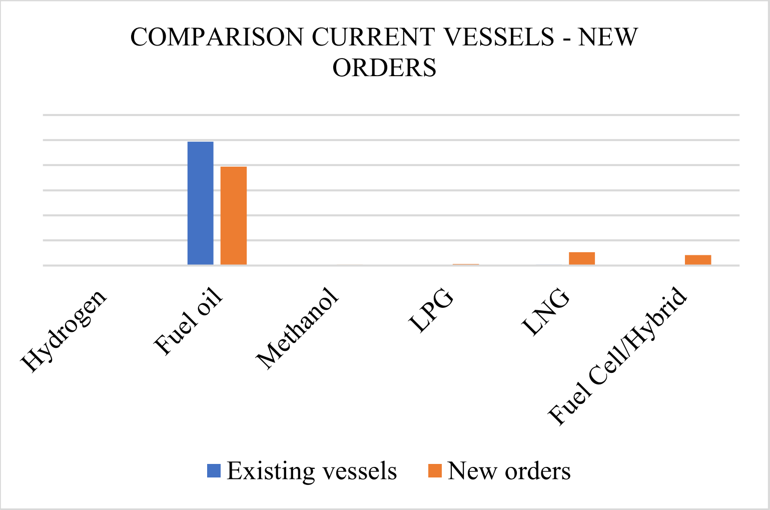


Fig. 13 Comparison between the percentages of existing vessels and vessels on order book

LNG is expected to continue to gain momentum until at least the 1930s, when regulations will begin to require greater efficiency from LNG equipment. It should also consider the evolution of the technology, which may keep it as one of the main fuels on the market from 2030 onwards or be replaced by other alternative fuels.

It should be noted that another point to consider will be the impact that the regulation will have on the cost of freight in the face of the approval of new regulations. In accordance with the Energy Taxation Directive (ETD) [89], this directive seeks to tax ships sold within and for use in the European Union according to the type of fuel implemented. In the case of FO/MDO, 0.9 €/GJ and LNG/LPG, 0.6 €/GJ in 2023, and by 2024, LNG/LPG will be taxed at 0.9 €/GJ.

This measure will have little impact given that most of these ships are built outside the EU, as can be seen from the analysis of the order book in 2021. In that year, 1.974 ship orders were registered of which: 46% were ordered in Chinese yards, 40% in South Korean yards, of which 45% were LNG carriers, and 8.5% in Japanese yards. The remaining 5.5% were shipyards around the world, including European yards [90].

In addition to this, European ports will not be able to offer fuel at competitive prices compared to other ports close to EU borders, which will result in shipping companies being able to avoid paying the tax and will not get the desired benefit, instead of offering fiscal incentives to reduce fossil fuel use and GHGs.

4.2 About new fuels markets

It is expected that after 2030 synthetic fuels will begin to occupy the role that LNG is currently occupying and, together with methane and ammonia, will evolve from blue to green fuel classification in the first instance, aiming for zero emissions throughout the manufacturing process.

The infrastructure necessary to guarantee the supply of these fuels, such as methanol, does not yet exist, so the dominance of LNG as a transition fuel towards decarbonisation will depend on the implementation of this infrastructure that can guarantee the supply of fuel over long distances.

It should also be noted that LNG itself is undergoing a transformation to Bio-LNG or synthetic LNG, with the goal of zero or close to zero pollutant emissions. Until 2030, LNG will clearly dominate alternative fuels, together with first- and second-generation biodiesel and methanol obtained from fossil or biomass sources. Thereafter, the development of Bio-LNG, Bio-Methanol and third generation Biodiesel is expected to have sufficient muscle to supply the market [91].

These new fuels are part of the strategy to reduce energy demand in the medium term, with the aim of achieving a 75% reduction in emissions in the long term (2050) with respect to 2020 and meeting the 1.5ºC scenario proposed as the lowest increase in the earth's temperature [92], as well as achieving the scenario highlighted in Figure 14.

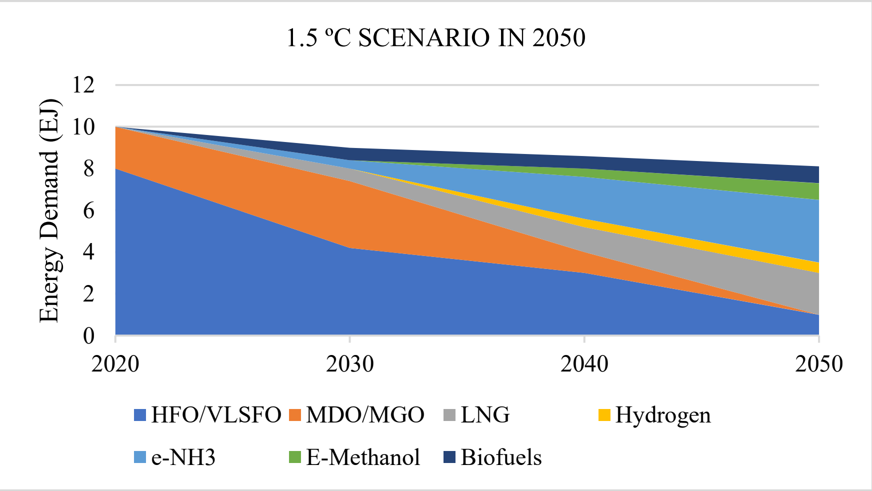


Fig. 14 Marine fuels evolution scenario

Likewise, not all the world's markets are equally developed, neither at the level of the necessary infrastructures, nor at the technological level.

Each vessel, depending on the area of operation, will be able to access a certain type of fuel, as Argus Marine Fuels explains in its latest study presented at the 2nd symposium on alternative low and zero carbon fuels for shipping by the OMI [93].

Table 7. Location of world fuel markets

	Europe and Baltic	**Mediterranean**	**Asia**	**Middle East**	**USA**	**South America**	**Caribbean**	**Africa**
Grey Ammonia	X	X	X	X	X	X	X	X
Grey Methanol	X		X		X			
Biomethanol	X							
LNG	X	X	X	X	X	X	X	X
Biofuels	X		X		X	X		
Green Ammonia	X							
Green or blue hydrogen	X	X	X	X	X	X	X	X

As can be seen in Table 7, there are fuels such as biomethanol or green ammonia that have no supply infrastructure outside European waters. To give an example, if a ship needed to make a voyage to the USA with biomethanol-type fuel, it would not have the supply to make the return voyage. Furthermore, about bio, blue and e-fuels, the development of electrolysis technology for obtaining hydrogen affects both the production of hydrogen as a fuel and its production for ammonia or methanol production processes, among others.

4.3 About the ship conversion

Under the new CII regulation, engine conversions to LNG will have a higher score on the indicator [94]. Current environmental regulations are favouring LNG to become the main fuel on board ships in the coming decades. In fact, the financial viability of ships is at a critical point where ships are being built at the same time as the regulations on ships are changing. According to the latest studies on the return on investment in 2-stroke propulsion [94], the 3 most cost-effective solutions are: Very Large Crude Carrier (VLCC) vessels operating on VLSFO, vessels with an improved HFO scrubbing system to clean the exhaust gas with water, or vessels converting directly to LNG.

In these situations where LNG will undoubtedly be the transition fuel while the development of new fuels continues, including LNG's own evolution to Bio-LNG or synthetic LNG (SYNGAS), companies such as Wärtsilä have already developed and patented new fuel injection systems for their engines to support LNG and the new generation of fuels. The Two-Stroke Future Fuels Conversion Platform system is prepared for the injection of LNG, methanol, or ammonia without the need for costly conversions on board the vessel. Because the fuel supply is injected at low pressure, no additional equipment is required to supply at high pressures, and it also offers the possibility to operate with HFO, MDO and VLSFO [95].

The cost of such measures varies depending on the type of vessel, as shown in Table 8, but in less than four years the investment could be amortised and allow a reduction of more than 20,000 tonnes of CO_2/year. In addition, these types of transformations allow a reduction of up to 4 categories in the EEXI certification in 6 years, with the corresponding economic savings in terms of emissions.

Table 8. Estimated cost of engine conversions as a function of ship type

Type of vessel	Engine	Cost
Container ship of 14000 TEU	12RT-flex96C	4,000,000.00 €
VLCC of 310000 TPM	W7X82	2,900,000.00 €
Newcastle Max 210000 TPM	W6X72	2,700,000.00 €

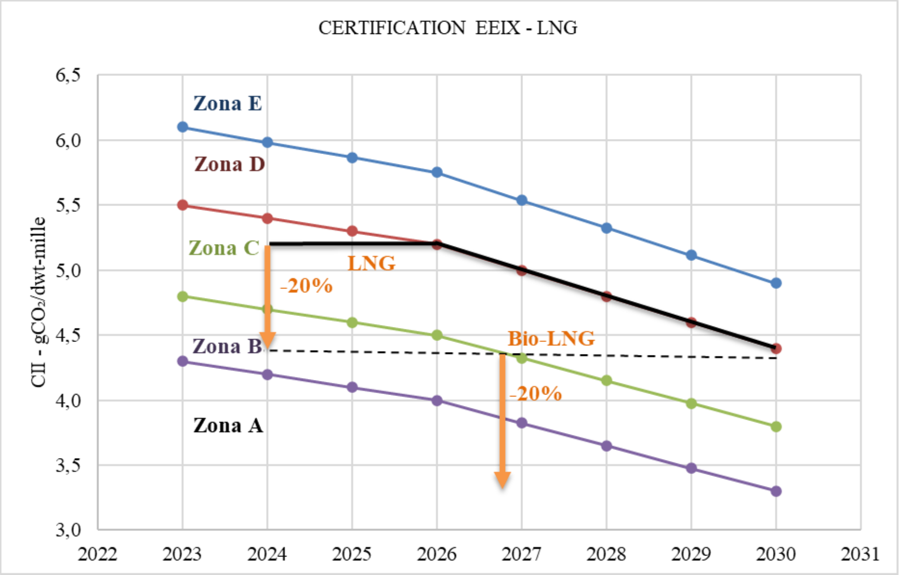


Fig. 15 Variation of EEIX certification as a function of fuel (LNG)

As can be seen in Figure 15, a 20% reduction in CO_2 emissions is obtained with the implementation of the system change, which with the subsequent change to bio-LNG would reduce up to a further 20%, placing ships with this type of fuel before 2030 in the qualification zone in accordance with the EEIX and CII standards.

If the mechanism were analysed with the fuel modification to methanol, this would result in an 18% emission reduction and a rating change from D to C, as shown in Figure 16.

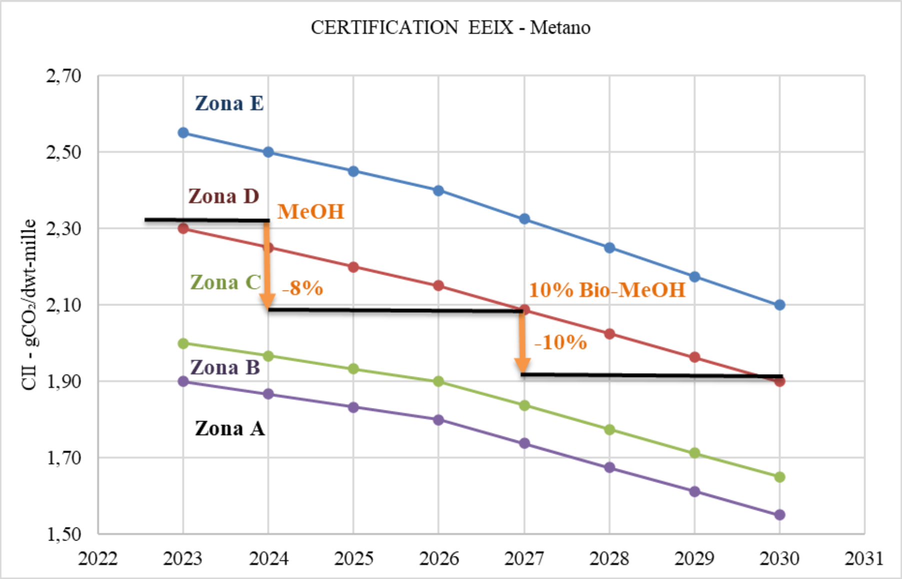


Fig. 16 Variation of EEIX certification as a function of fuel (Methanol)

5. Conclusions

It is undeniable that fossil fuels are currently doomed to be reduced to achieve a goal of zero emissions, however, to meet this goal, a period of several decades is needed in which the markets and the actors that make up the maritime sector adapt to the regulatory changes along with the technological discoveries that are being made.

At present, green hydrogen is one of the energies hopes as a fuel free of polluting emissions and environmentally friendly, although, today, electrolysis technology is not mature enough for the hydrogen obtained with it to compete with the hydrogen obtained from fossil fuels, and the possibility of implementing this technology on board ships is also far away.

There are several studies that support the problems of using hydrogen as fuel compared to liquefied natural gas, given its flammability, its characteristics in liquid form, its low temperature, or its danger in case of spillage, which do not make it a safe fuel in the marine environment.

Also, the lack of regulations makes its use impossible at present, since there is no ship or marine experience on which to develop a know-how that would allow its regulation.

For all these reasons, its main role in the maritime industry would be as an essential element in the synthetic fuels to be generated towards the 2050 frontier, being first natural gas and then methanol, the fuels that can lead this transition towards a future without emissions.

Synthetic fuels and blue fuels will underpin this direction and will allow to be the backup to the economic and market fluctuations that the price of gas may suffer, however, the culmination of the development of a nuclear technology that advances the existing one would be a real objective.

This is a type of energy that is already in operation in various high-performance ships, such as military vessels or icebreakers, whose main obstacle would be to put an end to the problem of the waste it generates.

Everything suggests that molten salt reactors could be the technology to be developed, which would not only allow the ship to be energy independent throughout its useful life but would also achieve a balance of zero polluting emissions.

On the other hand, the transformation of fuel injection systems, such as the one patented by Wärtsilä, are key to the transformation of existing ships, which will have to adapt to new emissions regulations to continue operating in terms of energy, environmental and even financial efficiency due to the taxes and fees generated by government agencies.

There is no single solution for the total decarbonization of the maritime sector, however, viable alternatives such as fuel blends and synthetics seem, a priori, the most solid solution to meet the first targets in 2030.

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