Journal of
Marine Science and Engineering

MDPI

Article

Life Cycle Greenhouse Gas Emission Assessment for Using Alternative Marine Fuels: A Very Large Crude Carrier (VLCC) Case Study

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Abstract: The International Maritime Organization (IMO) has set decarbonisation goals for the shipping industry. As a result, shipowners and operators are preparing to use low- or zero-carbon alternative fuels. The greenhouse gas (GHG) emission performances are fundamental for choosing suitable marine fuels. However, the current regulations adopt tank-to-wake (TTW) emission assessment methods that could misrepresent the total climate impacts of fuels. To better understand the well-to-wake (WTW) GHG emission performances, this work applied the life cycle assessment (LCA) method to a very large crude carrier (VLCC) sailing between the Middle East and China to investigate the emissions. The life cycle GHG emission impacts of using alternative fuels, including liquified natural gas (LNG), methanol, and ammonia, were evaluated and compared with using marine gas oil (MGO). The bunkering site of the VLCC was in Zhoushan port, China. The MGO and LNG were imported from overseas, while methanol and ammonia were produced in China. Four production pathways for methanol and three production pathways for ammonia were examined. The results showed that, compared with MGO, using fossil energy-based methanol and ammonia has no positive effect in terms of annual WTW GHG emissions. The emission reduction effects of fuels ranking from highest to lowest were full solar and battery-based methanol, full solar and battery-based ammonia, and LNG. Because marine ammonia-fuelled engines have not been commercialised, laboratory data were used to evaluate the nitrous oxide (N_2O) emissions. The GHG emission reduction potential of ammonia can be exploited more effectively if the N_2O emitted from engines is captured and disposed of through after-treatment technologies. This paper discussed three scenarios of N_2O emission abatement ratios of 30%, 50%, and 90%. The resulting emission reduction effects showed that using full solar and battery-based ammonia with 90% N_2O abatement performs better than using full solar and battery-based methanol. The main innovation of this work is realising the LCA GHG emission assessment for a deep-sea ship.

Keywords: life cycle assessment; greenhouse gas; MGO; LNG; methanol; ammonia; hydrogen; ship fuels

Citation: Huang, J.; Fan, H.; Xu, X.; Liu, Z. Life Cycle Greenhouse Gas Emission Assessment for Using Alternative Marine Fuels: A Very Large Crude Carrier (VLCC) Case Study. *J. Mar. Sci. Eng.* **2022**, *10*, 1969. https://doi.org/10.3390/jmse10121969

Academic Editor: Theocharis D. Tsoutsos

Received: 15 November 2022
Accepted: 9 December 2022
Published: 11 December 2022

1. Introduction

As the world enlarges its efforts against climate change, the shipping industry's greenhouse gas (GHG) emissions have gained more attention. Due to the large volumes of freight and long distances travelled, international shipping is responsible for about 3% of global anthropogenic GHG emissions on a carbon dioxide (CO_2) equivalent basis [1]. The Kyoto Protocol and the Paris Agreement officially handed responsibility for marine emissions to the International Maritime Organization (IMO). After years of efforts, in 2018, the IMO set the target to cut the carbon intensity of all ships by at least 40% by 2030 and reduce total GHG emissions from global shipping by 50% (compared to 2008 levels) by 2050 [2]. Further stringent requirements are expected by the climate change agenda of the IMO's Marine Environment Protection Committee (MEPC) after the 26th United Nations Climate Change Conference in Glasgow [3]. For example, the IMO MEPC's 78th session in June of 2022 considered phasing out GHG emissions from international shipping by 2050. The MEPC 80 meeting in July of 2023 may make the final decision [4]. Therefore, to meet the decarbonisation goals, switching to low-carbon or zero-carbon alternative fuels is urgent for the shipping industry [5,6].

Among alternative fuel options, liquified natural gas (LNG), methanol, and ammonia have gained traction for large ships. Liquified natural gas is considered a practicable transitional fuel to address GHG emissions because of its low-carbon nature, vast availability, proven technology, and affordability [7–9]. From a long-term perspective, some studies have concluded that using liquefied biomethane (bio-LNG) and green hydrogen-based LNG (synthetic LNG or e-LNG) as drop-in solutions will expand the use of LNG [10,11]. Biomass- or hydrogen-based methanol has the potential to achieve life cycle net zero emissions. It is liquid at standard temperature and pressure and thus easier to handle on ships [12]. As a hydrogen carrier, liquid ammonia has acceptable volumetric energy density and storage conditions (i.e., refrigerated at minus 33 °C at atmospheric pressure or 0.8–1.0 MPa under atmospheric temperature) and is considered a promising alternative fuel as well [13]. According to the Clarksons' database [14], as of October 2022, 4.8% of the global fleet including coastal and deep-sea ships and 43.8% in the order book in tonnage terms are capable of using alternative fuels. The tonnages of coastal ships are small, and their contributions to emissions are limited; thus, it can be seen from the database that deep-sea ships are playing important roles in reducing emissions. In the order book, 781 ships are set to use LNG, 42 ships will use methanol, and there are 130 ammonia-ready ships. However, there are still some hurdles, particularly the shortage of fuel supply chains [15], to be broken down for the scale-up to an alternative fuel ship fleet.

Currently, ships' GHG emission assessments are based on tank-to-wake (TTW) analysis. For example, the Energy Efficiency Design Index (EEDI), Energy Efficiency Existing Ship Index (EEXI), and Carbon Intensity Indicator (CII) requirements issued by the IMO are all TTW-based [16–18]. The TTW method considers the emissions from consuming fuel once it is already in the tank. The analysis does not include how a fuel is produced and transported to a ship's tank. Nevertheless, the well-to-wake (WTW) analysis, also known as life cycle assessment (LCA), considers emissions related to every stage of a fuel's life cycle, from its production, transport, and bunkering until consumption on a ship. Using a TTW approach could misrepresent the total climate impacts of shipping fuels. Therefore, the IMO has been developing life cycle GHG and carbon intensity guidelines to be utilised when assessing the overall climate impact of fuels [19]. A final draft of the guidelines is expected to be adopted by the IMO MEPC 80 meeting in July of 2023.

Some research studies have been conducted regarding the life cycle environmental impacts of using different marine fuels. Brynolf et al. compared the life cycle environmental performance of LNG, bio-LNG, methanol, and bio-methanol as ship fuels. They concluded that bio-LNG and bio-methanol could reduce climate impact [12]. Gilbert et al. evaluated conventional and alternative fuels' life cycle environmental performances in the shipping industry [20]. Law et al. compared 22 potential alternative marine fuel pathways in terms of LCA for the shipping industry [21]. Kanchiralla et al. conducted a life cycle evaluation of potential decarbonisation solutions for shipping regarding environmental impacts and costs [22]. For case studies, Hwang et al. [23] conducted an environmental LCA of various alternative ship fuels, including marine gas oil (MGO), LNG, and hydrogen, for a coastal ferry. They demonstrated the benefits of using hydrogen as a fuel [23]. Wang et al. implemented a life cycle environmental impact assessment for a battery-powered ferry [24]. Chen and Lam conducted an LCA to compare the environmental impacts of hydrogen fuel cell and diesel engine systems on tugboats, showing that hydrogen-powered tugboats can reduce GHG emissions significantly [25]. Similarly, Fernández-Ríos et al. compared the

LCA sustainability and environmental performances between hydrogen fuel cell systems and hydrogen internal combustion engine systems [26]. Wang et al. examined the environmental impacts of various alternative fuels, including MGO, LNG, methanol, biodiesel, and hydrogen for a yacht, and recommended using green hydrogen [27]. Seddiek and Ammar compared the LCA environmental and cost performances between diesel and renewable hydrogen-powered ships sailing in the Red Sea area [28]. Lee et al. compared the life cycle environmental impacts of using MGO, LNG, and hydrogen on a nearshore ferry in Republic of Korea [29]. These efforts have contributed to the literature regarding the life cycle performances of using alternative marine fuels; however, there are still gaps in utilising the LCA method to evaluate GHG emissions of using alternative fuels on large ships sailing internationally. According to the IMO's fourth GHG study report [1], large ships, including oil tankers, bulk carriers, and container ships, dominate the inventory of international shipping emissions. Therefore, choosing the optimal fuel for deep-sea ships is critical to reducing emissions in the shipping industry.

In this context, this study aimed to perform an LCA to compare the GHG emissions of a very large crude carrier (VLCC) using alternative fuels, including LNG, methanol, and ammonia. The conventional fuel, MGO, was also considered for a comparative purpose.

Of particular interest were the following questions to be addressed in this paper: How to consider the WTT, TTW, and WTW GHG emissions from using different marine fuels for a deep-sea ship? Which is the optimal GHG emission abatement fuel for the target ship?

The remainder of this article is structured as follows. Section 2 outlines the parameters of the VLCC, the LCA methodology, and the data. Section 3 presents the alternative fuels' LCA performances on the VLCC. Section 4 discusses the results. Finally, Section 5 presents the conclusions.

2. Methods and Materials

This section provides the parameters of the target ship, the framework of the LCA method, and the data.

2.1. Parameters of The VLCC

Table 1 presents the main parameters of the VLCC. Figure 1 shows the side view of the ship. The shipping route of the VLCC was from the Middle East to China, as shown in Figure 2. The loading port was Jebel Ali, and the unloading port was Zhoushan. The voyage of a round trip was 11,082 nautical miles (n.m.). Only one bunkering operation was conducted for each round trip. The ship was bunkered at anchorage in the Port of Zhoushan via ship-to-ship transfer.

Table 1. Parameters of the VLCC.

Parameter	Value	Unit
Maximum deadweight tonnage (DWT)	310,000	tons
Length between perpendiculars	333.0	m
Moulded breadth	60.0	m
Depth	30.0	m
Design draft	20.5	m
Scantling draft	22.0	m
Service speed	14.5	knots
Economical speed	13.5	knots
Main engine rated power	22,000	kW

Figure 1. Side view of the VLCC.

Figure 2. Shipping route and bunkering site.

2.2. Life Cycle Assessment Method

The ISO 14040 standard was used to perform the LCA [30]. This systematic tool enables the analysis of environmental loads of a product throughout its entire life cycle and the potential impacts of these loads on the environment. "Products" in this paper were marine fuels, which means the emissions from the ship's building, scraping, and recycling were not in the research scope. An LCA has four phases: goal and scope definition, life cycle inventory analysis (LCI), life cycle impact assessment (LCIA), and life cycle interpretation. The goal and scope and the LCI are presented in this section, the LCIA and the interpretation are reported in Sections 3 and 4.

2.2.1. Goal and Scope

This study aimed to compare the WTW GHG emission performances associated with using different fuels, including MGO, LNG, methanol, and ammonia. The primary GHG emissions, carbon dioxide (CO_2), methane (CH_4), and nitrous oxide (N_2O), were considered in this study. Carbon dioxide is the main contributor to GHG emissions, followed by CH_4. The CO_2 emissions mainly come from fuel combustion, with small amounts of CO_2 vented during processing. The main sources of the CH_4 emissions were vented, fugitive, and unburnt emissions. The N_2O only contributes to a minimal extent except in ammonia-fuelled engines. Black carbon emissions from MGO engines were not considered due to the high level of uncertainty and wide range of impact estimates of black carbon on the climate [7]. This represents a conservative approach to the potential benefits of alternative fuels, as CO_2-eq emissions from black carbon would increase the GHG emissions from MGO engines.

The mass (tons) of the ship's fuel consumption in one year was identified as the functional unit. The fuels' lower heating values (LHVs) (MGO: 42.7 MJ/kg; LNG:50 MJ/kg; methanol:19.9 MJ/kg; ammonia:18.6 MJ/kg) were used to describe the energy consumption in the ship engines. The GHG emissions were expressed in ton CO_2-equivalents (CO_2-eq).

To better understand the emissions, various fuel production pathways were considered. As the ship bunkering site was considered to be the Port of Zhoushan, China, from the status quo of China's energy supply [31], the MGO and LNG were considered imported from overseas, and methanol and ammonia were considered produced in China. Given that green methanol and green ammonia production have not yet been scaled up, grey productions, as transitional pathways, were also considered. It was assumed that the methanol and ammonia production factories were located in northwest China, where coal, natural gas, and solar energy resources were abundant [32]. The systems were thus split into nine subsystems:

- S1: MGO imported from overseas.
- S2: LNG imported from overseas.
- S3: Coal-based methanol produced in China.

Coal mining and processing, syngas production, methanol synthesis, and distillation were considered in this pathway.

- S4: Natural gas-based methanol produced in China.

In this pathway, natural gas extraction and processing, steam reforming processing, methanol synthesis, and distillation were considered.

- S5: Partial solar-based methanol produced in China.

The CO_2 capture, production of hydrogen by water electrolysis, and hydrogeneration of CO_2 to synthesise methanol were considered. The CO_2 source was exhaust gas from fossil-fuelled power plants, which supplied electricity and steam for the methanol synthesis system. Water electrolysis produces hydrogen powered by solar photovoltaic (PV).

- S6: Full solar and battery-based methanol produced in China.

Compared with S5, the CO_2 source was captured from the air in this pathway. All power requirements required in the system were provided by a solar PV power plant. Solar power generates electricity during the day. The excess PV electricity was stored in a lithium-ion battery to meet electricity requirements at night.

- S7: Coal-based ammonia produced in China.

Coal mining and processing, syngas production, air separation, ammonia synthesis, and purification were considered.

- S8: Natural gas-based ammonia produced in China.

In this pathway, natural gas extraction and processing, steam reforming processing, methanol synthesis, and distillation were considered.

- S9: Full solar and battery-based ammonia produced in China.

In this pathway, solar PV was used as the power source for the whole process, including water electrolysis-based hydrogen production, air separation, ammonia synthesis, and distillation. Similar to S6, a battery was needed for night production.

The produced methanol and ammonia fuels were transported to coastal storage tanks in the Port of Zhoushan through freight trains, and a transport distance of 2100 km was considered in this work. The bunkering ship was loaded at the port, then sailed to the bunkering anchorage to bunker the VLCC. The bunkering ship's round trip navigation distance was taken as 100 n.m. (between the fuel storage tanks and the anchorage of the VLCC).

The proposed supply chains for the fuels consist of standard processes such as the production of feedstock, production of fuels, storage, transportation, and utilisation as illustrated in Figure 3.

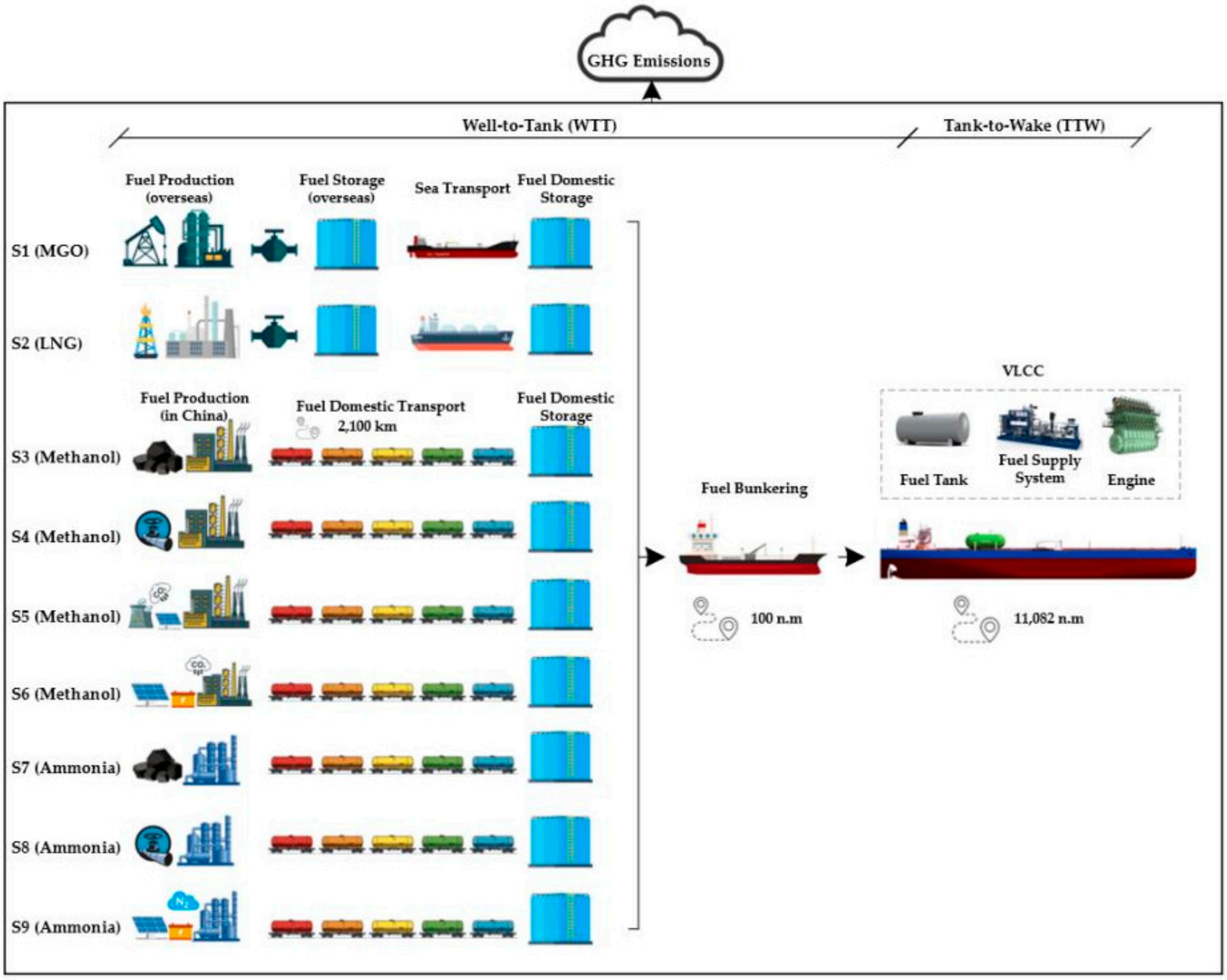

Figure 3. Supply chains of the fuels.

2.2.2. Life Cycle Inventory

The LCI analysis involved a systematic inventory of the input and output for the given systems. To assess the global warming potential in a 100-year timeframe, the following IPCC AR5 characterisation factors were used for calculating GHG emissions: 1 for CO_2, 28 for CH_4, and 265 for N_2O [33].

(1) Life cycle data of well-to-tank

Life cycle data of fuel productions and transport overseas and in China were mainly based on the literature. The data on production and transport for pathways S1 and S2 were taken from Sphera's report [7]. The data on production for S3–5 and S7–9 were taken from Zhu's research data [32], in which the emissions from the utilisations of resources, energy, and materials were considered. The data on production for S6 were taken from Nizami's study [34]. According to chapter 8 of the IPCC AR5 report [33], the GHG emissions of electric freight trains were 6–33 gCO_2-eq per ton of cargo per kilometre; conservatively, this work took 33 gCO_2-eq/ton/km as input. Therefore, for 2100 km of domestic train transport, 0.0693 tons of CO_2-eq were emitted per ton of cargo. An assumed newbuilt bunkering ship with a capacity of 10,000 DWT provides bunkering service for the VLCC. The emissions were estimated approximately based on the ship's EEDI calculation [2]. The maximum continuous rating (MCR) of the bunkering ship's main engine (ME) was estimated to be 5127 kW [35]; consequently, the power of auxiliary engines (AE) was 378 kW based on the calculation according to the IMO's EEDI guidelines [2]. The design speed was estimated to be 16.9 knots [35]. Conservatively, it was assumed that the bunkering vessel was running on MGO, whose carbon emission factor was 3.151. The fuel consumption rates of ME and AE were estimated to be 190 g/kWh and 250 g/kWh, respectively. As a result, the bunkering vessel's preliminary EEDI was estimated to be 15.38 g/ton/n.m., which means that 0.001538 tons CO_2-eq per ton of cargo were emitted for 100 n.m. of navigation. Table 2 presents the main data for WTT calculation.

Table 2. GHG emission data for WTT calculation (ton CO_2-eq/ton fuel).

Subsystem	Production [1]	Transport	Bunkering	In Total
S1	0.62		0.0015	0.62
S2	0.73	0.12	0.0015	0.85
S3	3.09	0.069	0.0015	3.16
S4	0.84	0.069	0.0015	0.91
S5	1.04	0.069	0.0015	1.11
S6	−0.32 [2]	0.069	0.0015	−0.25
S7	3.93	0.069	0.0015	4.00
S8	2.7	0.069	0.0015	2.77
S9	0.78	0.069	0.0015	0.85

[1] The data for S1 and S2 were taken from the literature [7]; The data for S3–5 and S7–9 were taken from the literature [32]. [2] The data for S6 were based on the literature [34]. The highest emission in this pathway was released from the lithium-ion battery production process. The CO_2 captured has a negative value due to its inputted to the process. As a result, the net emission is a negative value (−0.016 kg CO_2-eq/MJ methanol, which is equivalent to −0.32 tons of CO_2-eq per ton of methanol).

(2) Life cycle data of tank-to-wake

Using different fuels may lead to changes in the ship's loading capacity and deadweight. In this study, the LNG and ammonia fuel tanks were located on the open deck, and the methanol tanks were in the ship's wing tanks; thus, the loading capacity of the VLCC was not impacted. Compared with MGO, fuel, fuel tank, and system weight changes of LNG, methanol, and ammonia were −800 tons, +4500 tons, and +6300 tons, respectively, corresponding to −0.26%, +1.45%, and +2.03% compared to the ship's 310,000 DWT. These slight weight changes were ignored in the ship's ME power selection.

As the fuel consumption of the ship's ME varies significantly at different speeds, the following three main navigation conditions were considered:

- Two cruising speeds, 14.5 knots of the service speed and 13.5 knots of economical speed, were considered to assess the changes in fuel consumption of the engines. At service speed, the ME output was set to be at the MCR point; at the economical speed, the ME output was set to be at 70% of the MCR point, which was suggested by the ship operator.
- For safety considerations, the VLCC's speed was reduced when entering and leaving ports due to its large mass and inertia. In this regard, the speed of 6 knots was considered for 30 n.m. of in-ports navigation.
- The ship's speed was reduced when transiting the Malacca Strait. According to the navigation requirements [36], there were various speed restrictions from the One Fathom Bank to the Eastern Bank (482 n.m.), as shown in Figure 2. This paper considered that 40 h were needed to go through the strait at an average speed of 12 knots.

Some additional conditions were considered for the fuel consumption of the AEs, such as entering and leaving ports, berthing, and cargo loading/unloading. Table 3 presents the data on the navigation conditions.

Considering uncertain factors such as weather and restrictions on ship traffic when entering and leaving the ports, the ship is sometimes on standby. The standby time has uncertainty. In this paper, the standby times under 14.5 knots and 13.5 knots were artificially set to 78 h and 53 h, respectively, the purpose of which was to obtain a consistent annual number of voyages for both conditions, making the GHG emissions comparable. As seen in Table 3, a voyage would take 45 days; eight voyages per year can thus be completed.

Table 3. Data on the navigation conditions.

	Cruising			Entering and Leaving Ports			Across the Malacca Strait			At Ports		
	Speed (Knots)	Time (h)	Distance (n.m.)	Speed (Knots)	Time (h)	Distance (n.m.)	Speed (Knots)	Time (h)	Distance (n.m.)	Loading Time (h)	Unloading Time (h)	Standby Time (h)
At 14.5 knots	14.5	347	5029	6	5	30	12	40	482	36	36	78
ME Propulsion Power (kW)		22,000			5500			12,100			0	
AE Power (kW)		1400			1600			1200		1600	2000	800
At 13.5 knots	13.5	373	5029	6	5	30	12	40	482	36	36	53
ME Propulsion Power (kW)		15,400			5500			12,100			0	
AE Power (kW)		1200			1600			1200		1600	2000	800

The ME type series is MAN 7G80ME, a two-stroke diesel cycle low-speed engine with different versions for different fuels. When using LNG, methanol, or ammonia, a small amount of pilot MGO is needed. The fuel consumption data for each version of the engine are available on MAN's website [37]. Table 4 presents the fuel consumption and pilot MGO consumption of the ME at the specified maximum continuous rating (SMCR) point. Table 5 presents the fuel consumption and pilot MGO consumption of the AEs. The fuel mass consumptions of methanol and ammonia engines were much higher than MGO and LNG engines due to their differences in energy density.

Table 4. The ME's fuel consumptions at the SMCR point.

		MGO	LNG	Methanol	Ammonia
At 14.5 knots	ME Type	7G80ME-C10.5-EGRTC	7G80ME-C10.5-GI-EGRTC	7G80ME-C10.5-LGIM-EGRTC	7G80ME-C10.5-LGIA-EGRTC
	SMCR (kW)	22,000	22,000	22,000	22,000
	SFC (g/kWh)	159.3	129	318.9	376.5
	SPOC (g/kWh)	0	3.2	10.67	10.6
	Fuel Consumption (kg/h)	3505	2838	7016	8283
	Pilot Consumption (kg/h)	0	70	235	233
At 13.5 knots	SMCR (kW)	15,400	15,400	15,400	15,400
	SFC (g/kWh)	153.2	122.2	299.6	358.6
	SPOC (g/kWh)	0	4.06	13.53	13.4
	Fuel Consumption (kg/h)	2359	1882	4614	5522
	Pilot Consumption (kg/h)	0	63	208	206

Note: SFC = Specific fuel consumption; SPOC = Specific pilot oil consumption.

The four-stroke Otto cycle medium-speed AEs were used. The total fuel consumption of the AEs in a single voyage was calculated according to the engines' operating power and operating time under different conditions, as shown in Table 3. The total fuel consumption of ME and AEs, as shown in Table 6, was used to calculate the annual fuel consumption of the ship.

Table 5. The AEs' fuel consumptions.

		MGO	LNG	Methanol	Ammonia
At 14.5 knots	SMCR (kW)	1400	1400	1400	1400
	SFC (g/kWh)	187	155.3	395	406
	SPOC (g/kWh)	0	2.6	20	44
	Fuel Consumption (kg/round trip)	274,426	227,935	579,669	595,812
	Pilot Consumption (kg/round trip)	0	3816	29,350	64,571

Table 5. *Cont.*

		MGO	LNG	Methanol	Ammonia
At 13.5 knots	SMCR (kW)	1200	1200	1200	1200
	SFC (g/kWh)	187	155.3	395	406
	SPOC (g/kWh)	0	2.6	20	44
	Fuel Consumption (kg/round trip)	252,533	209,751	533,426	548,280
	Pilot Consumption (kg/round trip)	0	3511	27,009	59,420

Note: SFC = Specific fuel consumption; SPOC = Specific pilot oil consumption.

Table 6. Fuel consumption of ME and AEs.

Speed	Consumption (Ton/Year)	MGO	LNG	Methanol	Ammonia
At 14.5 knots	ME Fuel	20,736	16,766	41,405	48,881
	ME Pilot MGO	0	431	1438	1428
	AE Fuel	2195	1823	4637	4766
	AE Pilot MGO	0	31	235	517
At 13.5 knots	ME Fuel	15,350	12,234	29,972	35,832
	ME Pilot MGO	0	413	1377	1364
	AE Fuel	2020	1678	4267	4386
	AE Pilot MGO	0	28	216	475

Table 7 presents the CO_2 equivalent emission factors of the ME and AEs [1]. Ammonia-fuelled marine engines will be commercially available in 2024 [38,39]; there are no published N_2O emission data; therefore, the preliminary test data from a laboratory were used.

Table 7. The CO_2 equivalent emission factors (ton/ton fuel) of the engines.

Engine	Fuel	CO_2	CH_4	CO_2-eq (CH_4)	N_2O	CO_2-eq (N_2O)	CO_2-eq (Total)
Two-stroke low-speed Diesel cycle ME	MGO	3.21	6.53×10^{-5}	1.83×10^{-3}	2.22×10^{-4}	5.88×10^{-2}	3.27
	LNG	2.75	1.64×10^{-3}	4.58×10^{-2}	2.45×10^{-4}	6.51×10^{-2}	2.86
	Methanol	1.38	3.34×10^{-5}	9.35×10^{-4}	1.00×10^{-5}	2.65×10^{-3}	1.38
	Ammonia	0	0	0	5.42×10^{-4}	1.44×10^{-1}	0.14
Four-stroke medium -speed Otto cycle AE	MGO	3.21	5.35×10^{-5}	1.50×10^{-3}	1.60×10^{-4}	4.25×10^{-2}	3.25
	LNG	2.75	3.54×10^{-2}	9.92×10^{-1}	1.29×10^{-4}	3.41×10^{-2}	3.78
	Methanol	1.38	2.53×10^{-5}	7.09×10^{-4}	7.59×10^{-6}	2.01×10^{-3}	1.38
	Ammonia	0	0	0	5.02×10^{-3}	1.33	1.33

3. Results

This section presents the WTT, TTW, and WTW GHG emission results of the VLCC using different fuels.

3.1. Well-to-Tank Emissions

Figure 4 presents the annual WTT GHG emission results of subsystems S1–9. The WTT GHG emissions of fossil energy-based methanol and ammonia were significantly higher than those of fossil fuels, MGO, and LNG. Methanol emissions based on partial solar energy were also not competitive. Only methanol produced using a full solar and battery process had obvious advantages as its production process absorbed CO_2 as a feedstock and led to net negative emissions.

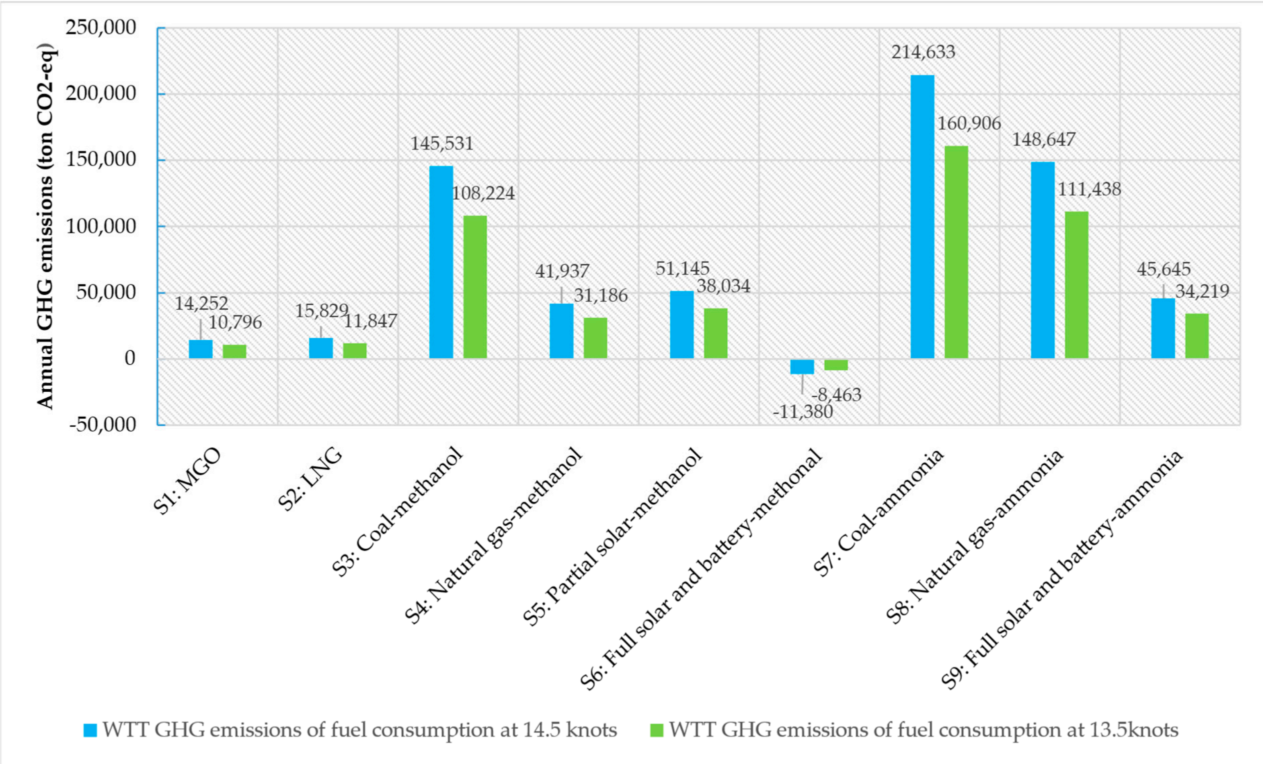

Figure 4. Annual WTT GHG emissions based on annual fuel consumption.

Figure 5 presents the annual WTT GHG emissions of pilot fuel consumptions for the subsystems.

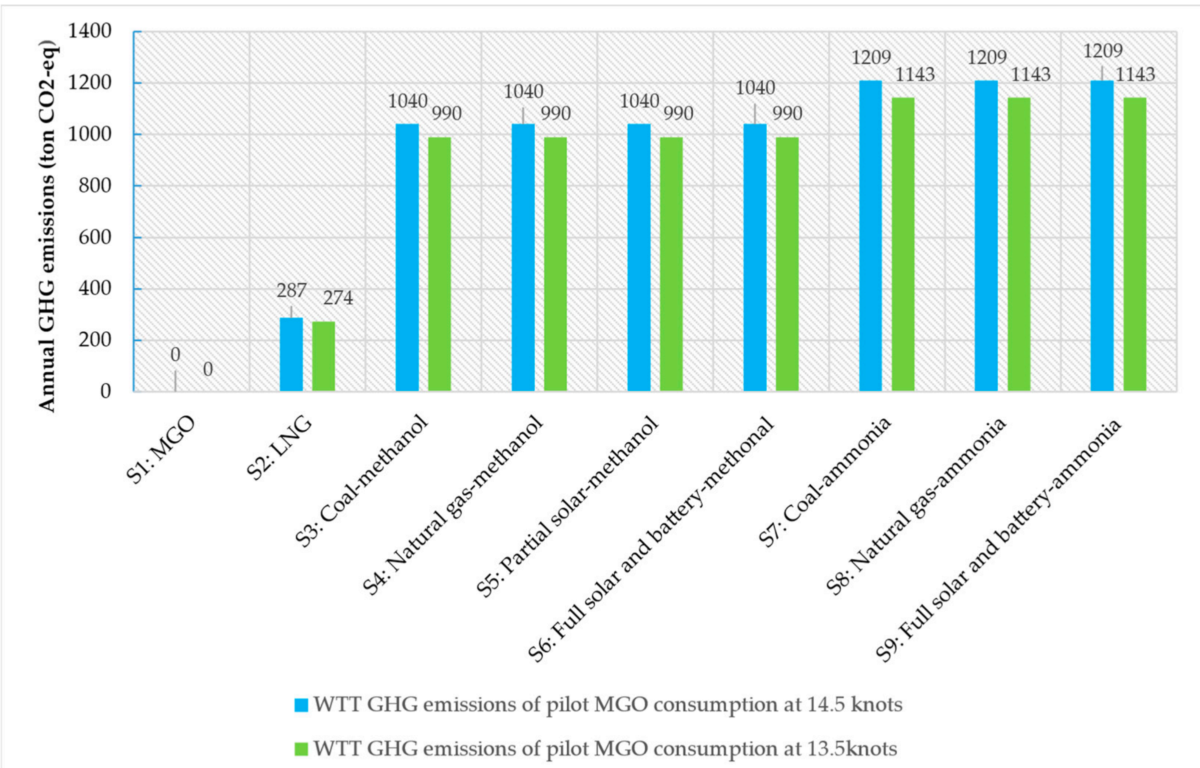

Figure 5. Annual WTT GHG emissions of annual pilot MGO consumption.

The WTT GHG emission calculation sheet is attached in Table S1 in the Supplementary Materials available online.

3.2. Tank-to-Wake Emissions

Figure 6 presents the annual TTW GHG emission results of the VLCC. First, the emission reduction effect of reducing speed was noticeable. Taking MGO for example, when the ship sailed at an economical speed of 13.5 knots, it reduced emissions by 24.26% compared to when it sailed at a service speed of 14.5 knots. Using alternative fuels shows varying degrees of advantages compared to MGO. At the speed of 14.5 knots, using LNG could reduce emissions by 24.73%, using methanol could reduce emissions by 7.94%, and using ammonia could reduce emissions by 73.68%. At the speed of 13.5 knots, using LNG could reduce emissions by 24.57%, using methanol could reduce emissions by 7.60%, and using ammonia could reduce emissions by 70.06%.

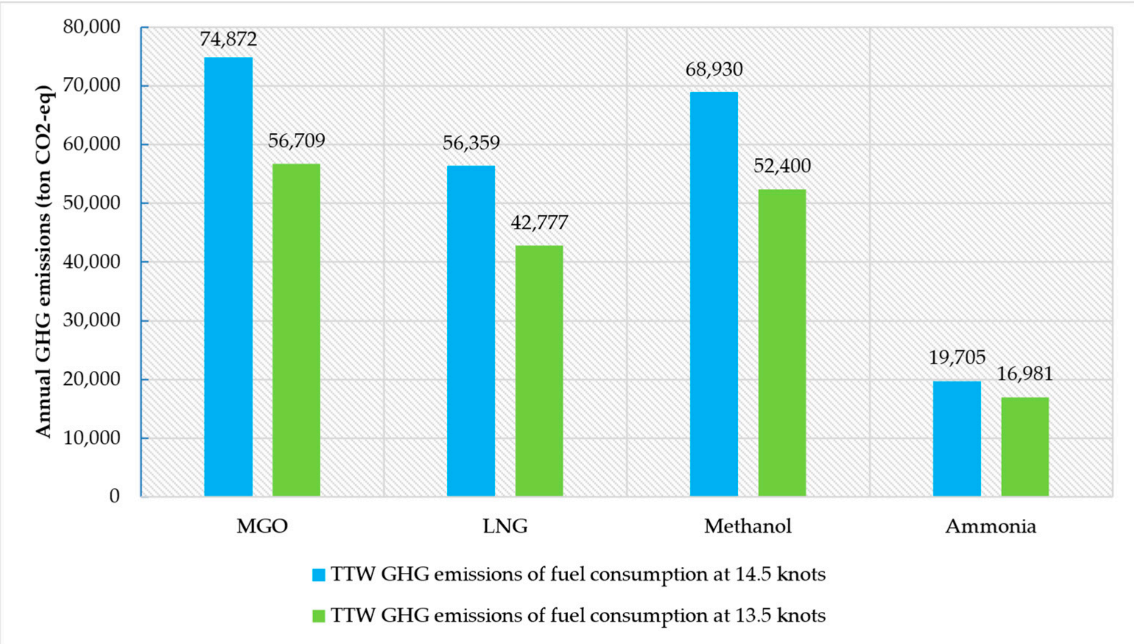

Figure 6. Annual TTW GHG emissions based on annual fuel consumption.

The TTW GHG emission calculation sheet is attached in Table S2 in the Supplementary Materials available online.

3.3. Well-to-Wake Emissions

Figure 7 presents the annual WTW GHG emission results of the VLCC. Fossil fuel-based methanol (S3 and S5) and ammonia (S7 and S8), and partial solar-based methanol (S5) had no emissions reduction effect. Compared with MGO, under the service speed of 14.5 knots, using LNG could reduce emissions by 18.68%; using full solar and battery-based methanol could reduce emissions by 34.26%; using full solar and battery-based ammonia could reduce emissions by 25.32%. Under the economical speed of 13.5 knots, using LNG could reduce emissions by 18.68%; using full solar and battery-based methanol could reduce emissions by 33.44%; using full solar and battery-based ammonia could reduce emissions by 22.46%.

The WTW GHG emissions calculation sheet is attached in Table S3 in the Supplementary Materials available online.

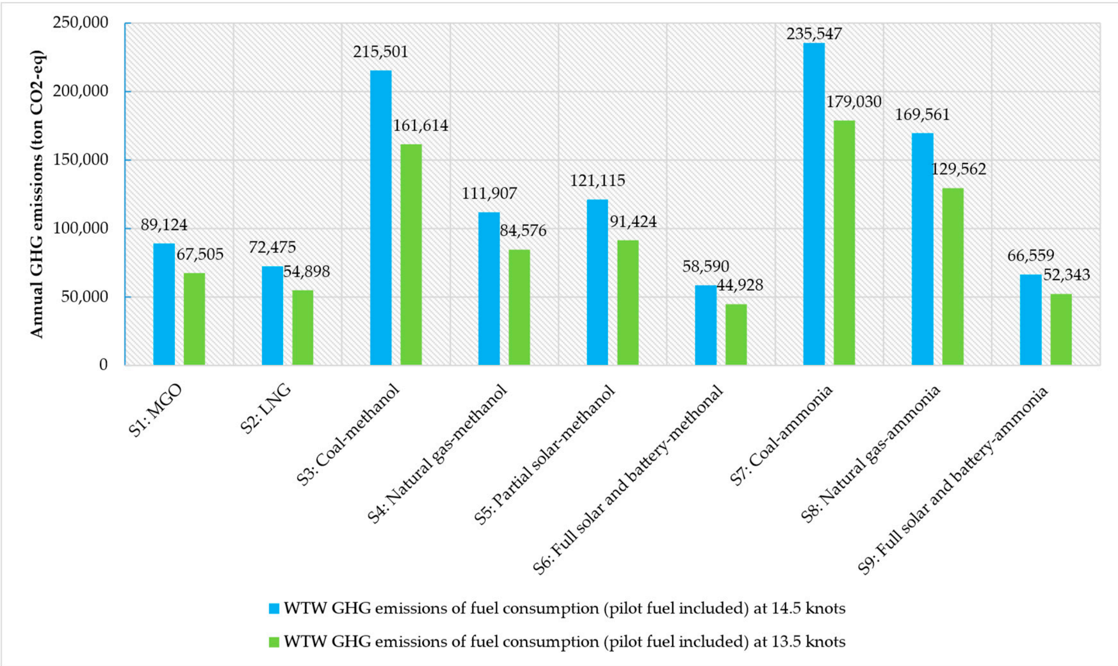

Figure 7. Annual WTW GHG emissions based on annual fuel consumption.

4. Discussion

This section discusses the N_2O emissions of ammonia engines and the emission reduction potentials of different fuels.

4.1. N_2O Emission Abatement from Ammonia Fuelled Engines

The only primary GHG emission from ammonia-fuelled engines is N_2O. However, it could be captured using after-treatment systems on ships, which the engine manufacturer has been working on [40]. This subsection assumed three N_2O emission abatement scenarios to study their sensitivity to the VLCC's TTW and WTW GHG emissions. The three scenarios were: (1) 30% N_2O was removed; (2) 50% N_2O was removed; (3) 90% N_2O was removed. The TTW and WTW results are illustrated in Figures 8 and 9, respectively.

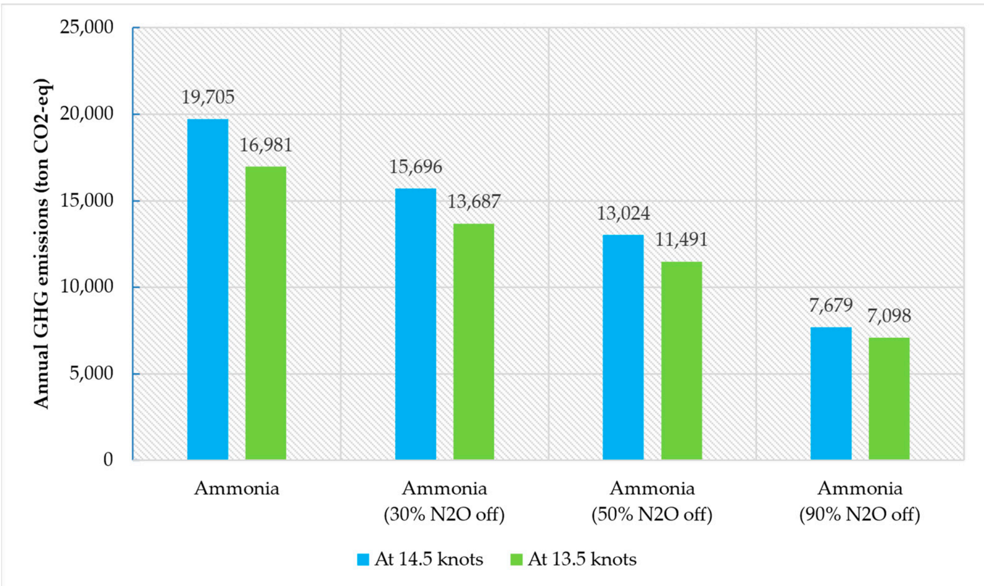

Figure 8. Annual TTW GHG emissions of using ammonia considering N_2O abatements.

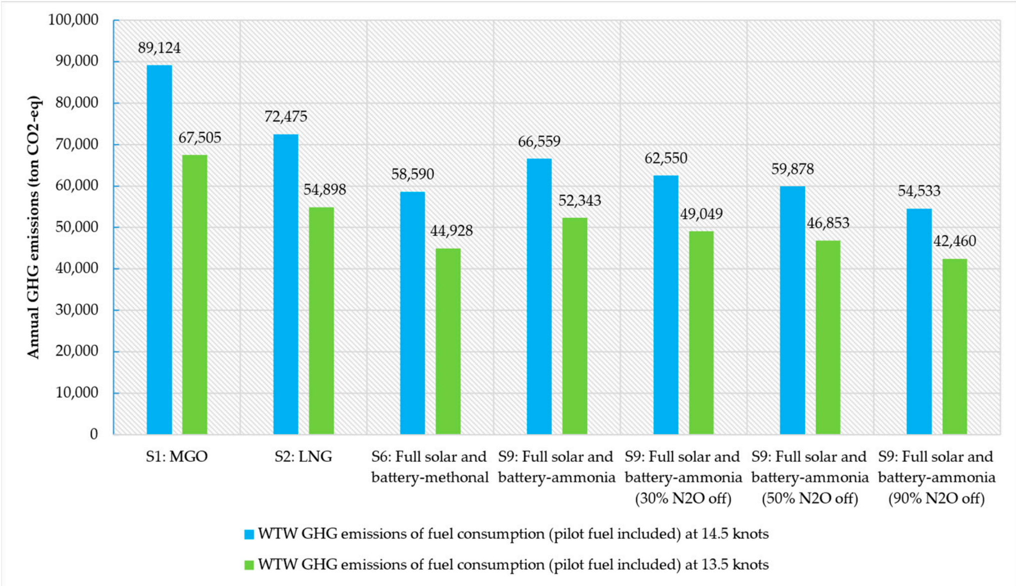

Figure 9. Comparison of annual WTW GHG emissions considering N_2O abatements of using ammonia.

Compared with emissions without N_2O abatement measures, under the service speed of 14.5 knots, 20.35% of TTW emissions could be reduced for the 30%-N_2O-off scenario, 33.91% for the 50%-N_2O-off scenario, and 61.03% for the 90%-N_2O-off scenario. Under the economical speed of 13.5 knots, 19.40% of TTW emissions could be reduced for the 30%-N_2O-off scenario, 32.33% for the 50%-N_2O-off scenario, and 58.20% for the 90%-N_2O-off scenario.

Figure 9 considers all scenarios with emission reduction advantages over MGO. Compared with MGO, under the service speed of 14.5 knots, using ammonia with 30%-N_2O-off measures could reduce the WTW GHG emissions by 29.82%, 32.81% for the 50%-N_2O-off scenario, and 38.81% for the 90%-N_2O-off scenario. Under the economical speed of 13.5 knots, by 27.34% for the 30%-N_2O-off scenario, 30.59% for the 50%-N_2O-off scenario, and 37.10% for the 90%-N_2O-off scenario.

The calculation sheet considering N_2O abatements can be found in Tables S2 and S3 in the Supplemental Materials available online.

4.2. GHG Emission Reduction Potential

According to the results, even full solar and battery-based methanol and ammonia have limited advantages over LNG in terms of total annual WTW GHG emissions. There were two main reasons for this:

- Solar PV cannot generate electricity at night; thus, electricity supply for fuel production relies on the electricity generated during the day stored in the battery system. The GHG emissions from battery manufacturing were also included in the total emissions of the fuel production process. This led to the conclusion that the emissions from the full solar and battery-based methanol and ammonia production were higher than expected.
- The calorific value of these low-carbon fuels was relatively low, resulting in more significant annual fuel consumption, which led to higher emissions.

Methanol and ammonia production will achieve ideal emission effects provided the electricity grid providing energy for fuel production processes is fully based on renewable energy. However, forming a fully green grid is still challenging [41]. The combined use of solar and wind energy can also achieve emission-free production of methanol and ammonia; however, this is only applicable to areas with abundant wind and solar resources.

5. Conclusions

The life cycle GHG emissions when using different fuels, including MGO, LNG, methanol, and ammonia, on a VLCC navigating on the Middle East to China route were investigated. The study had the following main results:

- The WTT GHG emissions of fossil energy-based methanol and ammonia were significantly higher than those of fossil fuels, MGO, and LNG. Partial solar-based methanol was also not competitive. Only full solar and battery-based methanol had apparent advantages.
- The TTW GHG emissions of using alternative fuels showed varying degrees of advantages compared to MGO. The emission reduction effect of ammonia was the most significant, followed by LNG and methanol.
- From a WTW perspective, fossil fuel-based methanol and ammonia and partial solar-based methanol had no emissions reduction effects. Compared to MGO, full solar and battery-based methanol was the optimal option, followed by full solar and battery-based ammonia and LNG. However, if the N_2O emitted from the ammonia engine was disposed of, then using full solar and battery-based ammonia with 90%-N_2O-off after-treatment technology would be preferable to using full solar and battery-based methanol.
- Within the scope considered in this paper, compared to MGO, the ranking of the WTW GHG emission reduction effect of alternative fuels was as follows: full solar and battery-based ammonia with 90%-N_2O-off, full solar and battery-based methanol, full solar and battery-based ammonia with 50%-N_2O-off, full solar and battery-based ammonia with 30%-N_2O-off, full solar and battery-based ammonia without N_2O-off, and LNG.

The main scientific findings can be summarised as follows:

- Pilot fossil fuels are required in current internal combustion engines, therefore, even using zero-carbon fuels, ships cannot achieve zero GHG emissions.
- Under ideal conditions, solar-based hydrogen-to-methanol could be approximately carbon-neutral over the entire life cycle. In fact, due to the discontinuity of solar power generation, lithium batteries are needed to store electricity. The GHG emissions of lithium batteries in the production process were included in the produced methanol, which makes the use of methanol as a marine fuel unable to achieve carbon neutrality. In the future, with the formation of a green power grid and the combined application of various renewable energy sources, the emission reduction potential of methanol could be further explored.
- Slowing the ship's speed had a significant emission reduction effect.

The findings of this research fill a gap in the literature regarding life cycle GHG emission assessment for VLCCs. However, due to the limitation of available data, the types of alternative fuels discussed in this paper were limited; for example, bio-LNG, hydrogen-based synthetic LNG, and biomass-based methanol were not included in this work. In future studies, the above fuels need to be considered.

This research was conducted to provide a clear image of applying the LCA GHG emission assessment to choosing suitable fuels for deep-sea ships. With the help of existing fuel production and transport data and ships' actual operational data, using the LCA method could potentially provide a solid basis for fuel selection.

It is worth noting that different production pathways for fuels have divergent effects on GHG emissions. Therefore, care must be taken when considering ships' GHG emissions reported in the literature because fuel supply chains' definitions are various.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/jmse10121969/s1. Table S1: WTT GHG emission calculation sheet; Table S2: TTW GHG emission calculation sheet; Table S3: WTW GHG emission calculation sheet.

Author Contributions: Conceptualization, J.H., H.F. and X.X.; methodology, J.H., H.F. and X.X.; validation, J.H., H.F., X.X. and Z.L.; formal analysis, J.H. and H.F.; resources, J.H. and H.F.; data curation, J.H. and H.F.; writing—original draft preparation, J.H. and H.F.; writing—review and editing, J.H., H.F., X.X. and Z.L.; project administration, J.H. and H.F. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

AE	Auxiliary engine
CH_4	Methane
CII	Carbon Intensity Indicator
CO_2	Carbon dioxide
CO_2-eq	Carbon dioxide equivalent
DWT	Deadweight tonnage
EEDI	Energy Efficiency Design Index
EEXI	Energy Efficiency Existing Ship Index
GHG	Greenhouse gas
IMO	The International Maritime Organization
LCA	Life cycle assessment
LCI	Life cycle inventory analysis
LCIA	Life cycle impact assessment
LHV	Lower heating value
LNG	Liquified natural gas
MCR	Maximum continuous rating
ME	Main engine
MEPC	Marine environment protection committee
MGO	Marine gasoil
N_2O	Nitrous oxide
PV	Photovoltaic
SFC	Specific fuel consumption
SMCR	Specified maximum continuous rating
SPOC	Specific pilot oil consumption
TTW	Tank-to-wake
VLCC	Very large crude carrier
WTT	Well-to-tank
WTW	Well-to-wake

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