

Maritime Energy Transition: Future Fuels and Future Emissions

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Abstract

The lifecycle greenhouse gas (GHG) emissions (Well-to-Wake) from maritime transport must be reduced by at least 50% in absolute values by 2050 to contribute to the ambitions of the Paris Agreement (2015). A transition from conventional fuels to alternative fuels with zero or lower GHG emissions is viewed as the most promising avenue to reach the GHG reductions. Whereas GHG and toxic pollutants emitted from the use of fossil fuels (heavy fuel oil (HFO) and marine gas/diesel oil (MGO/MDO)) are generally well understood, the emissions associated with the new fuel options are only now being measured and communicated. This review provides an outlook on fuels that could help shipping respond to the decarbonization effort including Liquefied Petroleum Gas (LPG), Liquefied Natural Gas (LNG), methanol, ammonia, and hydrogen. A quantification of the pollutants associated from the use of these fuels is provided and challenges and barriers to their uptake are discussed.

Keywords Greenhouse gas; Emissions; Maritime transport; Future fuels; Future emissions; Life-cycle assessment; Energy transition

1 Introduction

The downstream (Tank-to-Wake, TtW) greenhouse gas (GHG) emissions from maritime transport that are emitted from ships combustion engines are estimated at approximately one billion tons of carbon dioxide equivalents (CO_{2e}) annu-

ally (Buhaug et al., 2009; Faber et al., 2020; Lindstad et al., 2021; Smith et al., 2014). When the upstream (Well-to-Tank, WtT) GHG emissions from fuel production are included the total Well-to-Wake (WtW), or life-cycle emissions, increase to 1.25 – 1.5 billion tons of CO_{2eq} (Lindstad et al., 2020), which is 3% of the 50 billion tons of anthropogenic GHG emitted annually (BP, 2021).

In 2018, the International Maritime Organization (IMO) agreed to reduce GHG emissions, which includes carbon dioxide (CO₂), methane (CH₄) and nitrous oxide (N₂O), from international shipping by at least 50% by 2050 (relative to 2008) (IMO, 2018) as a pathway to reach the Paris Agreement goal to limit global warming to 1.5°C compared to pre-industrial levels (UN, 2015). Recent activities indicate that this target will most likely be revised, with a strong push to reduce GHG emissions by 100% by 2050 (Bush, 2022). There are several options (and their combinations) for the maritime industry to reach the required GHG reductions, including design and other technical improvements of ships, operational improvements, and, perhaps most promisingly, adopting energy carriers (fuels) with lower or zero GHG footprint (effectively moving away from the conventional use of fossil or carbon-based fuels) (Bouman et al., 2017). Considering that 99.5% of the current world fleet, which consists of approximately 110 700 vessels above 100 GT (not including inland waterways, non-merchant, and non-propelled vessels) is powered by diesel engines running on conventional marine fuel oils (such as heavy fuel oil (HFO) and marine gas/diesel oil (MGO/MDO)) (Figure 1), switching to fuels with lower or zero GHG emissions will be a disruptive transition for

Article Highlights

- Implementing renewably sourced zero carbon fuels, such as hydrogen and ammonia, is the most promising, and perhaps the only, option to deliver the desired greenhouse gas (GHG) reductions for the maritime industry.
- Although hydrogen produced from renewable sources can achieve a WtW GHG emission reduction of 79.9% compared to conventional fuels, if hydrogen is produced from NG, the WtW GHG emissions will contribute to 96.2% more GHG emissions compared to conventional fuels.
- Ammonia produced from renewable sources (green ammonia) can achieve a 71.0% GHG emission reduction, but if ammonia is produced from NG and the current N₂O emissions are not abated, the use of ammonia as a fuel will result in a WtW GHG emissions increase of 140.0%.
- Technical maturity, tank capacity and bunkering infrastructure are some of the key hurdles to overcome to implement ammonia and hydrogen across the worldwide fleet to realize a net-zero shipping future.

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the conservative industry (DNV, 2021; UNCTAD, 2021). As indication of the decarbonization efforts by ship owners, approximately 12% of current newbuilds are ordered with fuel systems that move away from conventional fuels (Figure 1), with an increase in use of fuels such as ammonia, hydrogen, methanol, Liquefied Petroleum Gas (LPG) and Liquefied Natural Gas (LNG).

At first glance, the use of carbon-free fuels, such as ammonia and hydrogen, are obvious candidates to reduce carbon dioxide (CO_2) emissions as the carbon-free molecules do not release CO_2 when combusted. It is also generally accepted that LNG combusted in the ship's engines delivers approximately 25% lower CO_2 emissions than conventional fuels (MGO and HFO) (Lindstad et al., 2020; Ushakov et al., 2019). However, these TtW emission reductions do not elucidate other issues arising from other pollutants that are released during combustion. For example, when one includes WtT estimates for the LNG supply chain (including extraction and transportation) and un-combusted methane (CH_4) from the ship's engine(s) (complete TtW), these additional emissions reduce and in the worst case negate any GHG benefits relative to HFO or MGO (Lindstad, 2019; Lindstad and Rialland, 2020). Furthermore, emissions of N_2O , a potent GHG with a Global Warming Potential (GWP) 273 times that of CO_2 on a 100-year timescale, formed in the combustion of ammonia can significantly contribute to CO_{2e} emissions (Zincir, 2022).

In an effort to compare the alternative fuels (LNG, LPG, methanol, hydrogen, and ammonia) being pursued by the shipping industry to reduce GHG emissions, there is first provided a summarized emission factor data (in both g/kWh and g/MJ) of all of the pollutant emissions (both toxic and GHG) that result from combustion of these fuels (complete TtW emissions); these values are compared against traditional bunker fuel (HFO) and diesel (MGO/MDO) (Tables 1 and 2). The emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are used to calculate CO_{2e} emissions as a metric to compare exhaust gas emissions based on their GWP on both a 20-year and 100-year perspective (Shine, 2009). The most recent GWP values provided by the International Panel on Climate Change (IPCC) in their 6th Assessment Reports (AR 6), (IPCC, 2022) are based on the most recent scientific work and therefore recommended as a charac-

terization factor of climate impact in life-cycle assessment (LCA) studies (Hauschild et al., 2013). Values for sulfur oxides (SO_x), nitrogen oxides (NO_x), ammonia (NH_3), particulate matter (PM), non-methane volatile organic compounds (NMVOC), and carbon monoxide (CO) emission values are also provided as they have both global climate effects and regional and local environment impacts on human health and nature (Lindstad et al., 2020). These TtW emissions are then presented with WtT emissions to provide a LCA summary of the alternative fuels (Table 3). In this way, one can clearly compare the GHG reduction potentials of LNG, LPG, methanol, hydrogen, and ammonia against HFO and MGO/MDO from both WtT and TtW perspectives.

There is also provided highlights of the key challenges to adopt alternative fuels in the shipping industry to put in context the difficulty in switching to these fuels. Typical key barriers include the retrofit cost (implementation of new or adaptation of existing machinery and storage), engine availability and technical maturity as an energy converter, increased and/or highly variable fuel prices (with unknown availability), lack of global bunkering infrastructure, increased tank capacity to store less energy-dense fuels (this is a substantial barrier for many alternative fuels to be used in deep-sea trading), and safety and handling considerations (particularly the currently unestablished rules and regulations) (DNV, 2021).

By first providing the most up-to-date and quantitative TtW emission factors of all the GHG and toxic pollutants that are released during combustion from alternative fuels, and then duly providing an LCA summary for complete WtW emission factors, one can weigh the GHG reduction potentials of LNG, LPG, methanol, hydrogen, and ammonia against the reality of implementing these alternative fuels across the global fleet with the highlighted key barriers to uptake in the shipping industry.

2 Future fuels and emissions

2.1 Liquefied natural gas (LNG)

There is a large interest in the use of Liquefied natural gas (LNG) in shipping to reduce emissions, including CO_2

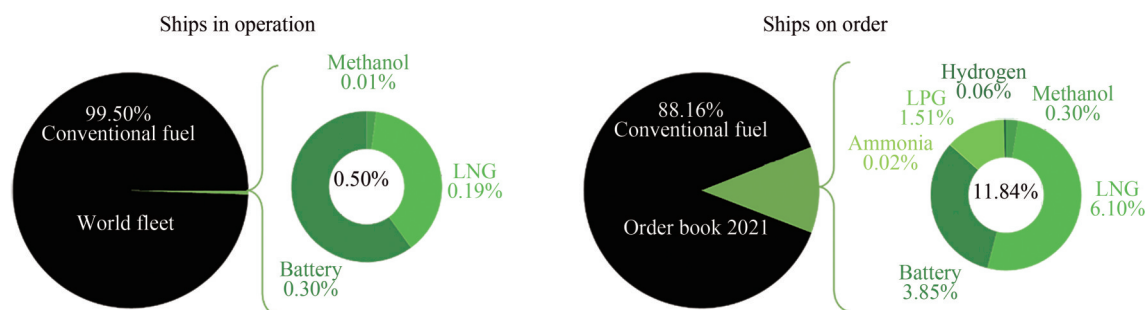


Figure 1 Uptake of alternative fuels for the world fleet (June 2021) (adapted from DNV, 2021)

Table 1 Tank-to-Wake (TtW) combustion emissions by fuel ($\text{g}_{\text{pollutant}}/\text{kWh}$)

Pollutant	HFO	MGO	LPG	LNG	Methanol	Hydrogen ²⁴	Ammonia ²⁵
CO ₂	561 ⁶	545 ¹¹	475 ¹⁶	418 ¹⁹	695 ²³	90 ²⁴	113 ²⁶
CH ₄	$1.08 \times 10^{-2,7}$	$1.02 \times 10^{-2,12}$	$1.00 \times 10^{-2,17}$	3.00 ²⁰	$2 \times 10^{-2,23}$	-	-
N ₂ O	$3.06 \times 10^{-2,8}$	$3.06 \times 10^{-2,13}$	$3.00 \times 10^{-2,17}$	$2.13 \times 10^{-2,21}$	-	-	1.95 ²⁶
SO ₂ ¹	2.00 ⁹	0.32 ¹⁴	0.60 ¹⁰	$3.00 \times 10^{-2,14}$	-	-	0.10 ²⁶
NO _x ²	14.4 ¹⁰	14.4 ¹⁴	12.9 ¹⁰	1.17 ¹⁴	6.5 ²³	4.0 ²⁴	28.2 ²⁶
NH ₃	$2.17 \times 10^{-3,9}$	$2.17 \times 10^{-3,9}$	-	-	-	-	10 ²⁷
PM _{Total}	0.67 ⁹	0.16 ¹⁴	0.20 ¹⁸	0.027 ¹⁴	0.093 ²³	0.015 ²⁴	0.035 ²⁶
NMVO _C ³	0.41 ⁹	0.43 ¹⁵	0.68 ¹⁰	0.38 ²²	1.6 ²³	0.30 ²⁴	20 ²⁷
CO	0.94 ⁹	0.73 ¹⁵	1.21 ¹⁸	1.86 ²²	3.7 ²³	0.11 ²⁴	50 ²⁷
CO ₂ e (100 year) ⁴	569	554	484	513	696	90	646
CO ₂ e (20 year) ⁵	569	554	484	671	697	90	628

Notes:

¹According to Annex VI of the International Convention for the Prevention of Pollution from Ships (MARPOL), the SO₂ emitted from HFO considers the limits of sulphur in the fuel oil used on board ships operating outside designated emission control areas to 0.50% m/m

²Pollutant abatement systems (e.g., SCR) not included

³Non-methane volatile organic compounds

⁴CO₂e (100 year) [g/kWh] = (CO₂ (g/kWh) * 1 (GWP_{CO₂})) + (CH₄ (g/kWh) * 29.8 (GWP_{CH₄})) + (N₂O (g/kWh) * 273 (GWP_{N₂O}))

⁵CO₂e (20 year) [g/kWh] = (CO₂ (g/kWh) * 1 (GWP_{CO₂})) + (CH₄ (g/kWh) * 82.5 (GWP_{CH₄})) + (N₂O (g/kWh) * 264 (GWP_{N₂O}))

⁶Source: Calculated from (Comer, 2021): TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh), consistent with (Lindstad et al., 2021): TtW (g/kWh) = 558

⁷Source: Calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021)

⁸Source: Calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021)

⁹Source: Calculated from TtW(g/MJ) reported from (Brynnolf et al., 2014a)

¹⁰Source: (Kristenen, 2015)

¹¹Source: Calculated from (Comer, 2021): TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh), consistent with (Lindstad et al., 2021): TtW (g/kWh) = 541

¹²Source: Calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021); consistent with (Gilbert et al., 2018): TtW (g/kWh) = 1.00×10^{-2}

¹³Source: Calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021); consistent with (Gilbert et al., 2018): TtW (g/kWh) = 2.60×10^{-2}

¹⁴Source: (Faber et al., 2020; Gilbert et al., 2018)

¹⁵Source: Calculated from TtW(g/MJ) reported from (S. Brynnolf et al., 2014)

¹⁶Source: (Lindstad et al., 2021)

¹⁷Extrapolated from (Lindstad et al., 2021) and consistent with (Comer, 2021)

¹⁸Calculated from (Wagemakers and Leermakers, 2012)

¹⁹Source: Calculated from (Comer, 2021): TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh), consistent with (Gilbert et al., 2018): TtW (g/kWh) = 412, and with (Lindstad et al., 2021): TtW (g/kWh) = 404

²⁰Conservative report of most common LNG engines (Otto-SS and MS) calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021): LNG-Diesel = 0.2 g/kWh; LNG-Otto-SS = 2.5 – 3.5g/kWh, LNG-Otto-MS = 5.5 – 6.5g/kWh; consistent with (Winnes et al., 2020)

²¹Source: Calculated (TtW (g/kWh) = TtW (g/g_{fuel}) * SFC (g/kWh)) and reported from (Comer, 2021); consistent with (Gilbert et al., 2018) : TtW (g/kWh) = 1.60×10^{-2}

²²Source: (Winnes et al., 2020)

²³Source: (Fridell et al., 2021) at 80% engine load

²⁴85% H₂ energy share with diesel in an inline-4 heavy-duty hydrogen (port injection)-diesel (direct injection) dual-fuel engine (Dimitriou et al., 2018); consistent with (Lilik et al., 2010) and (Dimitriou et al., 2018)

²⁵95% NH₃/ 5% MDO energy share (Zincir, 2022)

²⁶Source: (Zincir, 2022)

²⁶Source: (Hansson et al., 2020b)

(Burel et al., 2013). LNG consists mainly of methane and is favored since the emissions of air pollutants SO_x, PM and NO_x are significantly lower from LNG engines compared to traditional marine diesel engines burning HFO or MGO/MDO (Brynnolf et al., 2014a). The low sulfur content of LNG results in low SO_x emissions (although the sulfur content of the pilot fuel can contribute to SO_x emis-

sions), and corollary, PM emissions are low (the absence of polyaromatics and combustion specifics also contribute to low PM emissions). The lower NO_x emissions from LNG compared to HFO is mainly a result of reduced peak temperatures during combustion (Woodyard, 2009), and although can reach Tier III levels, are still significant. Also, CO₂ emissions per energy unit is relatively low from LNG

Table 2 Tank-to-Wake (TtW) combustion emissions by fuel ($\text{g}_{\text{pollutant}}/\text{MJ}$)¹

Pollutant	HFO	MGO	LPG	LNG	Methanol	Hydrogen	Ammonia
LCV ² (MJ/kg)	40.2 ⁶	42.7 ⁶	46.3 ¹¹	48 ⁶	19.9 ⁶	120 ¹⁵	18.6 ¹⁷
SFC ³ (g/kWh)	180 ⁷	170 ⁷	155 ¹²	152 ⁷	441 ¹⁴	57 ¹⁶	388 ¹⁸
CO ₂	77.5	75.1	66.2	57.3	79.2	13.1	15.7
CH ₄	1.49×10^{-3}	1.41×10^{-3}	1.39×10^{-3}	0.41	2.28×10^{-3}	-	-
N ₂ O	4.23×10^{-3}	4.22×10^{-3}	4.18×10^{-3}	2.92×10^{-3}	-	-	0.27
SO ₂	0.28 ⁸	4.41×10^{-2}	8.36×10^{-2}	4.11×10^{-4}	-	-	-
NO _x	1.99	2.04	1.80	0.16	0.74	0.58	3.91
NH ₃	$3.00 \times 10^{-4,8}$	$3.00 \times 10^{-4,8}$	-	-	-	-	1.39
PM _{Total}	$9.3 \times 10^{-2,8}$	2.20×10^{-2}	2.79×10^{-2}	3.70×10^{-3}	1.06×10^{-2}	2.19×10^{-3}	-
NMVOC	0.056 ⁸	0.059 ¹⁰	9.48×10^{-2}	5.21×10^{-2}	0.2	4.39×10^{-2}	2.8
CO	0.13 ⁸	0.1 ¹⁰	0.17	0.25	0.52	1.65×10^{-2}	6.9
CO _{2e} (100 year) ⁴	78.7 ⁹	76.3 ⁹	67.4 ¹³	70.3	79.3	13.1	89.5
CO _{2e} (20 year) ⁵	78.7	76.3	67.4	92.0	79.4	13.1	87.0

Notes:

¹All combustion emission values (g/MJ) calculated (unless indicated as reported) from values reported in Table 1 (TtW combustion emissions by fuel (g/kWh)), whereby:

$$\frac{\text{g}_{\text{pollutant}}}{\text{MJ}} = \frac{\text{g}_{\text{pollutant}}}{\text{kWh}_{\text{engine output}}} \times \text{engine efficiency} \times \frac{\text{kWh}_{\text{delivered to engine}}}{3.6 \text{ MJ}} = \frac{\text{g}_{\text{pollutant}}}{\text{kWh}_{\text{engine output}}} \times \frac{\text{kWh}_{\text{engine output}}}{\text{g}_{\text{fuel}}} \times \frac{\text{g}_{\text{fuel}}}{\text{MJ}}$$

²Lower Calorific Value

³Specific Fuel Consumption

⁴CO_{2e} (100 year) [g/MJ] = (CO₂ (g/MJ) * 1 (GWP_{CO₂))) + (CH₄ (g/MJ) * 29.8 (GWP_{CH₄))) + (N₂O (g/MJ) * 273 (GWP_{N₂O}))}}

⁵CO_{2e} (20 year) [g/MJ] = (CO₂ (g/MJ) * 1 (GWP_{CO₂))) + (CH₄ (g/MJ) * 82.5 (GWP_{CH₄))) + (N₂O (g/MJ) * 264 (GWP_{N₂O}))}}

⁶Source: (Faber et al., 2020; Lindstad et al., 2021)

⁷Source: (Comer, 2021; Faber et al., 2020)

⁸Source: (Brynolf et al., 2014a)

⁹Consistent with (Al-Aboosi et al., 2021; Pavlenko, 2020)

¹⁰Source: Reported from (Brynolf et al., 2014b)

¹¹Source: ("Resolution MEPC.281(70) – Amendments to the 2014 Guidelines on the Method of Calculation of the Attained Energy Efficiency Design Index (EEDI) For New Ships (Resolution MEPC.245(66), as Amended by Resolution MEPC.263(68))-(Adopted on 28 October 2016)," 2016)

¹²Source: ("MAN B&W ME-LGIP," 2020)

¹³Consistent with (Nikolaou et al., 2017)

¹⁴Source: (Fridell et al., 2021)

¹⁵Source: (Gilbert et al., 2018; Lindstad et al., 2021)

¹⁶Source: (Gilbert et al., 2018)

¹⁷Source: (Herdzik, 2021; Lindstad et al., 2021)

¹⁸Source: (Zincir, 2022)

combustion due to more chemically bound energy per carbon content in natural gas than in fuel oil (Winnes et al., 2020).

The marine engines operating on LNG (or equally Liquefied Biogas, LBG) are very often either a low-pressure or high-pressure type, with the low-pressure dual fuel engines being the most used on ships that are not LNG carriers. The low-pressure engines are either spark ignited (SI) (gas only) or use a dual fuel technology where a pilot fuel injection is used for ignition (referred to as LPDF or LNG Otto, medium speed (MS) and slow speed (SS)). Another type of dual fuel engine is the high-pressure engine that uses LNG as fuel in a diesel combustion cycle (HDPF or LNG diesel).

The drawback from the combustion in the low-pressure engines is a 2.3% – 4.1% slip of unburnt methane through

the combustion process for the most common LNG fueled-engines that are in operation today (Stenersen and Thonstad, 2017). The slip, measured as CO_{2e} from a 100-year perspective, is large enough to result in CO_{2e} emissions from LNG to be comparable to those from MGO (Pavlenko, 2020), and when measured from a 20-year perspective, results in emissions of CO_{2e} to exceed those from MGO (Winnes et al., 2020). The methane slip from ships engine contributes to the world's increasing global methane emissions, where the rising atmospheric methane levels represent a major challenge in the effort to limit global warming (Lindstad et al., 2020).

In a comparison between the engine types, the methane slip is lower from a HPDF engine (LNG diesel) (0.2 –

Table 3 Emission factors (WtT, TtW and WtW) of different shipping fuels (g CO_{2c}/MJ of fuel) and comparison to HFO/MGO (conventional shipping fuels) (GWP100)

Supply chain	HFO	MGO	LPG	LNG	NG	Methanol		Hydrogen		Ammonia	
						NG	Renewable	NG	Renewable	NG	Renewable
Well-to-Tank (WtT)	9.0 ¹	12.8 ²	7.2 ³	9.7 ⁴	20.4 ⁵	4.5 ⁶	159 ⁷	9.7 ⁸	121 ¹⁰		
WtT Difference to HFO	-	+42.2%	-20.6%	+7.6%	+126.7%	-50.0%	1 667.7%	+7.8%	1 244.4%		
Tank-to-Wake (TtW)	78.7	75.0	65.5	70.3	79.3	13.1	13.1	15.7 – 89.5 ⁹	15.7 – 89.5 ⁹		
TtW Difference to HFO	-	-4.7%	-16.8%	-10.7%	0.71%	-83.4%	-83.4%	-80.0% – +13.7%	-80.0% – +13.7%		
Well-to-Wake (WtW)	87.7	87.8	72.7	80.0	99.7	17.6	172.1	25.4 – 99.2	25.4 – 210.5		
WtW Difference to HFO	-	+0.1%	-17.2%	-8.8%	+13.6%	-79.9%	+96.2%	-71.0% – +13.1%	+55.9% – +140.0%		

Notes:¹Source: (Al-Aboosi et al., 2021) = 9.0; (Nikolaou et al., 2017) = 9.8; (Comer, 2021) = 10.8²Source: (Al-Aboosi et al., 2021) = 12.8; (Nikolaou et al., 2017) = 12.7; (Comer, 2021) = 13.6³Source: (Nikolaou et al., 2017)⁴Source: (Comer, 2021); consistent with (Brynnolf et al., 2014a) = 9.3⁵Source: (Brynnolf et al., 2014a)⁶Source: (Ozawa et al., 2017)⁷Source: Calculated from (Lindstad et al., 2021): WtT (g/kWh) = 1 086; consistent with (Ozawa et al., 2017)⁸Source: (Al-Aboosi et al., 2021); consistent with (Lindstad et al., 2021)⁹Range reported for 0 g/kWh and 1.95 g/kWh (Table 1) N₂O emissions, respectively¹⁰Source: Calculated from (Lindstad et al., 2021): WtT (g/kWh) = 874; consistent with (Al-Aboosi et al., 2021)

0.4 g/kWh) than a LPDF engine (LNG Otto) (average emission factors are reported as 5.5 – 6.9 g/kWh for LPDF MS (LNG Otto MS) and 2.5 – 3.2 g/kWh for LPDF SS (LNG Otto SS)) (Comer, 2021; Winnes et al., 2020). This is mainly a result of burning the fuel directly upon injection during the compression stroke in a HPDF engine, whereas a LPDF engines compress an air/fuel mixture (Ushakov et al., 2019). These emission factors will also change at different load conditions and from different engine manufacturers.

2.2 Liquefied petroleum gas (LPG)

Liquefied petroleum gas (LPG or LP-gas) consists of propane, propylene, butane, and butylenes (US EPA, 2020). Although the emissions from the use of LPG onboard a vessel have not been reported to date, it is known that gaseous pollutants such as NO_x, CO, and organic compounds are produced during combustion as are small amounts of SO₂ and PM. LPG combustion results in lower CO₂ emissions compared to oil-based fuels due to its lower carbon to hydrogen ratio (Nikolaou et al., 2017), but the CO₂ emissions are higher than that of LNG. Unburnt fuel emissions can also be released from LPG combustion, including propane (GWP100 = 0.02), n-butane and isobutane (GWP100 butane = 0.006) (IPCC, 2022), although any slip of un-combusted fuel through the engine would result in less GHG emissions for LPG than for LNG.

2.3 Methanol

Methanol is also a potential alternative fuel for shipping. It is a liquid at standard temperature and pressure,

which makes handling easier in comparison to LNG (Brynnolf et al., 2014b). On an industrial scale, methanol is predominantly produced from natural gas reforming and distilling the resulting mixture (Riaz et al., 2013). Methanol can also be produced from renewable resources, enabling lower WtT GHG emissions in the transition to non-fossil fuels (Fridell et al., 2021).

Recently, emissions of exhaust gases and PM from a dual fuel marine engine using methanol as fuel with MGO as pilot fuel have been reported for an operating ferry (Fridell et al., 2021). It was determined that the emission factor for NO_x was between 6.5 and 12.3 g/kWh, which is lower than what is typically found for MGO, but does not reach the Tier III limit. The emissions of CH₄ was determined to be 0.020 g/kWh, which is low when compared to the 5.5 – 6.9 g/kWh reported for dual fuel LNG engines of similar type (Stenersen and Thonstad, 2017). The PM emission (as mass of particles) was measured as approximately 0.1 g/kWh, which is lower than what is normally reported when using MGO as fuel, although there is a significant range in results from MGO reported in the literature (from 0.1 to 0.4 g/kWh) (Winnes et al., 2016). The black carbon (BC) represented approximately 17% of the mass of the PM in the data reported and the BC emissions are also lower than what is expected from MGO (Fridell and Salo, 2016). Furthermore, the measured emissions of THC and NMHC were both 1.6 g/kWh, which is higher than what has been reported when using fuel oil in a medium speed engine (approximately 0.2 g/kWh) (Cooper and Gustafsson, 2004). Although emissions of aldehydes are a concern for alcohol fuels, the emission factor measured for formaldehyde was 4.9×10^{-4} g/kWh, which is well below the US HD limit of

0.013g/kWh (“Worldwide Emissions Standards Heavy Duty and Off-Highway Vehicles,” 2016). Importantly, it was also determined that the emission factor of CO₂ was 28% higher than the use of MGO.

2.4 Hydrogen

Hydrogen has been attracting attention across all energy sectors as a clean and flexible energy carrier with perceived zero GHG emissions (World Economic Forum, 2022). Hydrogen can be produced from hydrocarbon feedstocks via chemical processes (e.g., steam reforming of NG and coal gasification), and by using electricity to electrolyse water (Holladay et al., 2009; Navarro et al., 2007). “Renewable hydrogen” is produced using renewable energy or electricity sources that results in a decrease or zeroing of the GHG emissions (Barbir et al., 2016). At the other end of the supply chain, hydrogen can be consumed by diverse end-use applications including fuel cells and internal combustion engines (Ozawa et al., 2017).

Hydrogen combustion does not produce CO₂ (or other greenhouse gases), CO, HCs, SO_x, smoke, lead (or other toxic metals), sulphuric acid, ozone (or other oxidants), benzene (or other carcinogenic compounds), or formaldehydes (Masood et al., 2007). Instead, its main product of combustion is water (Bose and Maji, 2009). There can be, however emissions of CO, CO₂ and HCs in exhaust gas because of the burning of lube oil and pilot fuel that is required for combustion (Bose and Maji, 2009). The only pollutant is NO_x, which is due to high combustion temperature in hydrogen fuelled engines; the exhaust gas temperature for hydrogen enrichment is 505 °C at 80% load whereas that of diesel is 260 °C (Bose and Maji, 2009).

The application of hydrogen injection in internal combustion engines was proposed in the 1970s (Pan et al., 2014) and can be dated back two-hundred years (Cecil, 1822). Many studies have implemented the use of hydrogen as a fuel in SI engines (Haragopala Rao et al., 1983), but these studies illustrated issues with backfire and knocking problems at high loads due to the spontaneous combustion of hydrogen, as well as a substantial drop in power output (Pan et al., 2014). Nevertheless, the implementation of hydrogen in SI engines has demonstrated excellent energy conversion with extremely low harmful emissions (Verhelst et al., 2006; White et al., 2006). Because of hydrogen’s high self-ignition temperature (576 °C), it is not possible to use hydrogen directly in compression ignition (CI) engines as fuel (Bose and Maji, 2009), and an energy source is needed to provide ignition (Gomes Antunes et al., 2009). Combustion triggering devices such as installation of glow plugs in the combustion chamber has been used, but more widely investigated and implemented is the addition of a lower auto-ignition fuel to the combustion chamber (Bose and Maji, 2009). Hydrogen can be used in small energy share ratios for improving the engine’s per-

formance and provide reductions in carbon, smoke and NO_x emissions, or can be used in high energy share ratios with the (diesel) fuel injected close to the engine’s top dead centre to act as the combustion trigger (Dimitriou et al., 2018). Although work has been reported for cases with hydrogen energy share ratio to be less than 5% or even more than 95%, most demonstrations investigate the effects of hydrogen energy share ratios between 10 and 40% (Dimitriou et al., 2018).

A recent review of H₂ supply in CI engines concludes that the use of H₂ as an energy carrier provides significant reduction in HC, CO, CO₂ and smoke in comparison to conventional fuels, but NO_x formation was a significant issue (Dimitriou and Tsujimura, 2017). In one example, hydrogen fuel (0-98% energy share ratio) was tested at low and medium operating loads in a heavy-duty hydrogen-diesel dual-fuel engine (Dimitriou et al., 2018). At medium load (with a maximum of 85% H₂ energy share ratio), the CO emission was reduced by up to 88%, the CO₂ emission was decreased by up to 84% (compared to diesel), the soot formation was up to 87% reduced, and the THC were at the same level (compared to diesel) for the dual-fuel operation. However, NO_x emission increased four times higher than the conventional engine due to the high energy content of hydrogen fuel. Similar results were reported when the energy share of hydrogen co-combusted with diesel was changed in the range from 0 to 30% in a single-cylinder 4-stroke diesel dual-fuel engine (Jamrozik et al., 2020). The addition of up to 25% hydrogen to the CI engine resulted in an 85% reduction in soot emissions, 57% reduction in CO, and 27% reduction in CO₂. The disadvantage of using hydrogen as a fuel for a CI engine was increase in HC emissions and a significant increase in NO emissions (by over 80%).

2.5 Ammonia

Towards meeting the IMO’s goals, the use of ammonia as a shipping fuel is gaining significant interest because, like hydrogen, it is a carbon-free molecule and will not produce CO₂ when combusted (Al-Aboosi et al., 2021; Hansson et al., 2020a). However, it is important to account for all of the emissions emitted during combustion, as other significant GHGs, such as N₂O, are known to be emitted in the exhaust gas from the use of ammonia as a fuel (Zincir, 2022). Furthermore, the emissions associated with the use of pilot fuels, which are required for combustion as ammonia has a high resistance to autoignition, can produce CO_{2e} emissions and need to be considered.

Although ammonia has been used in combustion engines since the second world war, there are a limited number of combustion tests (with emission data) published. Ammonia has rather poor ignition and combustion properties and an ignition fuel is needed for both CI engines (e.g., diesel oil, methanol or dimethyl ether (DME) (Gross and Kong, 2013;

Pochet et al., 2017; Reiter and Kong, 2011, 2008) and SI engines (e.g., hydrogen or alcohols (Frigo and Gentili, 2013; Mørch et al., 2011)) (Hansson et al., 2020b; Rehbein et al., 2019). In the CI engine application it was found that the successful approach was to supply ammonia vapor to the air intake system and use diesel fuel to provide ignition energy (Pearsall and Garabedian, 1968). The other approach of directly injecting liquid ammonia into the cylinder without using diesel fuel was not successful even though the engine compression ratio was increased to 30 : 1.

The available tests on combustion engines show issues with ammonia slip (Bro and Pedersen, 1977; Reiter and Kong, 2011), NO_x (Frigo and Gentili, 2013; Gray et al., 1966; Gross and Kong, 2013; Mørch et al., 2011; Ryu et al., 2013) and N_2O (Pochet et al., 2017) emissions and potentially emissions of CO and hydrocarbons (Gross and Kong, 2013; Ryu et al., 2013) (depending on pilot fuel). Ammonia that is released into the atmosphere can have health risks (if at high concentrations) and contributes to eutrophication. Emissions of N_2O are of significant concern due to its high GWP. Recently, a case study of the environmental and economic effects of an ammonia-diesel dual-fuel marine engine onboard a general cargo ship has been reported (Zincir, 2022). There were three fuel options in the study: 100% MDO, 60% NH_3 /40% MDO, and 95% NH_3 /5% MDO (this fraction is the highest energy fraction for the stable combustion of the ammonia-diesel dual-fuel engines in the literature). It was reported that the SO_x and PM emissions were decreased up to 95% by ammonia usage. The NO_x emissions were 19.4% lower than MDO at 60% NH_3 energy fraction but increased 133.1% at 95% NH_3 energy fraction. Although it was reported that blue and solar green ammonia comply with IMO2030 CO_{2e} reduction target of 40% and green ammonia (from wind energy) complies with IMO2050 CO_{2e} reduction target of 70%, the full TtW emissions, including the N_2O emissions and carbon-based emissions from the pilot fuel, were not taken into consideration. Importantly, the N_2O emissions of the ammonia-fueled engines with 60% and 95% energy fractions were calculated as 1.55 g/kWh and 1.95 g/kWh, respectively (calculated using values reported by Yousefi et al., 2022). The NO_x and N_2O emissions can likely be handled with after treatment systems (achieving Tier III NO_x values and near zero N_2O values), either three-way catalyst (TWC) if the combustion is stoichiometric or Selective Catalytic Reduction/Exhaust Gas Recirculation (SCR/EGR) for lean combustion. However, the high fraction of the pilot fuel (specifically the emissions that result from the pilot fuel), the ammonia slip, and the N_2O emissions are factors that need to be addressed (Hansson et al., 2020b).

3 Emissions discussion

The TtW combustion emissions (i.e., onboard emissions)

for LPG, LNG, methanol, hydrogen, and ammonia are presented in Table 1 ($g_{\text{pollutant}}/\text{kWh}$) and Table 2 ($g_{\text{pollutant}}/\text{MJ}$); the emission factors for HFO and MGO are shown for comparison. The emissions of carbon dioxide (CO_2), methane (CH_4) and nitrous oxide (N_2O) are used to calculate CO_{2e} emissions as a metric to compare exhaust gas emissions based on their GWP on both a 20-year and 100-year perspective (Shine, 2009).

For LPG, the CO_2 emissions are 13% and 15% less than MGO and HFO, respectively, and with lower emissions of SO_x and PM; NO_x and CO remain similar to the conventional fuels. Although CO_2 emissions for LNG are reduced by 25% when compared to HFO, including the conservative value of 3 g/kWh of methane slip (reflecting the most common LNG engines of Otto-SS and MS, in which $\text{LNG-Otto-SS} = 2.5 - 3.5$ g/kWh and $\text{LNG-Otto-MS} = 5.5 - 6.5$ g/kWh) detract from the CO_{2e} reduction potential of the fuel; lower values of SO_x , NO_x , and PM are still advantageous for LNG. Methanol has little advantage over HFO/MGO other than lower SO_x and PM values, but the higher CO_2 and CH_4 emissions nullify any CO_{2e} reduction potential. The emission factors reported for hydrogen considers an 85% H_2 energy share with diesel in an inline-4 heavy-duty hydrogen (port injection)-diesel (direct injection) dual-fuel engine (Dimitriou et al., 2018). The benefits of hydrogen are clear (83% CO_{2e} reduction), with reduction or removal of most pollutants, other than CO_2 (from the pilot fuel) and high NO_x emissions. Similar to hydrogen, the emissions factors reported for ammonia considers a 95% NH_3 /5% MDO energy share (Zincir, 2022). Although the CO_2 reduction in comparison to HFO/MGO is 80%, including the N_2O emissions surpasses the CO_{2e} emissions for HFO/MDO; the high NO_x and HC emissions are also of concern. The TtW combustion emission factors for all considered fuels are combined with WtT emissions to provide a LCA summary of the alternative fuels (Table 3).

Considered on a lifecycle perspective, LPG production is associated with lower emissions than oil-based fuels. The combination of low production and combustion emissions yields an overall GHG emissions reduction of 17.2% compared to HFO or MGO (consistent with Nikolaou et al., 2017). For LNG, by including a conservative estimate of methane slip in the TtW emissions, the overall GHG emissions reduction is only 8.8% compared to HFO or MGO. Methanol, overall, has higher GHG emissions (13.6%) than the conventional fuels. If hydrogen is produced from a renewable source (hydro, wind or solar), the WtW GHG emission can be reduced by 79.9%; (Bicer and Dincer, 2018) reported a 40% decrease in GHG emissions per tonne-kilometre when hydrogen was used as dual fuel with heavy fuel oils (50%). Unfortunately, if hydrogen is produced from natural gas, as is common practice today, the use of hydrogen as a marine fuel contributes to 96.2% more GHG emissions than the use of conventional fuels. An interesting trend is calculated for ammonia: even if am-

monia is produced from a renewable source (green ammonia), the use of ammonia can reduce GHG emissions by 71% if N₂O emissions are completely removed nearing the advantages of hydrogen, otherwise will contribute to 13.1% GHG emissions; (Bicer and Dincer, 2018) reported a 30% decrease in GHG emissions per tonne-kilometre when ammonia was used as dual fuel with heavy fuel oils (50%). If ammonia is produced from natural gas (brown ammonia), the WtW GHG emissions increase by 140.0% including N₂O emissions and 55.9% without including N₂O emissions; note that although the production of blue ammonia (produced from fossil sources with carbon capture) results in 85% less CO₂ emissions than brown variants, only green ammonia can provide the up to 71% GHG emission reduction and is a zero-carbon fuel (Brinks and Chryssakis, 2022).

4 Challenges and barriers to uptake

Table 4 identifies seven key challenges in the uptake of alternative fuels identified above for shipping.

4.1 Retrofit cost

In order to maintain comparability across all fuels, one category of vessels is presented: LR1 tankers. The retrofit

costs are based on the American Bureau of Shipping's (ABS) MarE-fuel study, published in late 2021.

On the higher end, LNG's retrofit cost of \$26.5 million compares to a less costly retrofit for a methanol operation at \$15 million. Both LPG and ammonia have similar retrofit costs with \$18.5 million and \$20 million, respectively. A hydrogen retrofit cost is not included as none have been identified for this vessel type.

4.2 Engine availability

Engine technologies for LNG, LPG and methanol are readily available today. Methanol engines today are developed by MAN and WinGD's engine is expected to be available from 2024. The first ammonia engine will be ready end of 2024 (developed by MAN Energy Solutions). WinGD and Wartsila are also working on ammonia engines to be delivered in 2025. For hydrogen, it is estimated that the first engines for this vessel type will only be available beyond 2030. It is also worth noting that engine manufacturers, such as MAN, have developed innovative dual-fuel two-stroke engines that can run on LNG, LPG, ethane and methanol nearly interchangeably (Anner, 2022); fuel-agnostic engine platforms, which offer different versions of the same base engine with unique cylinder heads designed to accommodate a different low or zero carbon fuel, are also being pursued in addition to fuel flexible en-

Table 4 Key challenges for the uptake of alternative fuels for shipping

Category	LNG	LPG	Ammonia	Methanol	Hydrogen
Retrofit Cost (LR1) (in \$m) ¹	26.5	18.5	20	15	Unknown
Engine Availability	Yes	Yes	2024	Yes	2030+
Technology Maturity	Mature	Mature	Immature	Immature	Immature
Fuel Price (\$/mt) ²	1 200	590	Natural Gas: 770 Renewable: 700	Grey: 470 Green: 650	Natural Gas: 2 000 Renewable: 3 500 – 7 000
Bunkering and Tank Infrastructure	Existing	Only LPG carriers use cargo for fuel	Not established (ability to piggyback on LPG infrastructure)	Not established (technically feasible to piggyback on liquid infrastructure)	Not established
Tank Capacity ³	1.6×	1.5×	3.1×	2.3×	4.2×
Safety and Handling Considerations	Liquefaction @ -160 °C	Liquefaction @ -33 °C	Liquefaction @ -33 °C (safety Ignition fuel required)	Liquid at ambient temp and pressure; inert nitrogen gas needed requires very clean tanks as it is colorless	Liquefaction @ -253 °C

Notes:

¹Retrofit costs are based on American Bureau of Shipping (ABS) MarE-fuel study, link: <https://orbit.dtu.dk/en/projects/electro-fuels-for-long-range-maritime-transport>

²Prices for green methanol, green ammonia and green hydrogen are based on Trafigura market analysis and project reviews. All prices used in this table are indicative (<https://www.methanol.org/wp-content/uploads/2020/04/Nitrogen-Blanketing-for-Ships.pdf>). Pricing assumptions: Natural Gas and Renewable – determine feedstocks used in the process, agnostic of technology (SMR, ATR, Alkaline, PEM...); LNG Singapore cal 2023; LPG Singapore cal 2023; Methanol – grey spot Singapore and green is based on production cost modelling; Ammonia Far East cal 2023 is 700 vs. USG is 240 for cal 2023 (green based on production cost modelling); Hydrogen – grey USG today, green based on production cost modelling

³Tank Capacity is based on low heating values in MJ/L vs. VLSF – share values

gines that can run on multiple fuels (White, 2022). Existing optimizations of diesel engines (Altosole et al., 2017; Tadros et al., 2019) and application of established after-treatment exhaust systems (Lu et al., 2022) can be applied to future engine developments using alternative fuels to provide the most sustainable engine technologies (Triviza et al., 2022).

4.3 Technology maturity

Both LNG and LPG use mature technology, with approximately 1,050 LNG and 37 LPG vessels in operation today (according to Clarkson's research). Conversely, methanol has not been deployed to the same scale with only 16 vessels deployed and 23 on order. Both ammonia and hydrogen have the lowest technology maturity at this stage compared to the other alternative fuels.

4.4 Fuel price

Price visibility is a key challenge for the renewable fuels. Fuels such as ammonia, methanol and hydrogen are not as readily traded as their counterparts. As much as possible the fuels are priced based on the same delivery location in Singapore. In addition, their renewable production pathway is not readily priced, heavily depending on current project development. As a result, renewable pathways are priced based on production cost in this analysis. These prices should only serve as indicative for the purpose of this comparative exercise.

Fuel prices (June 2022) are presented in \$/1 000 MJ to compare fuel prices adjusted for energy density and can be parallelly compared to prices in \$/mt (Table 5).

Using Very Low Sulphur Fuel (VLSF) oil as a reference to compare against alternative fuels, LPG is more cost-effective than VLSF based on equal energy density. Meanwhile, LNG and ammonia are expected to be approximately 50% and 150% more expensive than VLSF, respectively. Methanol would be similar to LNG, ranging from 50% to 100% more expensive than VLSF. Hydrogen's cost compared to VLSF depends on its feedstock, with it being competitive if produced from gas or 80% to 260% more expensive otherwise.

4.5 Bunkering and tank infrastructure

In terms of ease of adoption, LNG is the most broadly used and possesses existing global bunkering and infrastructure. LPG is almost wholly used on LPG carriers only. Today there is very limited (if any) bunkering and infra-

structure for methanol, ammonia, and hydrogen. Methanol can technically use existing liquid infrastructure whereas ammonia can "piggyback" on LPG infrastructure. Today both methanol and ammonia are waterborne traded. Ammonia traded volumes are approximately 20 million tonnes per annum and are even larger for methanol, both with existing handling and safety considerations in use today which will need to be transposed to the bunkering industry.

4.6 Tank capacity

Tank capacity was used as a measure for space requirements on board. The size of the tanks directly affects the ease of retrofitting and, consequently, the adoption of the fuel. In comparison to VLSFO (the base case for comparison here), LNG and LPG require approximately 60% and 50% more tank space, respectively. Methanol, with a 130% increase in tank capacity, can also be more readily adopted. Ammonia requires a 210% increase in tank space and may require space optimization. Hydrogen poses the greatest challenge, requiring a 320% increase in tank space, making it particularly challenging to adopt in deep-sea shipping.

4.7 Safety and handling considerations

Lastly, each fuel presents their own handling and safety considerations, making it more (or less) straightforward to adopt them. LNG, LPG, ammonia, and hydrogen all require liquefaction, with ammonia and LPG at a required temperature of $-33\text{ }^{\circ}\text{C}$, needing the least amount of energy and isolation in the infrastructure. LNG, at a required temperature of $-153\text{ }^{\circ}\text{C}$, requires entirely dedicated and costly infrastructure whereas hydrogen, at $-253\text{ }^{\circ}\text{C}$, a temperature close to absolute zero, will also need dedicated and expensive infrastructure. All liquefaction comes at an energy cost, in line with the temperature required. Hydrogen and LNG will require the most energy to liquefy, with hydrogen liquefaction consuming up to 30% of the energy contained in the hydrogen. Methanol is liquid at atmospheric conditions however requires very clean tanks to avoid contamination. In addition, methanol requires inert gas, such as nitrogen, to be used during loading and discharge to prevent an explosive air mixture in the cargo tanks. Finally, ammonia does not easily ignite and hence requires a low autoignition temperature fuel such as diesel or even hydrogen to be injected in the engine. This entails availability of these fuels on board and dedicated tanks.

Table 5 Alternative marine fuel prices in \$/mt and \$/1000 MJ (June 2022)

Marine Fuel Price	VLSF	LNG	LPG	Ammonia	Methanol	Hydrogen
Fuel price (\$/mt)	700	1 200	590	Natural Gas: 770 Renewable: 700	Natural Gas: 470 Renewable: 650	Natural Gas: 2,000 Renewable: 3 500 – 7 000
Fuel price (\$/1 000 MJ)	16.4	24	12.8	Natural Gas: 41.4 Renewable: 37.6	Natural Gas: 23.6 Renewable: 32.7	Natural Gas: 16.7 Renewable: 29.2 – 58.3

5 Conclusions

Adopting energy carriers (fuels) with lower or zero GHG footprint is a promising route for shipping to cut carbon emissions. Implementing renewably sourced zero carbon fuels, such as hydrogen and ammonia, is the most promising, and perhaps the only, option to deliver the desired GHG reductions for the maritime industry (Lindstad et al., 2021); although not the focus of this review, it must be noted that the upstream WtT emissions across all fuels can vary widely (European Parliament, Council of the European Union, 2018). Hydrogen produced from renewable sources can achieve a WtW GHG emission reduction of 79.9% compared to conventional fuels. Similarly, ammonia produced from renewable sources (green ammonia) can also achieve a 71.0% GHG emission reduction.

However, these GHG emission reductions are only achievable under the “cleanest” conditions. If hydrogen is produced from NG and used in the shipping industry as a fuel, the WtW GHG emissions will contribute to 96.2% more GHG emissions compared to conventional fuels. Furthermore, if uncombusted hydrogen is released as a slip, it would amplify the GHG emissions as hydrogen has a GWP100 of 11 ± 5 (Warwick et al., 2022). Similarly, if ammonia is produced from NG and the current N_2O emissions are not abated, the use of ammonia as a fuel will result in a WtW GHG emissions increase of 140.0%.

Equally as important to considering these LCA emissions is the barriers to overcome to implement ammonia and hydrogen across the worldwide fleet: technical maturity, tank capacity and bunkering infrastructure are some of the key hurdles to overcome to realize a net-zero shipping future.

Competing interest The authors have no competing interests to declare that are relevant to the content of this article.

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