



Research article

Comparative analysis among different alternative fuels for ship propulsion in a well-to-wake perspective

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ABSTRACT

The shipping sector is required to give a significant contribution to the reduction of Green House Gas (GHG) emissions, according to the ambitious goals fixed by the International Maritime Organization (IMO). To achieve these targets, new technologies and measures are required, related to logistics, digitalization, hydrodynamics, machinery, energy, and aftertreatment. A large potential to reduce GHG emissions is offered by alternative fuels. In this perspective a Well-to-Wake (WtW) approach is due for a comprehensive analysis. The paper is focused on the evaluation of WtW CO₂ equivalent emission factors for LNG, methanol, and ammonia. The extensive bibliographic research on this topic outlines the large differences occurring when considering grey or green fuel production pathways. A case study based on a cruise ship allows to compare alternative fuels produced from fossil or renewable sources, considering two typical cruise profiles. Results in terms of Carbon Intensity Indicator confirms that the WtW approach points out the great potential of alternative green fuels for GHG emissions reduction.

1. Introduction

The maritime sector accounts for about 3% of global greenhouse gas (GHG) emissions [1]. Despite being among the most efficient mean of transport which accounts for approximately 80% of global trade by volume, and 70% by value [2], the shipping sector is under a strong renewal process due to an increase in mandatory requirements regarding energy efficiency and emissions reduction.

The IMO (International Maritime Organization) is a specialized agency of the United Nations engaged in safety rulemaking within the maritime sector. In 1997, the IMO adopted the Annex VI of MARPOL Convention (International Convention for the Prevention of Pollution from Ships) to limit the air pollution from ships. It was the first step of an extensive strategy to reduce emissions of the worldwide fleet, still under development (Fig. 1). Regulations from the Annex VI of the MARPOL Convention initially addressed the main air pollutants contained in ships exhaust gas, including sulphur oxides (SO_x) and nitrogen oxides (NO_x), and prohibited deliberate emissions of ozone depleting substances (ODS).

In 2011, amendments to MARPOL Annex VI were adopted to introduce the compulsory employ of energy efficiency components to ship design and management, promoting the use of less polluting equipment and engines [1].

In 2016, in order to gather data from shipboard fuel consumption, hours underway and distance travelled, the Data Collection

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System (DCS) was introduced.

In 2023, through the Marine Environmental Protection Committee (MEPC, 80th session) the IMO strengthened its own goals in terms of emission reductions that will be achieved through the “IMO GHG reduction strategy” [3]. According to these goals, net-zero GHG emissions should be achieved by 2050. Intermediate milestones are also present, such as the 40% decrease of the Carbon Intensity of the global fleet (measured as the ratio between the CO₂ emissions and the transport work) and a minimum of 5% fuel energy share provided by alternative fuels by 2030.

To meet these goals different solutions took part to the strategy for GHG reduction. From January 1, 2023, it is mandatory for all the ships to calculate the attained Energy Efficiency Existing Ship Index (EEXI) in order to measure the energy efficiency and to collect the data for the reporting of annual operational Carbon Intensity Indicator (CII) and the related CII rating. Such a rating will be included in the Part III of the SEEMP (Ship Energy Efficiency Management Plan), mandatory for ships from 2013.

The Carbon Index Indicator is a measure of the ship emission performance evaluated over a calendar year; it is defined as the ratio between the mass of CO₂ emissions and the corresponding transport work. According to the current definition, only the Tank-to-Wake (TtW) emissions of the vessel are considered, i.e., the emissions from the fuel consumption onboard.

However, as reported in Ref. [1], a comprehensive approach is needed to effectively limit the global warming, in a lifecycle assessment (LCA) perspective. Attention has to be paid to GHG emissions from the fuel production to the end-use by a ship (Well-to-Wake), resulting from the combination of a Well-to-Tank part (WtT, from primary production to carriage of the fuel in a ship tank, also known as upstream emissions) and a Tank-to-Wake (or Tank-to-Propeller) part (from the ship fuel tank to the exhaust). To this regard, the European Union is adopting the LCA method to evaluate ships' emissions considering also the WtT contribution.

A large number of investigations based on the WtW approach, as well as LCA of conventional and alternative fuels, are currently available in literature. On the other hand, a limited number of papers has compared the different outcomes for the same fuel and among the different ones, hence allowing for a selection of the best option based on a quantitative approach. Furthermore, it is quite difficult to find a “practical” application of the WtW emission factors, which is mainly required by stakeholders of the maritime sector to support their decision-making process. Therefore, in this paper the research gaps are.

- To collect data on WtW emission factors of the alternative fuels expected to represent feasible options in the short- and medium-term, comparing them in order to assess the relevant uncertainties, lack of information, and reliability.
- To apply the data in a real case study, referring also to the expected development of regulations on carbon intensity and efficiency indicators.
- To make an extended comparison of grey and green alternative fuels.

The paper is organized as follows: Section 2 presents an overview of the technical measure available to decarbonize the maritime sector. Section 3 is related to the main characteristics of the selected alternative fuels. Section 4 outlines the literature research for the definition of Well-to-Wake Green House Gas emission factors. Section 5 presents the selected case study with the relevant values of quantities influencing the comparison and the sensitivity analysis. Finally, in Section 6 results are presented and discussed.

An added value of the present research activity is the collection and harmonization of the most relevant data about the emission factors present in literature; this overview has allowed the selection of proper coefficients for a quantitative investigation regarding the emissions of a cruise ship. The results have evidenced the positive effect of the fuel green production on ship emissions.

2. Decarbonization of the worldwide fleet

The research on the ship decarbonization is currently engaging all the stakeholders of the maritime sector and nowadays there is not a silver bullet being suitable for all of the needs. To achieve the level of ambition set by the IMO and the EU, it is necessary a case-

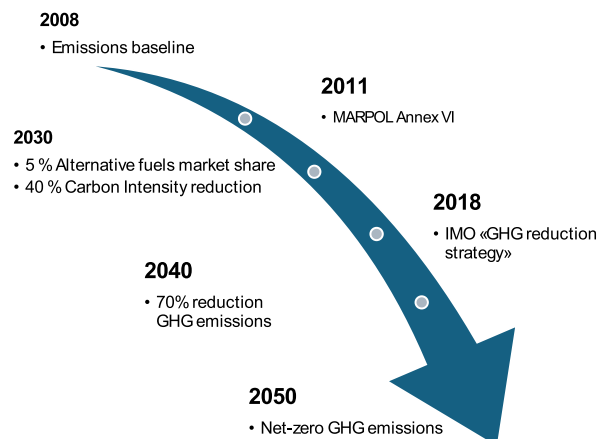


Fig. 1. IMO initiatives for ship emissions reduction.

by-case study to identify the most suitable solution in relation to the specific requirements from different ship types and mission profiles.

A wide analysis on the solutions currently available and the impact they have on emissions is reported in Ref. [4], while in Ref. [5] a review on research, technology development, and innovation proposals for a greener shipping is presented.

In general, in the following paragraph several areas are identified where action can be taken to reduce emissions or equally to increase the efficiency of marine transport. A summary of the selected different options is presented in Fig. 2. The alternative fuels are one of the most important topics toward the decarbonization of the worldwide fleet.

It is worth mentioning that among the several strategies presented in Fig. 2 some are considered particularly promising, besides alternative fuels, such as wind assisted propulsion and slow steaming that are already included by mean of proper coefficients in the metrics proposed by IMO i.e. EEDI and EEXI.

2.1. Emissions evaluation criteria

To carry out the assessment on the complete Well-to-Wake track, it is necessary to identify a suitable metric for the two sub-tracks, Well-to-Tank and Tank-to-Wake. Basing on the common literature, the unit of measurement g_{CO_2e}/MJ_{fuel} is unanimously recognized as suitable for the first phase (i.e., WtT). Differently, two approaches may be used for the second phase, as explained in Ref. [6]. In the first one, only the engine efficiency is addressed focusing on the engine output. In this case, the functional unit is $g_{CO_2e}/kWh_{engine\ output}$ or $g_{CO_2e}/MJ_{Shaft\ work}$, if the propeller shaft work is considered. The second option also analyses the impact of operational factors on the ship activity (routes, range, sea and environmental conditions, etc.), therefore referring to the fuel consumption. In this second case, the functional unit is referred to the transport work (i.e., the distance travelled by the ship multiplied by the cargo capacity of the ship) or to the fuel input expressed as mass or energy. The corresponding measuring units are $g_{CO_2e}/tonne\text{-}nm$, g_{CO_2e}/MJ_{fuel} or t_{CO_2e}/t_{fuel} .

2.2. Hydrodynamics – hull design

Hull resistance is a primary characteristic of ships and is under continuous development to be reduced to consequently reduce fuel consumption. The development of new hull forms and appendages, aided by CFD can reduce the resistance of about 5–15% [7].

Energy efficiency devices (e.g., Mewis duct, pre-swirl fins, Boss Cap) and air lubrication are able to reduce the resistance up to 15% [8]. Stern hydrodynamic ESDs may increase the ship performance by up to 14% [9]. Nevertheless, careful hull polishing from marine growth and use of low friction hull coatings help ships in reduction of resistance during the useful life.

2.3. Logistics & digitalization

The shift towards greener shipping and the technological and digital innovation that the whole world is facing cannot be separated. Digitalization can be a player in emissions reduction too. Digitalization can assist decarbonization with data analysis to optimize the management of voyage plans, ship speed and weather routing. Including environmental factors such as wind speed, currents, and wave height in the choice of the planned route may result in a reduction of emissions and a higher safety for the crew and the cargo.

From a logistic point of view, the digitalization is an aid helping the operators to best manage loading and unloading operations, ship arrivals avoiding unnecessary and uneconomic waiting at anchor outside the port. Through the “just in time” arrivals it is also possible to take advantage of the slow steaming that allows for a further reduction in ships emissions avoiding useless stops at anchor nearby busy ports. Moreover, the optimization and use of scale factors can greatly increase the transport efficiency of the ship as shown in Ref. [4].

2.4. Renewable energy sources and energy vectors

2.4.1. Renewable energy

A complete decarbonization can be achieved producing energy from different renewable energy sources. Several studies have focused on the possibility to directly use the wind power for the ship propulsion. Some examples are wind sails, kites and Flettner rotors, from which renewable energy can be obtained from the wind in new buildings and as retrofits for some types of ships. The wind propulsion systems are dependent on the weather conditions and are not always able to guarantee the necessary power for ship

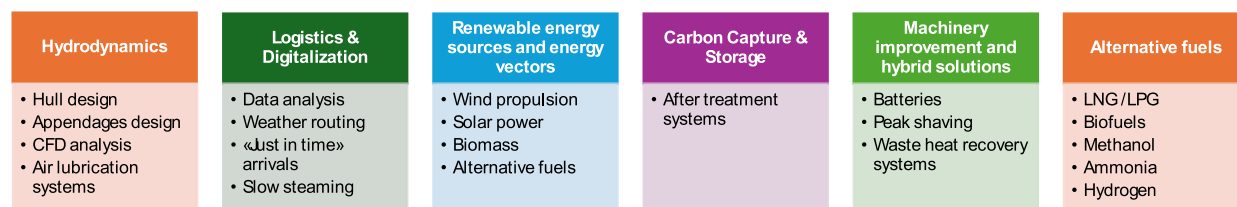


Fig. 2. A summary of identified technical and operational solutions for emissions reduction.

propulsion, requiring their integration as auxiliary propulsion systems [10]. Nevertheless, if a reduction in speed is acceptable wind energy may also serve as main propulsion system [11].

Similar conclusion applies to the solar power which cannot satisfy the power request from commercial ships. This power is harvested directly from the exposure to sunlight of PhotoVoltaic (PV) panels. The technology is swiftly evolving but is still needing a surface area for PV panels which do not fit on commercial ships. Some applications have been implemented but for limited amount of power.

Lastly, energy harvested from biomass can be considered renewable as the fuel production from plants or vegetable oils is based on a theoretically infinite source of natural feedstock. These feedstocks are usually related to the production of biodiesel and bio-gas which are a viable candidate for shipping decarbonization as they can be a drop-in fuel for most of the engines already installed with minor modifications.

2.4.2. Energy vectors

Alternative fuels can reduce emissions by up to 100% and are useful as energy vector for renewable and green energy. Alternative fuels can be divided in zero carbon emission fuels (hydrogen and ammonia) and low-carbon fuels such as alcohols, LNG, and LPG.

To better describe the potential in terms of emission reduction of each of these fuels it is necessary to consider two fundamental characteristics: the feedstock from which they are produced, which is related to the emission in the well-to-tank process, and the converter used to transform the energy contained in these energy carriers into energy useful for the ship, which is related to the emissions from the tank-to-wake. Moreover, a green production path also requires renewable energy.

Furthermore, not only the suitability in terms of the emission reduction should be addressed, but a major impact will come from the physical and chemical characteristics of the fuel, strongly influencing vessel design and safety.

2.5. Carbon capture & storage

Shipping has always relied on fuels such as HFO, MDO and MGO. These traditional fuels originate from fossil feedstock and have ensured ships a safe unrestricted navigation for decades. Given the challenges in the integration onboard of alternative fuels and the difficulties of completely setting aside traditional fuels, a solution which in the medium/long term may guarantee a reduction in emitted CO₂ is carbon capture. Carbon Capture and Storage (CCS) can reduce CO₂ emissions by about 30%–80% [12]. Research on CCS systems is going on, but there are still no wide commercial applications. The integration onboard of these CCS systems also requires additional energy for the liquefaction of CO₂ and a reduction in the available payload due to the installation of the CO₂ capture system and on-board storage.

2.6. Machinery improvement and hybrid solutions

With the entry into force of the EEXI and CII regulations the “slow steaming” has become the first and simplest response available to shipowners to become compliant through an engine de-rating. This solution can also be adopted on a voluntary basis if deemed necessary by the owner and compatible with the minimum power required for safety and manoeuvrability.

The electrification of ships may also induce a reduction in emissions. To power a ship with batteries large volumes and weights are needed to obtain the required ship range for commercial applications. Batteries are not a viable power source when it comes to commercial ships (bulk carrier, ro pax, etc.). The main aim of batteries is therefore reduction of emissions nearby the port, peak shaving, and boosters. It is understood that the use of electricity from fossil sources undermines the effectiveness of batteries from an emission point of view and can even lead to increased emissions considering the efficiencies of the systems involved (batteries, electric motors, converters, etc.).

Considering that almost all ships to date sail using internal combustion engines, waste heat recovery (WHR) systems can be used to reduce emissions and improve fuel efficiency (although from fossil source). An extensive review of all heat recovery systems that can be implemented on board ships is presented in Ref. [13]. Some WHR are for steam production, other uses the power from the main engine exhaust gases to power a steam turbine and produce electricity.

2.7. Alternative fuels production pathways

As will be extensively described, and defined by the purpose of this article, the different pathways that can be followed in the production of an alternative fuel have a major influence on the GHG emissions reduction. As already outlined, a Well-to-Wake approach allows to consider both the production, distribution and bunkering of the fuel (Well-to-Tank) and the on board emissions (Tank-to-Wake).

Referring to production feedstocks, alternative fuels are defined using a different colour to identify the different raw material, green for renewable sources, grey for natural gas, blue for NG associated with CCS, brown from coal [14].

2.7.1. Biofuels

Biofuels are mainly composed of oil crops and biomass. They are currently commercialized and used for road transport, often blended with conventional fuels [15]. Food and energy crops, forest and agricultural residues, waste fats or municipal waste are among the most widely used raw materials. Each of these shows problems of scalability making complex the large-scale production that would be necessary to allow for a progressive phase out of traditional fuels in favour of biofuels [16,17]. European Union is also requiring to

move from first generation to advanced biofuels [18,19], to comply with sustainability criteria and to avoid the fuel versus food conflict. As raw materials are derived from crops or waste, their composition is dependent on the zone in which they are cultivated or collected. For example, soybean oil is the most used in America, while rapeseed oil in Europe, among the first generation feedstock, or used cooking oil for the advanced feedstock.

For transport applications, biofuels have the advantage of being drop-in fuels already available on the market. These fuels have physical characteristics like traditional fuels, requiring minimal changes to the infrastructure adapting perfectly to the existing one and requiring minor changes in the mostly used converters (internal combustion engines).

The emissions related to the production of biofuels are mostly due to the energy required for the field to be harvested and from the transport of the fuel, which is still based on fossil fuels both for road and marine.

2.7.2. LNG – BioLNG

LNG, short form of Liquefied Natural Gas, is a fossil fuel composed of natural gases extracted in several countries such as Algeria, Australia, Nigeria, Norway, Qatar, and the United States. The chemical composition of LNG depends on the source of the Natural Gas and on the type of treatment it has undergone before or for the liquefaction.

LNG is usually a mixture of methane, ethane, propane, and butane with small amounts of heavier hydrocarbons and some impurities. In particular, impurities like nitrogen, sulphur, water, carbon dioxide and hydrogen sulphide, that may be present in the feed gas and must be removed before liquefaction. In fact, the process of production and transport of the LNG passes through 5 different phases [20]: production, purification, liquefaction, transport and off-loading and distribution. From this it follows that the emissions due to the production of LNG derive mainly from the composition of the extracted gas, the type of liquefaction process/gasification process used and the transport distance.

However, LNG can also be produced from renewable sources such as biomass. Bio-LNG suffers the same disadvantages of biodiesel due to land use and availability. The production process of biomethane (then liquefied in bio-LNG) arises from the degradation of biomass. It can be produced according to three main routes: landfill gas recovery, anaerobic digestion, and thermal gasification [21].

2.7.3. Methanol

Methanol is widely used on a large scale to produce a variety of chemicals and products. The industrial synthesis of methanol was first developed in the 1920s based on the Fischer-Tropsch process, which involves reactions that convert hydrogen and carbon monoxide (syngas) in liquid hydrocarbons. While the process originally used coal as the raw material for syn-gas, NG is currently by far the most used raw material and accounts for about 70% of world production. Nevertheless, methanol can be produced from a wide range of feedstocks in addition to fossil fuels, such as agricultural products and municipal waste, wood, and various biomasses.

From the biomass, syngas can be produced, which can then be synthesized into methanol, producing green methanol. Similarly, green methanol is obtained from hydrogen produced by the electrolysis of water through green electricity and renewable CO₂ [14]. Blue methanol, instead, is produced by natural gas reforming applying CCS and producing hydrogen, then combined with renewable or non-renewable CO₂ [14]. Methanol will be grey or brown if the syngas is produced entirely from natural gas or coal, respectively, without CCS. Each colour has a different impact on emissions from production to the tank, with only the green option referring to a renewable pathway.

2.7.4. Ammonia

About 90% of ammonia produced worldwide is used as fertilizer, being a source of nitrogen for growing plants in agriculture. Ammonia is also used in various industrial processes, in additives such as AdBlue® for the control of NO_x from ICEs, in the production of domestic cleaners or nitric acid, used to produce dyes, fibres and plastics, etc. It has excellent properties as a refrigerant, due to its volatility greater than water, therefore undergoing with greater ease the passage of liquid-steam status.

Ammonia production methods can be classified according to the CO₂ emissions that the process entails. The mostly common reaction to produce ammonia is the Haber-Bosch process, in which nitrogen reacts with hydrogen to form ammonia. The production of the hydrogen itself has a strong influence on the overall emissions.

The current commercial production of ammonia is mainly based on the same process. It involves the catalytic reaction of hydrogen and nitrogen at high temperature and pressure. Overall, brown ammonia production is energy intensive, consuming 8 MWh of energy per ton of ammonia. However, most energy consumption and about 90% of carbon emissions come from hydrogen production. Hydrogen is generated almost exclusively through the steam reforming process of fossil fuels. Most ammonia plants rely on reforming natural gas to produce hydrogen and carbon dioxide. Coal, heavy fuel oil and naphtha may also be used, but they have higher CO₂ emissions. The production of blue ammonia involves the steam reforming of methane (SMR) with CCS. Methane reforming emits carbon dioxide in concentrated form, particularly suitable for carbon capture and storage.

In the green ammonia production process [22], hydrogen is produced through water electrolysis. Nitrogen is obtained directly from air using a separation unit that represents 2–3% of the energy used. In this case, therefore, ammonia is produced using the Haber-Bosch process powered by renewable energy.

2.7.5. Hydrogen

Hydrogen is a gas (H₂) that has the potential to reduce GHG emissions up to 100%. It is characterized by a very low boiling temperature which makes it difficult to storage and handle. The storage is also a critical point as it has low volumetric energy density requiring more space than conventional fuels. As for the other alternative fuels, it is possible to assign different colors depending on the raw material from which energy is derived for the hydrogen production. Indeed, although being the most common element in the

universe, hydrogen is not available in nature, and it is produced through the process of electrolysis which requires large amounts of energy.

2.8. Converters

To achieve the goals set by the IMO in terms of reduction of greenhouse gas emissions, the use of alternative fuels is the most promising solution. In particular, the use of carbon-free fuels (such as green hydrogen and ammonia) can allow for a complete decarbonization of shipping in compliance with the IMO objectives presented in Section 2.1. Nowadays ships are mainly fuelled by conventional fuels and there are still few alternative solutions commercially available. In recent years there has been a growth in the number of ships fuelled by LNG [23] which is paving the way for the entry of new fuels. LNG, even though reduces the amounts of SO_x and CO_2 emitted, is still a fossil fuel which cannot be considered as a long-term solution for emissions reduction. All the alternative fuels have different chemical and physical characteristics (Table 1): some are liquid at ambient temperatures (such as methanol, ethanol, and biodiesel) and other are gaseous such as hydrogen and ammonia. Every fuel offers challenges and opportunities; there is no single solution, but it will be necessary to identify the best solution on a case-by-case base.

To employ the energy contained in different energy carriers (alternative fuels) it is necessary to identify which converter is most suitable for each fuel. Internal Combustion Engines (ICEs) or Fuel Cells (FC) may be used for the conversion of the chemical energy (Fig. 3) contained in the fuel into mechanical energy valid for ships propulsion.

2.8.1. Internal combustion engines

Internal combustion engines have dominated and are still prevalent in ship propulsion. There are a few examples of ships that do not rely on ICEs, being propelled by electric motors powered by batteries (suitable only for smaller application), gas or steam turbines, or by sails.

The most used internal combustion engines are diesel engines. In recent years there have been many developments in relation to alternative fuels. In the following sections the main advances for methanol, ammonia, and hydrogen ICEs are reported.

2.8.1.1. Methanol ICEs. Methanol has historically been used in spark-ignition internal combustion engines due to the high Octane Number which limit the risk of detonation. Similar benefit is obtained in supercharged engines, thanks to the high latent heat of vaporization which makes possible to compensate the increase in the intake temperature resulting from air compression.

Typical applications were racing engines and for aviation applications (although limited to takeoff and maximum power demand phases) [24]. In the field of road traction, extensive field testing was conducted in the 1980s–1990s in California, using vehicles fuelled with M85 blend (85% methanol): no problems were found, but the California Air Resources Board (CARB) later chose other alternative fuels for meeting air quality goals [24].

For the use of methanol in diesel engines many technologies have been identified. They are based on dual-fuel concept, in which the diesel fuel injection allows the ignition of the air-methanol mixture. For the dual-fuel applications different strategies are viable.

Table 1

Physical, chemical, air-fuel mixture, and combustion characteristics for conventional and alternative fuels.

	MGO	Methane/LNG	Ammonia	Methanol
Density (STP ^a) [kg/m ³]	<900	0.72/430–470 ^a	0.73/682 ^a	790
Boiling point @1 bar [°C]	170–350	–161.5	–33	65
Evaporation heat [kJ/kg]	270–300	510	1370	1100
Chemical formula	C10 – C22	CH ₄	NH ₃	CH ₃ OH
O ₂ content (mass) [%]	0	0	0	49.93
H content (mass) [%]	14	25.13	17.79	12.58
C content (mass) [%]	86	74.87	0	37.49
Lower heating value [MJ/kg]	42	50	18.7	19.7–20.26
Energy density [MJ/m ³]	35,700	32,50/21,500–23,500	13,7/12,750	15,560–16,000
Stoichiometric AFR [kg/kg]	14.5	17.65	6.06	6.50
CO ₂ specific emission [g/MJ]	72.8	54.87	0	68.44
Auto-ignition temperature [K]	500	813–859	930	712–738
Adiabatic flame temperature [K]	2300	2225	1850	1910–2143
Evaporation heat for air unit of mass [kJ/kg] (stoich. condition)	18.6–20.7	28.9	226.1	170.9
Energy per unit mass of mixture [MJ/kg] (stoich. condition)	2.71	2.68	3.04	3.07
Lower flammability limit referred to λ	0.48	0.59	0.70	0.23
Higher flammability limit referred to λ	1.35	1.99	1.54	1.81
Minimum ignition energy [mJ]		0.28	8	0.14
Cetane Number	>35	–10	–	3
Laminar flame front speed [m/s] (stoich. condition)	–	0.34–0.38	0.015–0.07	0.36–0.43

^a STP = standard temperature and pressure (except for ammonia, values in liquid state at 10 bar, $t = 25^\circ\text{C}$ or 1 bar $t = -33^\circ\text{C}$; LNG, value in liquid state at 1 bar, $t = -161.5^\circ\text{C}$).

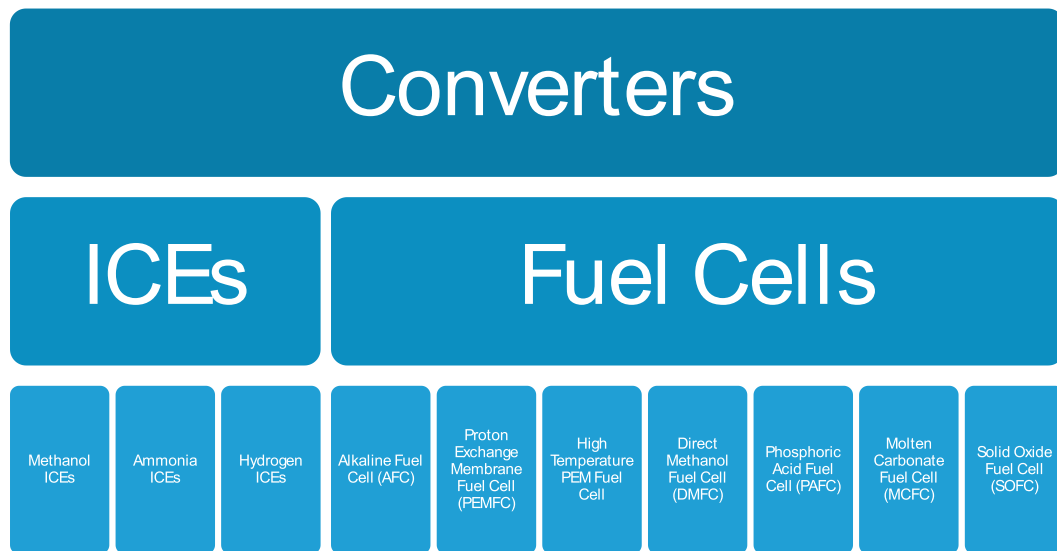


Fig. 3. A selection of energy converters for alternative fuels exploitation onboard.

- Injection of methanol into the intake duct. Methanol evaporates and mixes with air. The charge is then drawn into the cylinder, where it is ignited by a pilot injection of conventional fuel (HFO or MDO) near the top dead center (TDC) at the end of the compression phase. This method is also referred to as “fumigation”.
- Direct injection of a conventional diesel/methanol mixture near the TDC, using a single injector.
- A single injector that injects diesel fuel and methanol separately near the TDC, directly into the combustion chamber. The injector has separate injection channels and nozzles.
- Two separate injectors for conventional fuel and methanol, with direct injection into the cylinder near the TDC.

2.8.1.2. Ammonia ICEs. Ammonia offers the advantage of containing no carbon in its molecule: therefore, the combustion occurs without formation of carbon dioxide. A second advantage is its high hydrogen content, which allows the storage of large quantities of this energy carrier, which can be made available through appropriate processes.

As in the case of methanol, the high octane number is a positive feature for use in spark-ignition engines, but it results in very extended ignition delay in the case of application to compression-ignition engines. To start the combustion process in a diesel engine, it is therefore necessary to use a second fuel, making dual-fuel engines as in the case of LNG and methanol. In the case of ammonia, combustion is also penalized by the limited flame speed (Table 1), in contrast to methanol, for which, once started, combustion proceeds more rapidly than for conventional fuels.

Possible approaches for using ammonia in diesel engines are [25].

- Injection of ammonia into the intake duct. The ammonia evaporates and mixes with air. The charge is then drawn into the cylinder, where it is ignited by a pilot injection of conventional fuel (HFO or MDO) near the top dead center at the end of the compression phase.
- Direct injection of ammonia into the combustion chamber near the TDC. Conventional fuel pilot injection is also required to ignite the charge. A single injector or two separate injectors can be used.

2.8.1.3. Hydrogen ICEs [26]. Hydrogen has been tested in both Spark-Ignition ICEs and Compression Ignition ICEs. Due to its properties, hydrogen is particularly suitable for Spark Ignition ICEs even though the low ignition energy may cause backfire and pre-ignition in presence of a hot spot in the combustion chamber or due to residual electrical energy in the spark plug. The high autoignition temperature is however an advantage in SI ICEs as it can support higher compression ratios with benefits in terms of the maximum achievable thermal efficiency.

Research showed that an increase in the engine efficiency is achieved, with respect to gasoline one, using both hydrogen/gasoline mixtures or in pure form due to the higher LHV, short quenching distance, flame propagation velocity and higher compression ratios. Regarding the emissions, an increase in the production of NO_x is expected due to the higher adiabatic flame temperature which triggers the reaction between the nitrogen and oxygen in the air fuel mixture.

In CI, as already mentioned, the high auto-ignition temperature is significantly reducing the feasibility of pure hydrogen application of. Therefore, dual-fuel operation is a mean to overcome this issue and trigger the combustion of hydrogen. As per the SI engines, hydrogen can enhance the combustion efficiency of the CI ones, ensuring a more complete combustion of the injected fuel.

2.8.2. Fuel cells

A FC is an electrochemical cell that converts chemical energy from a fuel and an oxidizing agent (often oxygen from the air) into electricity through redox reactions ensuring almost no GHG emissions. Different fuel cell types are available, and can be characterized by the materials used in the membrane.

- Alkaline Fuel Cell (AFC)
- Proton Exchange Membrane Fuel Cell (PEMFC)
- High Temperature PEM
- Direct Methanol Fuel Cell (DMFC)
- Phosphoric Acid Fuel Cell (PAFC)
- Molten Carbonate Fuel Cell (MCFC)
- Solid Oxide Fuel Cell (SOFC)

As per [27], the most promising solutions for the application in the maritime sector are the Low Temperature (LT) PEMFC, High Temperature (HT) PEMFC and SOFC.

The PEM FC requires pure hydrogen to be powered and can go up to 50–60% in efficiency. The hydrogen and air oxygen are converted into H₂O avoiding any GHG emission. On the other hand, these cells are particularly sensitive to contamination by CO and have a moderate lifespan. Conversely, HT PEMFC, even though is a less mature technology and still under development, guarantees a minor sensitivity against CO and impurities in fuel supply. Therefore, the high temperature allows for the use of hydrogen coming from the steam reforming of methanol, overcoming the challenges regarding the storage of hydrogen onboard. Moreover, the HT PEMFC may be coupled with a Waste Heat Recovery system to improve the overall efficiency of the plant. SOFC, as for the HT PEMFC, operates at even higher temperatures and may be fuelled by LNG, methanol, diesel, or hydrogen. When hydrocarbon is used as fuel the reforming to hydrogen take place internally in the cell and generates as products CO₂ and NO_x.

3. Selected innovative fuels (LNG, ammonia, methanol)

As discussed in Section 2, LNG, methanol, and ammonia are among the alternative fuels which may allow the achievement of IMO targets for the reduction of future GHG emissions in the maritime sector. They have been selected for the analysis and the application case investigated in this paper since LNG fuel has already been introduced in shipping operation in the latest years; methanol is expected to gain important shares in the short term [23], while ammonia is recognized as an interesting option but in the medium-term because of the safety and technical issues it implies. Ammonia is corrosive and toxic, causing lung damages and death if inhaled for different exposure levels/time. Methanol is corrosive and toxic as well. Furthermore, always from a safety point of view, it must be underlined that all these options are classified as low flashpoint fuels, requiring technical measures to avoid uncontrolled combustion. An extended analysis of health and safety problems is presented in Ref. [28] for ammonia and in Ref. [24] for methanol.

Hydrogen and biofuels (except for bio-LNG) are not included in the analysis, as hydrogen technology for use onboard is still under development and it is still under discussion whether the biofuels production in support for the whole marine sector is sustainable in the long term.

Table 1 presents the main characteristics of conventional (MGO = marine gasoil) and alternative fuels/energy vectors. Physical and chemical properties are firstly considered. Then, the most important features of the air and fuel mixture are outlined, together with the corresponding quantities related to the combustion process. Data were obtained comparing information from Refs. [24,28–37].

The comparison of the different characteristics listed in Table 1 allows to outline important differences among the selected options, focusing on technical aspects related to their use in internal combustion engines and their application to the maritime sector. Fuels in the gaseous state in standard conditions have density lower than the air one. To liquify methane and ammonia and to keep them in the liquid state, low temperatures are required, but with a significant advantage for ammonia. Increasing pressure up to 10 bar allows to increase boiling point to −125 °C for LNG and to ambient temperature for ammonia. The evaporation heat is always higher for the alternative fuels, with LNG, ammonia, and methanol requiring 1.8, 4.8, and 3.9 times the thermal energy to evaporate the same amount of conventional fuel.

Carbon, hydrogen, and oxygen content justify variations of other quantities, such as lower heating value, stoichiometric value of air-fuel ratio and CO₂ specific emission. The first consequence is the difference in the energy density values, with reduction of 37, 64, and 56% respectively for LNG, liquified ammonia, and methanol. This influences the volume required to store the same amount of energy in the ship tanks or the travelled range for a fixed value of storage volume. In the case of LNG and ammonia, further space is requested for insulation purpose and tank reinforcement. Stoichiometric value of air-fuel ratio (AFR_{st}) is significantly reduced for ammonia and methanol. This point must be considered when evaluating thermal energy available in exhaust gases for waste heat recovery, because the corresponding mass flow rate may be different from the operations with conventional fuel. Further quantities are linked to the stoichiometric air-fuel ratio, such as the evaporation heat for air unit of mass and the energy per unit mass of mixture. For the first parameter, the limited level of AFR_{st} leads to a further increase of the ratio between heat required by ammonia and methanol compared to MGO (11.5 and 8.7 times higher for the alternative fuels, respectively). On the other hand, the second quantity outlines that the thermal energy supplied to the engine is about 12–13% higher for the two alternative fuels. In this case, a more suitable comparison should consider the actual mixture conditions, applying the air-fuel ratio related to the use of lean strategies.

CO₂ specific emission identify the contribution of the combustion process. It is clear the advantage offered by ammonia, not including carbon in its molecule, while the potential reduction of methane compared to MGO is equal to 24.6%. Methanol advantage is

limited to only a 6% decrease. As explained in Sections 2, 4 and 6, a proper comparison of GHG emissions must include the Well-to-Tank phases.

Flammability limits are expressed in terms of excess air ratio λ (given by the ratio between actual and stoichiometric air-fuel ratio = AFR/AFR_{st}). In the lean side, the more extended range is offered by methane, due to its gaseous state. On the rich side, methanol allows for the minimum λ value, because of its oxygen content.

Alternative fuels generally show low values of cetane number. This results in a large extension of ignition delay if these fuels are applied in compression ignition engines. The current approach is based on the adoption of dual-fuel engines, with the conventional fuel injected in a pilot event to ignite the mixture. In dual-fuel engines, substitution rate allows to define the energy contribution of each fuel, according to equation (1):

$$\text{Substitution rate} = m_{\text{alternative fuel}} \times \text{LHV}_{\text{alternative fuel}} / (m_{\text{alternative fuel}} \times \text{LHV}_{\text{alternative fuel}} + m_{\text{MGO}} \times \text{LHV}_{\text{MGO}}) \quad (1)$$

where $m_{\text{alternative fuel}}$ and m_{MGO} are the masses of the two fuels per single thermodynamic cycle and $\text{LHV}_{\text{alternative fuel}}$ and LHV_{MGO} represent their relevant Lower Heating Value.

In the case of ammonia, further difficulties to start the combustion are related to the level of auto-ignition temperature and ignition energy, significantly higher than the corresponding values of the other fuels. After the start of combustion, the process is expected to be slower for ammonia, as shown by the value of flame front speed in laminar conditions for the stoichiometric mixture and confirmed in rich and lean operations in Ref. [33], where the comparison of methane and ammonia shows a large disadvantage for ammonia. In Ref. [24], a similar comparison between methane and methanol outlines slightly higher values for the second fuel.

Finally, the adiabatic flame temperature is lower for methanol and, mainly, for ammonia. This may result in a limited formation of thermal NO_x . In the case of ammonia, fuel NO_x may represent a significant contribution, as suggested in Ref. [33].

4. Definition of WtW GHG emission factors (fossil or renewable fuels)

The definition of emission factors to evaluate green-house gas emissions on a Well-to-Wake basis is a fundamental step to allow a proper comparison between conventional and alternative fuels, including all the phases required to produce the fuel, to bunker it in the ship tanks, to consider potential evaporative emissions occurring in transportation, storage and inside the supply system to the engine, and finally to assess emissions produced within the combustion process.

To this aim, extended bibliographic research has been made, collecting papers, reports and documents published by researchers, classification societies, expert panels, and EU or IMO Committees and Working Groups.

The initial database included about 40 documents, whose emission factors were mainly derived from different LCA tools, such as Ecoinvent, European Reference Life Cycle Database, GREET, Gabi, and SimaPro. In other papers, a literature review was developed. Details on the selected fuels and applied tools within the investigations presented in these documents are reported in Table A1. Among them, a selection was made for this study, considering different criteria.

- The availability of emission factors for the considered emissions (CO_2 , CH_4 , and N_2O) or an overall value related to the two contributions (WtT and TtW).

Table 2

Well-to-Wake green-house gas emission factors from selected references.

Fuel	MGO	LNG	Bio-LNG	Grey Methanol	Green Methanol	Grey Ammonia	Green Ammonia
References	Well-to-Wake green-house gas emissions in [gCO_2/MJ]						
[16]	87.0	63.0	10.0	–	10.0	–	0.0
[18,41]	90.7	76.4	–	102.9	10.4	126.3	–
[38]	93.0	87.8	–	–	–	129.8	5.4
[39]	173.9	166.0	105.4	200.3	–	–	–
[40]	81.8	–	12.5	–	33.0	–	–
[43]	–	80.9	51.1	89.4	18.2	–	–
[44]	88.9	93.8	55.5	93.8	6.0	–	–
[45]	87.8	84.5	20.3	91.2	7.4	–	–
[46]	85.5	–	–	94.2	25.6	–	–
[47]	85.3	66.6	20.0	93.5	7.6	–	–
[48]	92.0	82.1	32.1	–	–	–	–
[49]	–	–	–	–	–	–	36.3
[50]	86.7	78.9	–	95.9	4.5	–	–
[51]	91.6	84.9	33.9	–	–	–	–
# values	12	11	9	8	9	2	3
Average ^a	88.2	79.9	29.4	94.4	13.6	–	13.9
Standard deviation ^a	3.4	9.3	17.0	4.3	9.9	–	19.6
Minimum	81.8	63.0	10.0	89.4	4.5	126.3	0.0
Maximum	173.9	166.0	105.4	200.3	33.0	129.8	36.3
CoV [%] ^a	3.9	11.7	57.6	4.6	72.3	–	140.8

^a Average, standard deviation, and CoV do not include values of Ref.39.

- A clear definition of the applied functional unit, as discussed in Section 2.1.
 - The comparison of different conventional and alternative fuels (documents referring to a single fuel were not included in the following evaluation).
- A well-defined description of the considered pathways to produce the renewable fuels.

Applying these criteria, the database was reduced to 14 documents. Two papers [38,39] were included in the list by processing emission factors (whose functional unit was $[\text{gCO}_2\text{e/kWh}_{\text{engine output}}]$) through the application of the efficiency of the propulsion system connecting the engine shaft to the propeller for the cruise ship considered in the case study. As data reported in Ref. [40] are referred only to carbon dioxide, levels of CH_4 and N_2O emissions available in Ref. [41] for the different fuels were added. In the case of ammonia, N_2O emission were taken from Ref. [38].

When separate emission factors for CO_2 , CH_4 , and N_2O were stated, the overall GHG emission factor was calculated applying the 100-year global warming potentials for climate pollutants according to the Sixth Assessment Report (AR6) of the Intergovernmental Panel on Climate Change (IPCC) [42]. In this report, the global warming potentials are equal to 1, 29.8, and 273, respectively for CO_2 , CH_4 , and N_2O .

For fossil and Bio-LNG, methane slip was also considered, adding the term listed in Annex II of the Fuel EU Maritime Regulation [41].

Well-to-Wake green-house gas emission factors expressed in $[\text{gCO}_2\text{e/MJ}]$ are listed in Table 2, for the four selected fuels: MGO, LNG, methanol, and ammonia. For the three alternative fuels, a fossil option was considered, meaning that primary feedstock to produce methanol and ammonia is natural gas. A renewable pathway for each of them was also taken into account, with reference both to the energy required for their production and to the feedstock (biomass or waste for methanol, renewable hydrogen for ammonia).

From Table 2, some general considerations can be derived. The number of values available for the considered fuels are very different. For the conventional fuel and the most common alternative (LNG) information is generally included in each document. The renewable pathway of natural gas and methanol (both for the fossil and the renewable options) is frequently considered, while a limited number of documents already deals with ammonia. A relationship between the number of values, the current use of the fuels and their expected penetration in the market is therefore apparent, as an increasing share of the ships order are currently based on LNG and methanol [23].

Generally, emission factors are quite similar except for those reported in Ref. [39]. Therefore, average, standard deviation, and coefficient of variation values were obtained without including this reference, whose factors were considered as maximum levels for MGO, LNG, Bio-LNG, and grey methanol. For grey ammonia, these statistics were not calculated, as only two levels were available.

The highest values of GHG emission factors are apparent for methanol and ammonia with the fossil pathway. This outcome confirms that the contribution to emissions in the production and delivery phases may represent a large share. Therefore, the Well-to-Wake approach has to be followed for a proper comparison of conventional and alternative fuels, because it allows to include this contribution to the overall balance, leading to identify choices to achieve real benefits.

The highest values of coefficient of variation correspond to the renewable options. This is partly due to the reduced level of emission factors, but it probably outlines that further investigations are required, to reduce the uncertainties on these aspects.

Calculations of simulated CII for the selected single profiles were made applying average (minimum for grey ammonia) and maximum values of WtW emission factors.

5. Application case

To ingrate the effect of the Well-to-Tank emissions contribution in the overall GHG emission, a cruise ship has been selected as Case Study. Although, as previously mentioned, the main focus on the present investigation is about the WtW emission evaluation, nevertheless the use onboard of alternative fuels should take into account the safety issues implied by their physical/chemical characteristics, especially when considering passenger ships. In this perspective it is important to point out the toxicity of ammonia that requires attentive hazards identification and relevant countermeasures. The cruise ship is an interesting case also for the significant technical discussion about the proper metric to be considered related to the specific operational profile: in fact, the present CII formulation is deemed to strongly penalize the cruise market since does not properly account for the operational time spent by cruise ship at berth. The CII formula, as conveyed during the MEPC 78 (the IMO committee meeting regarding marine pollution), is negatively affected by port stops, vital for the service performed by cruise vessel. Nevertheless, in this paper the CII is being used as a metric to evaluate the emission performance of a cruise ship. The main data of the selected Case Study are reported in Table 3.

Table 3
Main characteristics of the selected cruise ship.

Characteristics	
Lwl	330 m
Beam	42 m
Gross Tonnage	Over 150,000 GRT
Propulsive power	2×20 MW
Installed Power	60 MW
Passengers	Abt. 5000
Crew	Abt. 1500

The propulsion plant of the Case Study ship is composed of 5 dual-fuel diesel engines (fuelled by LNG and MGO) which, through alternators, power two Propulsive Electric Motors (PEMs) and the hotel loads. This is a typical arrangement for diesel-electric cruise vessels.

Two different cruise profiles are assumed for the estimation of the fuel consumption and distance travelled need for the CII evaluation.

- Profile 1 (ISO condition and 14 days long cruise)
- Profile 2 (Tropical condition and 7 days long cruise)

Significant parameters of the cruise profiles are shown in Table 4, with reference to time spent in navigation, manoeuvring and at berth.

Actually, the CII calculation is based on real annual ran miles and relevant fuel consumption (therefore emissions) as already explained in Section 1. Such comprehensive data are not available for the case study and at the same time, due to the comparative perspective of our investigation, they are neither strictly necessary. Hence, a simulated CII has been defined, as if the two profiles were repeated an appropriate number of times in order to provide the consumption and distance travelled over one calendar year.

Manoeuvring and berth time are also known (Table 4). Further available data are related to the fuel consumption when LNG is used as the main fuel, together with the amount of MGO supplied through the pilot injection to ignite the air-fuel mixture. This allows to evaluate the energy required for the different phases of the cruise profiles. When the reference fuel (LNG + MGO) is replaced by the alternative fuels (ammonia or methanol), values of engine efficiency and substitution rate have to be selected to calculate the amount of the two fuels (MGO and ammonia or MGO and methanol) to be supplied. The selected concept is based on dual-fuel engines, with both fuels directly injected in the combustion chamber. This is in line with the approach followed by the main engine manufacturers developing converters for the maritime sector for the use of the considered alternative fuels.

In the case of methanol, an extended investigation [52] showed a slightly better efficiency of methanol compared to diesel oil, when direct injection applies. This result may be related to the higher laminar flame front speed of methanol. In a conservative approach, the baseline engine efficiency was assumed to be the same of the reference case also when using methanol. In the sensitivity analysis more favourable engine efficiency values are discussed. In the case of ammonia, different characteristics (evaporation heat, auto-ignition temperature, minimum ignition energy, laminar flame front speed, Table 1) may imply that mixture formation, ignition and combustion development are negatively affected, leading to larger thermodynamic losses when compared to other conventional or alternative fuels. Therefore, a reduction of 0.04 on the whole engine load range was considered, compared to the reference case. As far as substitution rate is concerned (equation (1)), in both cases the baseline level was 85%. In this case, targets of the main engine manufacturers for the maritime sector were considered, again coupled to a conservative approach.

Taking into account the uncertainties on the two parameters and the limited experimental information currently available, a sensitivity analysis was also carried out for ammonia and methanol, referring to their green option. From Table 5, it is possible to identify the two baseline cases, already introduced, and the 8 cases investigated to assess the influence of variations in engine efficiency and substitution rate.

Sensitivity cases 1 and 2 were defined keeping the substitution rate at the baseline level (85%), while increasing engine efficiency values. As a consequence the same efficiency of the reference LNG engine is applied for ammonia in case 1 (Ammonia sensitivity case 1 = S1 ammonia) and an increase in efficiency of 0.04 on the whole engine load range is applied in case 2 (Ammonia sensitivity case 2 = S2 ammonia).

For methanol case 1 and case 2, an increase in engine efficiency of 0.03 (Methanol sensitivity case 1 = S1 methanol) and 0.06 (Methanol sensitivity case 2 = S2 methanol) is selected respectively, again on the whole engine load range.

These increases are meant to represent potential improvement and optimization of the propulsion system achieved by engine manufacturers in the development of these alternative solutions. They can be considered reasonable values, as long as they will be confirmed in literature.

On the other hand, while keeping the engine efficiency equal to the baseline case, the substitution rate values were set equal to 75% (Ammonia sensitivity case 3 = S3 ammonia and Methanol sensitivity case 3 = S3 methanol) and to 95% (Ammonia sensitivity case 4 = S4 ammonia and Methanol sensitivity case 4 = S4 methanol). As previously mentioned, these variations are related to the expected ranges of this parameter for the two alternative fuels, which may be limited, especially at low engine load, by the high evaporation heat and, in the case of ammonia, by the slow flame front speed.

6. Results and discussion

The selected case study allows for a quantitative evaluation in terms of GHG metrics based on emission factors described in Section 4. Fig. 4 ÷ 10 present the simulated “extended CII” calculated according to the details given in Section 5, respectively referring to

Table 4
Main characteristics of the selected cruise profile.

Cruise Profile	Time [h]	Distance [nm]	Time in cruise mode [%]	Time in manoeuvring mode [%]	Time at berth [%]
1	338	4102.5	77.2	1.2	21.6
2	169	1366	55.0	1.8	43.2

Table 5

Selected cases for the sensitivity analysis.

Green Ammonia + MGO				
Ammonia baseline case	Ammonia sensitivity case 1	Ammonia sensitivity case 2	Ammonia sensitivity case 3	Ammonia sensitivity case 4
BS ammonia	S1 ammonia	S2 ammonia	S3 ammonia	S4 ammonia
$\eta = \eta_{LNG} - 0.04$	$\eta = \eta_{LNG}$	$\eta = \eta_{LNG} + 0.04$	$\eta = \eta_{LNG} - 0.04$	$\eta = \eta_{LNG} - 0.04$
SR = 85%	SR = 85%	SR = 85%	SR = 75%	SR = 95%
Green methanol + MGO				
Methanol baseline case	Methanol sensitivity case 1	Methanol sensitivity case 2	Methanol sensitivity case 3	Methanol sensitivity case 4
BS methanol	S1 methanol	S2 methanol	S3 methanol	S4 methanol
$\eta = \eta_{LNG}$	$\eta = \eta_{LNG} + 0.03$	$\eta = \eta_{LNG} + 0.06$	$\eta = \eta_{LNG}$	$\eta = \eta_{LNG}$
SR = 85%	SR = 85%	SR = 85%	SR = 75%	SR = 95%

MGO, LNG + MGO, methanol + MGO, and ammonia + MGO. For the alternative fuels two sets of results are considered with reference to the production mode: a “grey” option (Figs. 7 and 9) implying natural gas as feedstock; a green option (Figs. 6, 8 and 10) based on renewables. In each figure, the five CII ratings obtained with the TtW approach presently in force are shown as a function of time range from 2023 to 2026. The two cruise profiles are reported where the black lines are referred to cruise profile 1, the blue lines to cruise profile 2 (Table 4). Values corresponding to TtW CO_{2e} emission factors are shown by means of continuous lines while those related to average values of WtW CO_{2e} emission factors, reported in Table 2, are represented through dashed lines. Finally, simulated CII levels obtained applying maximum values of the WtW CO_{2e} emission factors (Table 2) are indicated by dotted lines.

The analysis of the figures outlines the following general considerations.

- Referring to the TtW emission factors, all the fuels allow the ship to be rated A in the considered period (2023–2026). This can be related to the advanced design of the cruise ship considered as case study, with enhanced energy efficiency solutions. From this point of view, the application of energy and carbon intensity indicators promotes the improvement of design measures and techniques to save fuel, but has a minor effect, for the moment, on boosting the alternative fuels adoption.
- For renewable LNG and methanol, TtW emission factors are related to the combustion process regardless of the carbon source, therefore equal to the case for fossil/grey path. When considering the WtW emission factors, carbon credits related to the feedstock production are applied, leading to lower values of CII for the average EFs (Bio-LNG) or in both cases (average and maximum EFs for green methanol).
- Simulated CII (both TtW and WtW) are higher for Cruise profile 2 compared to values of Cruise profile 1, with an increment between 21 and 22% for all the different fuels and analysed emission factors. As reported in Table 4, the Cruise profile 2 shows a shorter navigation period (with a lower relevant distance travelled) and a higher time spent in port (evidenced by a higher percentage of hotel mode), while the manoeuvring time is limited in both cases. The conclusion would be that for a conservative approach while investigating the CII, calculations should take into consideration longer periods spent at berth since they are the more challenging profiles. This is due to the formulation of the CII: in fact, that formulation is at present under discussion at IMO specifically for Passenger/Cruise ships, characterized by operational profiles, not only significant in terms of distance travelled, but in terms of comprehensive cruise time (inclusive of time spent in port). Meanwhile, zero-emission target for energy used at berth

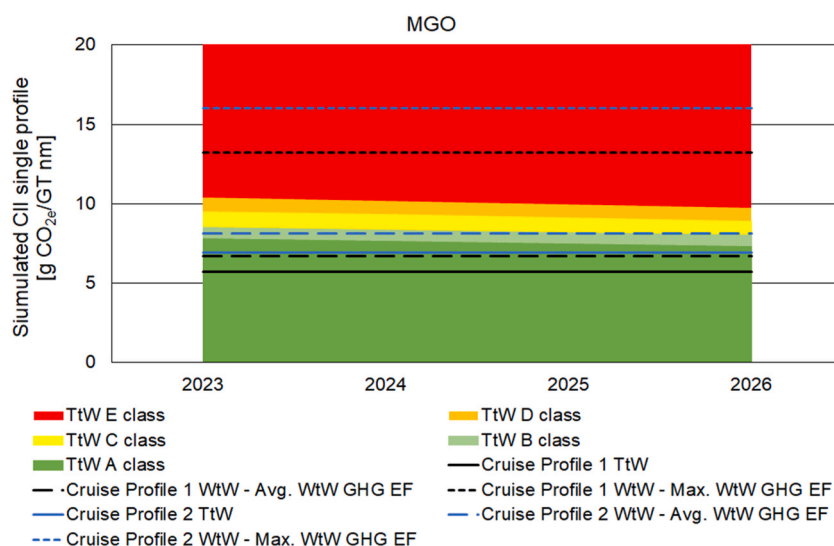


Fig. 4. Tank-to-Wake and Well-to-Wake GHG emissions for the conventional fuel (MGO).

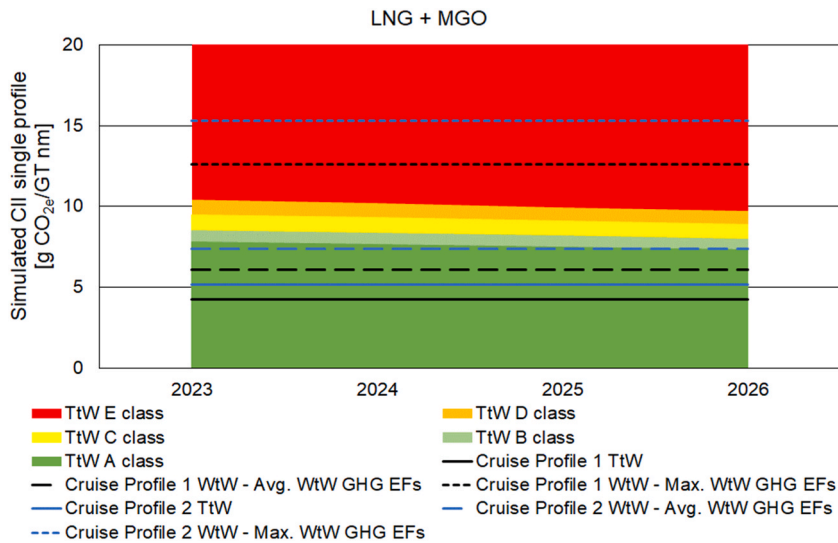


Fig. 5. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using fossil LNG + MGO.

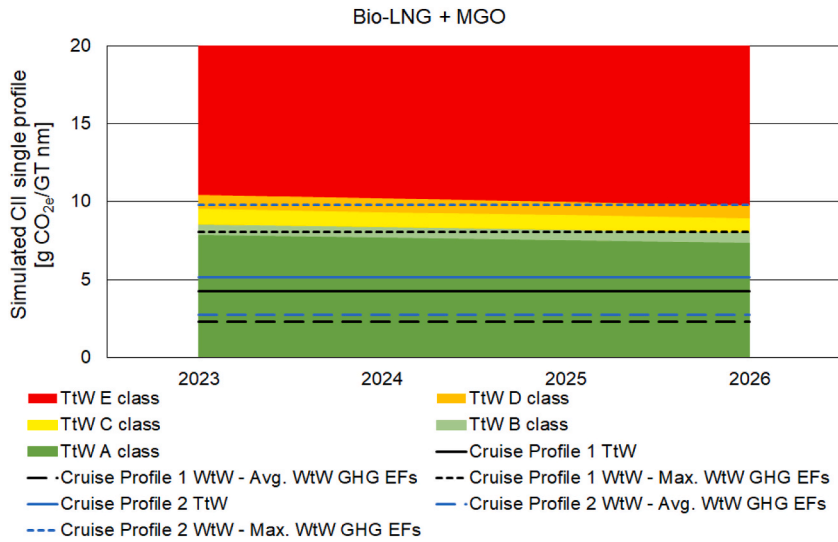


Fig. 6. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using bio-LNG + MGO.

are defined by the Fuel EU Maritime Regulation [41], prescribing the connection to on-shore power supply (OPS) system starting from January 2030 or January 2035 for mooring longer than 2 h.

- As expected, the application of WtW maximum emission factors results in an increase of the simulated CII. The smallest impact is apparent for grey ammonia (with an increment of more than 10%). The largest increase (more than 200%) is observed for Bio-LNG, in line with the emission factors in Table 2. Consequently, for the conventional fuel and the alternative ones (i.e., MDO, LNG, ammonia, and methanol) still obtained through a fossil pathway, the simulated CII belongs to the worst class for both the cruise profiles.
- The influence of the selected time period shown on the X axis of Fig. 4 ÷ 10 is evidenced by the decrease of the threshold values defining the class limits, with a reduction of 6% moving from 2023 to 2026. As a consequence, some figures show a worsening of ranking with reference to different combinations of fuel, cruise profile and emission factors. For example, simulated CII for MGO moves from class B to class C in the case of cruise profile 2 when applying average WtW EF, Fig. 4; on the other side simulated CII for LNG moves from class A to class B for the same cruise profile and EF, Fig. 5. For Bio-LNG, Fig. 6, simulated CII moves from class B to class C in the case of cruise profile 1 and from class D to class E for cruise profile 2, when applying maximum WtW EF.

When focusing on the different fuels, further remarks can be listed as follows.

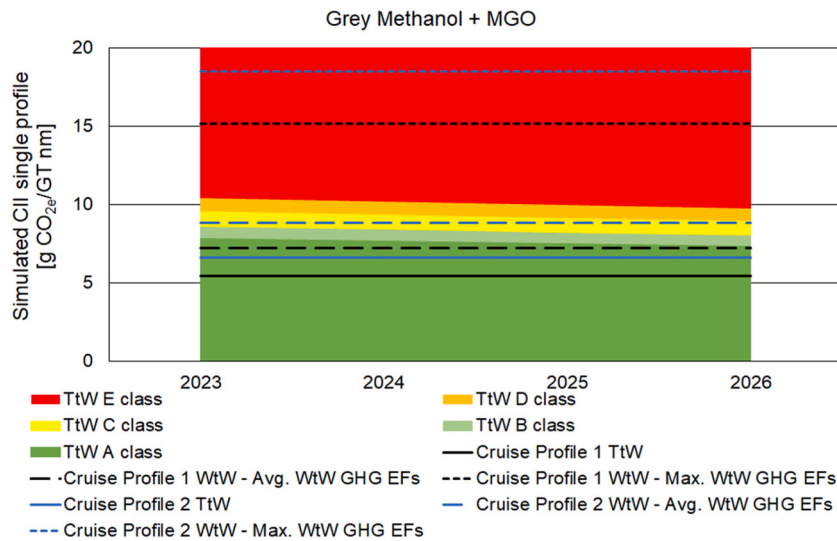


Fig. 7. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using grey methanol + MGO.

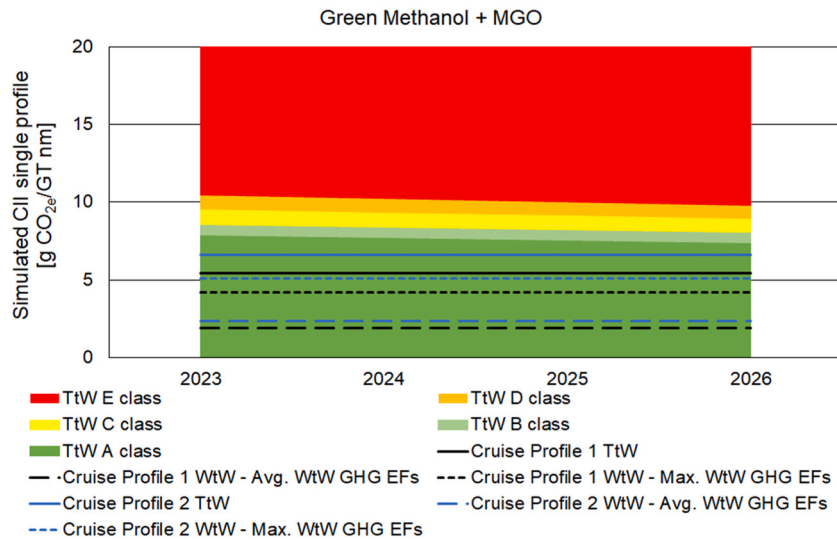


Fig. 8. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using green methanol + MGO. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

- Green methanol and green ammonia allow to obtain values of simulated CII belonging to class A for both the cruise profiles and the three emission factors (TtW, average and maximum WtW).
- For Bio-LNG, the maximum WtW emission factor leads to a value of the simulated CII in class B for the first profile and class D for the second profile.
- For ammonia, values of the simulated CII applying TtW emission factors are only due to the contribution by MGO, as the considered SR is equal to 85%. Therefore, technologies to maximize the substitution rate and the corresponding reduction of GHG emissions are required when applying this energy vector to internal combustion engines for the maritime sector.
- For the alternative fuels, the WtW approach indicates that the availability of *green* fuels is mandatory to fulfil the IMO decarbonization targets.
- Best options can be identified according to the different EFs. When considering the TtW approach, ammonia allows to achieve the lowest CII values for both the cruise profiles (without distinction between grey or green). When switching to the WtW approach, green methanol is the fuel with the lowest values of CII, when applying average or maximum emission factors for its calculation.

From these considerations, it can be concluded that only the WtW approach will allow for a comprehensive reduction in GHG emissions, forcing the exploitation of renewable pathway to produce alternative fuels. Furthermore, a strict procedure is strongly

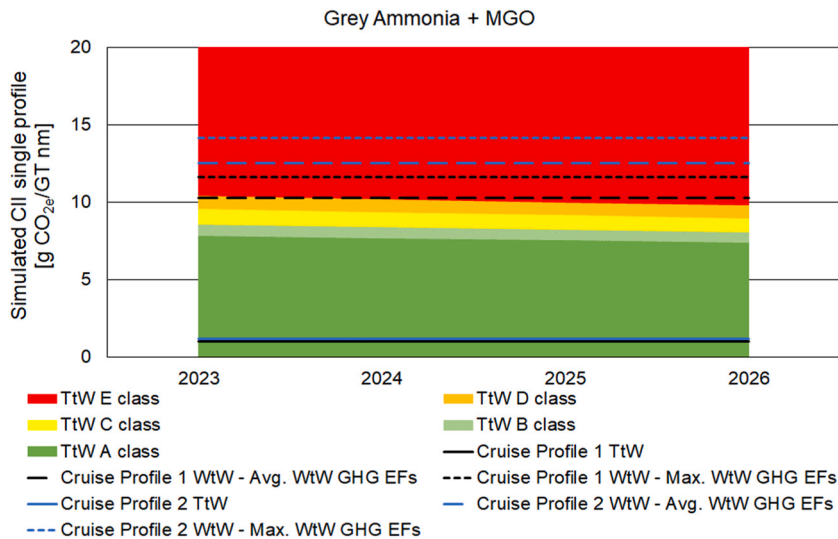


Fig. 9. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using grey ammonia + MGO.

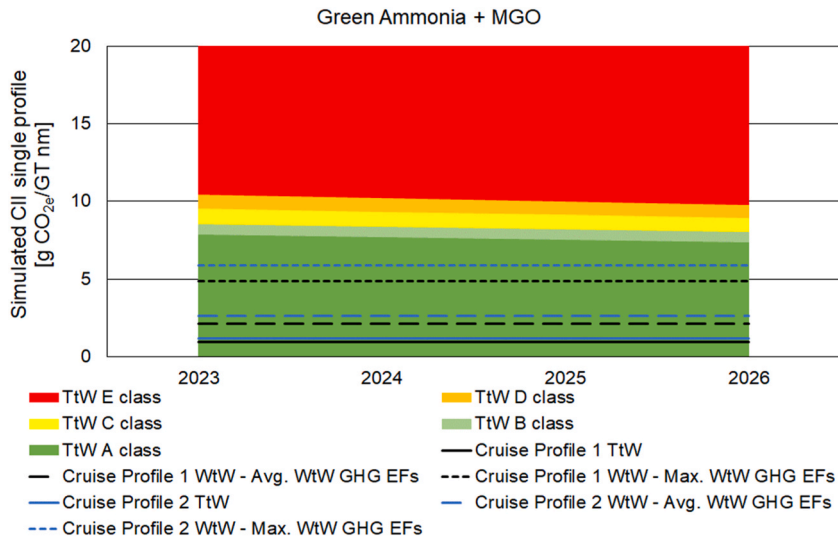


Fig. 10. Tank-to-Wake and Well-to-Wake GHG emissions for dual-fuel engines using green ammonia + MGO. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

recommended for a reliable assessment of WtW CO_2e emission factors, as the current situation shows a large variability of the available data, leading to a consequent variability on related energy and emission indicators.

Two further parameters strongly influence the observed results, i.e., engine efficiency and substitution rate. To quantify their influence, the sensitivity analysis described in Section 5 was carried out and results are presented in Fig. 11 for green ammonia and in Fig. 12 for green methanol. Both cruise profiles are considered as well as the three emission factors: TtW, average WtW, and maximum WtW CO_2e . As reference, the threshold value for Class A in 2026 (i.e., the minimum level referring to the considered time period) is also shown in the two graphs. The sensitivity cases (a combination of energy efficiency and substitution rate values) named as S1, S2, S3, S4 and the baseline cases (BS) are described in Table 5.

As expected, when higher values of engine efficiency are considered, lower (therefore better) simulated CII levels are obtained. For ammonia, the decrease is around -8.5% for all the considered emission factors in case S1, and -15.5% in case S2. For methanol, the corresponding reductions are around -6.0% and -11% . The differences between the two fuels are due to the applied increases of efficiency.

The effects of the variations in substitution rate (cases S3 and S4) are related to the contribution to emissions given by MGO and the relevant larger emission factors of the conventional fuel. The inverse relationship entailing higher simulated CII when SR is lower has been quantified. The largest variations in simulated CII, around 66% , are evident in the case of the TtW approach, as ammonia and

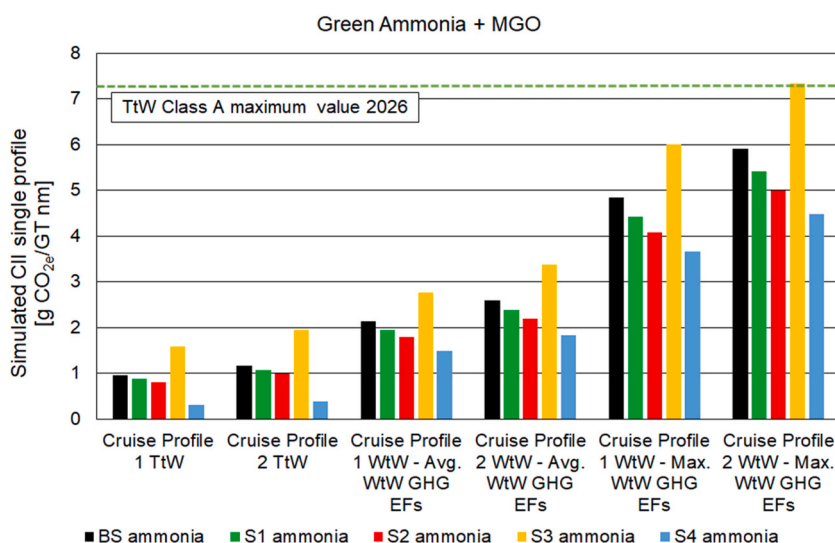


Fig. 11. Sensitivity analysis on Well-to-Wake GHG emissions for dual-fuel engines using green ammonia + MGO. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

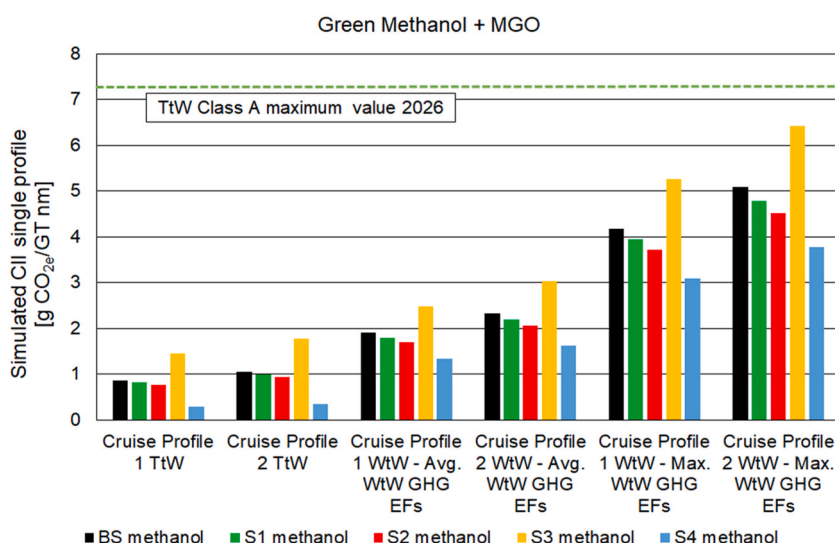


Fig. 12. Sensitivity analysis on Well-to-Wake GHG emissions for dual-fuel engines using green methanol + MGO. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

methanol emission factors are equal to 0 in this case. As the average and maximum WtW CO_2e emission factors for ammonia and methanol are quite close (Table 2), changes of simulated CII are consistently similar, around 30% for the average levels, and 25% for the maximum ones. Finally, variations do not depend on the cruise profiles.

Referring to absolute values, only the case of ammonia, cruise profile 2, with maximum value of WtW emission factors appears to be critical with reference to the selected threshold (TtW class A upper limit in 2026). All the other values are below this limit, both for ammonia and methanol.

7. Conclusions

The investigation about the definition of Well-to-Wake GHG emission factors and their application to a case study based on a cruise ship allowed to outline a range of interesting outcomes. For the analysis conventional and alternative fuels were selected (MGO, LNG, Bio-LNG, grey and green methanol, grey and green ammonia).

An extended literature on WtW GHG emission factors is available but relevant documents are significantly reduced when consistency criteria are applied on GHG emissions (CO_2 , CH_4 and N_2O), for the different fuels, together with a detailed description of

calculation procedure.

The largest data availability was observed for MGO and LNG, followed by an acceptable level for Bio-LNG, grey and green methanol. On the other side, limited information is reported for grey and green ammonia.

Following this first step, an application case based on two different cruise profiles was developed. For each of them a simulated Carbon Intensity Indicator was evaluated, considering three sets of emission factors (Tank-to-Wake, average Well-to-Wake and maximum Well-to-Wake) and comparing CII values with the current required standards.

Based on these calculations, the following remarks can be underlined.

- The advanced design of the selected ship allows to obtain the best CII rating (i.e., A) for all the fuels, proving that energy and Carbon Intensity Indicator rule's constraints are improving design solutions for fuel saving, rather than the adoption of alternative fuels.
- Simulated CII values for Cruise profile 2 is always higher (+21–22%) than values of Cruise profile 1. Profile 2 is characterised by a longer time spent in port (covering 43.2% of the time, versus 21.6% for profile 1) and by a shorter navigation time (55% vs. 77.2%), therefore it can be concluded that time at berth has a negative influence on the CII values.
- As expected, the application of WtW emission factors strongly affects the CII values for the different fuels, leading to low rankings for fossil and grey options. From the quantitative analysis carried out in the paper, it is evidenced how the green options are mandatory to comply with the decarbonization targets set by IMO and EU.
- The large variability of WtW CO_{2e} emission factors strongly suggests further investigations on their definition and the normalised procedure to assess them with a reliable and shared approach.
- Sensitivity analysis confirms the strong importance for the maximization of both engine efficiency and substitution rate for CII values reduction.

Future work will be focused on refining the available WtW emission factors, extending their definition also to other options (grey and green hydrogen). The further activity will also include data for pollutants such as NO_x, SO_x and PM, as well as energy required to produce the different fuels/energy vectors.

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Data availability statement

Data associated with this study is confidential, therefore they are not available and has not been deposited into a publicly available repository.

Ethics declarations

All participants provided informed consent to participate in the study.

CRediT authorship contribution statement

Giorgio Zamboni: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. **Filippo Scamardella:** Conceptualization, Investigation, Methodology, Supervision, Writing – original draft. **Paola Gualeni:** Conceptualization, Supervision, Validation, Writing – review & editing. **Edward Canepa:** Conceptualization, Project administration, Supervision, Writing – review & editing.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Giorgio Zamboni reports financial support was provided by Fincantieri Spa. Paola Gualeni reports financial support was provided by Fincantieri Spa. Edward Canepa reports financial support was provided by Fincantieri Spa.

Table A.1

List of references analysed for the definition of Well-to-Wake GHG emission factors.

References	Type of fuels	Emissions	Functional unit	Global Warming Potential	Life cycle inventory database/tool
[14]	Bio-methanol, Fossil methanol, E-methanol,	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	–	Literature review

(continued on next page)

Table A.1 (continued)

References	Type of fuels	Emissions	Functional unit	Global Warming Potential	Life cycle inventory database/tool
[15]	HFO, MDO, NG, FAME, HVO	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	–	Literature review (IEA Bioenergy)
[16]	HFO, MGO, LNG, RNG, Biodiesel, Methanol, H ₂ (liquid), Ammonia (liquid)	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	Literature review (IEA Bioenergy)
[18,41]	MGO, LNG, Methanol (NG), Bio-LNG, Bio-methanol, NG-ammonia, E-ammonia, H ₂ (NG), etc.	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	–	–
[38]	MGO, LNG, NG-ammonia, E-ammonia, LH ₂ (NG), E-LH ₂ , HFO	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/kWh shaft output	GWP100	Literature review
[39]	LSHFO, MDO, LNG, Bio-LNG, LH ₂ (w/o and with CCS), Ren LH ₂ , Methanol, biodiesel	CO ₂ , CH ₄ , N ₂ O, NO _x , SO _x , PM	g CO ₂ e/kWh shaft output	GWP100	Ecoinvent, ELCD
[40]	MDO, Bio-methanol (wood and waste stream), Bio-LNG, Biodiesel, E-methanol, E-LNG, E-ammonia, NG-ammonia, E-H ₂ , NG-H ₂	CO ₂	g CO ₂ /MJ fuel	–	–
[42]	HFO, LSFO, MGO, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	GREET
[43]	HFO, LNG, Methanol, bio-LNG, Bio-methanol	CO ₂ , CH ₄ , N ₂ O, NO _x , SO ₂ , PM ₁₀ , NH ₃ , NMVOC, CO	g CO ₂ e/MJ fuel	GWP100	ELCD, JEC
[44]	HFO, MGO, LNG, Bio-LNG, Methanol, Bio-methanol, HVO, Biodiesel	CO ₂ , CH ₄ , N ₂ O, NO _x , SO _x , PM _{2.5}	g CO ₂ e/MJ fuel	GWP100	Literature review
[45]	Ren Methanol, Methanol (NG), Bio-LNG, LNG, MDO, LH ₂ -NG, Ren LH ₂ , HFO, Biodiesel	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	–	from a 2014 DNV LCA study
[46]	HFO, MGO, Methanol (NG), Methanol (biomass)	CO ₂ , CH ₄ , N ₂ O, NO _x , SO _x	g CO ₂ e/MJ fuel	GWP100	Literature review, ELCD, JEC
[47]	HFO, MGO, LNG, Methanol (NG), Bio-methanol, Biodiesel, LBG, H ₂ (NG), Ren H ₂	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	DNV GL calculations, EU RED II
[48]	HFO, MGO, Rapeseed methyl ester (RME), Synthetic bio-diesel (BTL), LNG, Bio-LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	ELCD, JEC
[49]	HFO, Hydrogen, Ammonia	CO ₂ , CH ₄ , N ₂ O	emission per tonne-kilometre (g CO ₂ e/MJ fuel)	GWP500	GREET
[50]	MDO, Methanol, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	GREET, TEAMS
[51]	MDO, LNG, Bio-LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	Literature review
[53]	HFO, MGO, LNG, Bio-LNG, Methanol, Bio-methanol, Bioliquids, LH ₂ , HVO, FT	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/kWh shaft output	–	Literature review
[54]	HFO (w/o and with scrubber), MGO (w/o and with SCR), LNG (fossil), GTL (w/o and with SCR)	CO ₂ , CH ₄ , N ₂ O	1 t cargo transported 1 km with a roll-on-roll-off (g CO ₂ e/MJ fuel)	GWP100	ELCD, JEC
[55]	Biogas, Dimethyl ether, Ethanol, LNG, LPG, Methanol, Ammonia, Biodiesel	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	SimaPro
[56]	HFO, MGO, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/kWh shaft output	GWP100	OPGEE, GREET
[57]	H ₂	CO ₂ , CH ₄ , N ₂ O	emission per 1 kWh of energy	GWP100	Gabi
[58]	HFO, MGO, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	Gabi
[59]	HFO, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	Literature review
[60]	Diesel, electricity	CO ₂ , CH ₄ , N ₂ O, SO _x , NO _x , PM	g CO ₂ e/MJ fuel	GWP100	Gabi
[61]	LNG, Bio-LNG, Bio-methanol, NG-ammonia, E-ammonia, LH ₂ (NG), E-LH ₂ , Biodiesel	CO ₂	g CO ₂ /MJ fuel	–	Lloyd's Register and UMAS, 2020
[62]	HFO, LSFO, MGO, LNG	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/kWh shaft output	GWP100	Gabi, GREET, JRC
[63]	HFO, MDO/MGO, ULSD, LNG (fossil)	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	DOE, EPA
[64]	Bio-methanol, Fossil methanol, E-methanol, MGO	CO ₂ , CH ₄ , N ₂ O	emission for a voyage with a RoPax vessel travelling	GWP100	ELCD
[65]	LNG	CO ₂ , CH ₄ , N ₂ O	–	GWP100	GREET, GHGenius
[66]	MGO, VLSFO, HFO, LNG (fossil)	CO ₂ , CH ₄ , N ₂ O	g CO ₂ e/MJ fuel	GWP100	Greet
[67]	Methanol, Dimethyl ether, LNG, Hydrogen, Biodiesel, Electricity	CO ₂ , CH ₄ , N ₂ O	tons of CO ₂ e	GWP100	GREET
[68]	LNG, Methanol (NG), Biofuels	CO ₂ , CH ₄ , N ₂ O, NO _x , SO _x , PM	g CO ₂ e/kWh shaft output	–	Literature review
[69]	LNG, HFO, MGO, VLSFO	CO ₂ , CH ₄ , N ₂ O, SO _x , NO _x , PM	g CO ₂ e/kWh shaft output	GWP100	Gabi
[70]	HFO, LNG	CO ₂ , CH ₄ , N ₂ O	emission per “1 t of cargo transported for 1 km (1 tkm)” and “1	GWP100	ELCD, Ecoinvent

(continued on next page)

Table A.1 (continued)

References	Type of fuels	Emissions	Functional unit	Global Warming Potential	Life cycle inventory database/tool
[71]	HFO, LNG	CO ₂ , CH ₄ , N ₂ O, SO _x , NO _x	passenger transported for 1 km (1 pkm)'' g CO ₂ e/kWh shaft output	GWP100	GREET
[72]	HFO, biofuels	CO ₂ , CH ₄ , N ₂ O, NO _x , SO ₂	g CO ₂ e/MJ fuel	GWP100	Literature review
[73]	HFO, LNG, MDO, Biofuels	CO ₂ , CH ₄ , N ₂ O, SO _x , NO _x	g CO ₂ e/MJ fuel	GWP100	Literature review

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Abbreviations

AFR	Air-Fuel Ratio
CCS	Carbon Capture and Storage
CH ₄	Methane
CII	Carbon Intensity Indicator
CO ₂	Carbon Dioxide
DCS	Data Collection System
EEDI	Energy Efficiency Design Index
EEXI	Energy Efficiency Existing Ship Index
EF	Emission factor
GHG	Green House Gas
HFO	Heavy Fuel Oil
IMO	International Maritime Organization
LCA	Life Cycle Assessment
LHV	Lower Heating Value
LNG	Liquified Natural Gas
LPG	Liquified Petroleum Gas
Lwl	Length waterline
MDO	Marine Diesel Oil
MGO	Marine Gas Oil
N ₂ O	Nitrous Oxide
NO _x	Nitrogen Oxides
ODS	Ozone Depleting Substances
OPS	On-board Power Supply
PEM	Propulsive Electric Motors
SEEMP	Ship Energy Efficiency Management Plan
SMR	Steam Methane Reforming
SO _x	Sulphur Oxides
SR	Substitution Rate
TDC	Top Dead Centre
TtW	Tank-to-Wake
WHR	Waste Heat Recovery
WtT	Well-to-Tank
WtW	Well-to-Wake

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