Prospects for carbon-neutral maritime fuels production in Brazil

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Abstract

The International Maritime Organization (IMO) has compromised to reduce its greenhouse gas (GHG) emissions in the medium and long term. Besides energy efficiency measures, the development of potentially carbon neutral fuels in the upcoming years are key to achieve the sector's goals. In this context, this study presents a multicriteria methodology to compare possible alternative fuels for the Brazilian maritime trade. To this end, 13 fuel options were evaluated according to technical, economic and environmental criteria to which different weights were assigned. The ranking of results indicates that drop-in fuels such as Fischer-Tropsch diesel, Alcohol-based diesel, straight and hydrotreated vegetable oils and e-diesel stand out as promising alternatives. Biomass-based liquefied natural gas (Bio-LNG) performance in the evaluation is hampered mostly by the risk of methane slip. Green hydrogen seems to be a distant alternative for the Brazilian case such as green ammonia, that may be an alternative for cabotage transport in the long-term.

Keywords: biofuels, marine, carbon-neutral, electrofuels, shipping, IMO

Abbreviations[*]:

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[*] GHG: Greenhouse gas
IMO: International Maritime Organization
SVO: Straight vegetable oil
HVO: Hydrotreated vegetable oil
HDPO: Hydrotreated pyrolysis oil
FT-diesel: Fischer-Tropsch diesel
ATD: Alcohol-to-Diesel
Bio-LNG: Liquefied bio-methane
Bio-CH3OH: Bio-methanol
Bio-C2H5OH: Bio-ethanol
Green H2: Renewable-based hydrogen
Green NH3: Renewable hydrogen-based ammonia
e-diesel: Electrodiesel
e-LNG : Electromethane
e-CH3OH: Electromethanol

1. Introduction

The international shipping industry has set ambitious targets for reducing its greenhouse gas (GHG) emissions. The strategy defined by the International Maritime Organization (IMO) proposes a quantitative reduction in carbon intensity and GHG emissions in the sector which includes, among other targets, a 50% reduction in GHG emissions by 2050 compared to 2008 levels [1]. Among the main potential measures to be adopted in the medium- and long- terms, neutral emission fuels are listed. Several alternatives can be considered, such as distilled biofuels, bio-Liquefied Natural Gas (bio-LNG), bio-alcohols, hydrogen, ammonia and the so-called electrofuels (e-fuels).

Maritime transport is the most efficient way to promote medium- and long-distance trade around the world. Despite the cargo containerization process observed in the recent past, long-haul shipping still focuses heavily on the transportation of mineral and agricultural commodities [2]. Additionally, while the trade of higher value-added products (typically containerized) is concentrated on the intra-Asia, Asia-North America and Asia-Europe routes, on a mass basis, the major part of the sea trade is associated with the supply of raw materials by countries of the Global South. These are typically low-value-added products sold in bulk and transported in large vessels [2].

Brazilian foreign trade, for example, is strongly based on primary products. The main goods exported are iron ore, soybeans, crude oil and sugar, which are low-value-added commodities with notorious discrepancy in terms of mass and value. On a mass basis, these four products account for more than three-quarters of Brazil's exports while, in terms of value, they represent only a quarter of the country's exports [3]. Furthermore, Brazil has an unfavorable geographical position for of its maritime trade. Far from East Asia, Europe and the United States, and with no access to the Pacific Ocean, the country must deal with longer travel distances and higher fuel expenses and carbon intensities[1].

Deep-sea shipping includes mostly large, ocean-going vessels covering long routes and often without a regular schedule (except for containerships). Vessels operating in long-

[1] In the period 2001-2018 China was, by far, the main destination of Brazil's exports, accounting for 46% of the iron ore, 64% of the soybeans and 27% of the crude oil shipments of these products. The shipping distance between the Brazilian coast and China's main importing centers is around 11,900 nautical miles (Santos-Shanghai taken as a reference), a very high value compared to the average haul length of 4,200 nautical miles [3].

distance transportation require fuels that are globally available and have good energy density in order to maximize the space availability for cargo and ensure fuel autonomy. Therefore, the choice of mitigation measures in the Brazilian shipping sector should be carefully evaluated given the economic impacts this might have on the country's foreign trade.

From a technical and economic perspective, various potentially carbon-neutral fuels could serve as medium- to long- term alternatives to replace fossil fuels used in marine engines. Possibilities are diverse, ranging from the direct use of vegetable oils to the use of synthetic fuels produced from hydrogen and recycled carbon dioxide. In addition, technological routes optimized to produce high-quality biofuels, such as biomass-derived jet (bio-jet), could also co-produce fuels suitable for maritime transportation.

Brazil can be considered a potential producer of marine biofuels in view of the high availability of biomass resources and its expertise in biofuels production [4–6]. Also, the significant participation of renewable energy sources and the low emission factor of the Brazilian power grid would benefit the production of green hydrogen, green ammonia and e-fuels. Therefore, Brazil may have competitive advantages to produce fuels suitable for long-sea shipping that could be used in its major trade routes and/or make it an important international exporter of such fuels.

Previous studies have assessed the possibilities of using alternative marine fuels. While some of them focused on the benefits and challenges of specific options [7], others tried to understand the potential pathways and scenarios for the future of international shipping as a whole [8,9]. A number of these studies points out hydrogen as a promising alternative to reduce shipping's emissions. DNV GL, an accredited certification company, conducted three studies regarding alternative low-carbon energy sources for the maritime transportation sector [10–12]. The most recent one assessed the commercial and operational viability of six alternative fuels compared to LNG according to several criteria based on existing literature [12]. Lloyd's Register, another classification group investigated the potential of zero-emission vessels to 2030, by examining the application of distinct technological options to different types of ship [13] and performed a techno-economic analysis of zero-carbon fuels for shipping in view of their economic viability, technological feasibility and emissions [14].

While relevant, previous studies did not perform context-specific analyses that consider particularities regarding foreign trade, such as cargo, ship types and transportation routes. Also, some fuel alternatives, such as ammonia and e-fuels, pointed by some studies as the most promising ones, would be better suited for short-distance transportation. Even though it is expected that these alternatives benefit from learning rates in the long-term, they may not be ready in the time span of the IMO goals, given also the extended lifetime of long-haul vessels [15].

To fill this gap, this study performs a comparative analysis of potentially carbon-neutral fuels produced in Brazil for maritime transportation. It is the first preliminary assessment of the operational, commercial and sustainable aspects of fuel alternatives for the maritime transport sector within a country-specific approach. To this end, a comparative analysis that evaluates the alternatives according to a set of indicators is performed. This kind of analysis is critical for assessing the potential of different alternatives according to the inherent characteristics of the country. Also, it would support local decision makers to define the best strategies to comply with the sector's GHG emissions reduction goals in the upcoming years.

This paper is structured as follows. Section 2 details the technological pathways to produce non-fossil maritime fuels. Section 3 presents the methodology developed to perform a comparative analysis of the alternatives. Section 4 presents the results and ranking of the most promising ones. Finally, section 5 discusses the results obtained and section 6 presents the final remarks and suggestions for future studies.

2. Non-fossil alternative fuels for ships

Currently, there are various options of potentially carbon-neutral maritime fuels produced from renewable energy sources, which could serve as alternative, in the medium- to long- term, to petroleum fuels currently used for the propulsion2 of ships [14] .

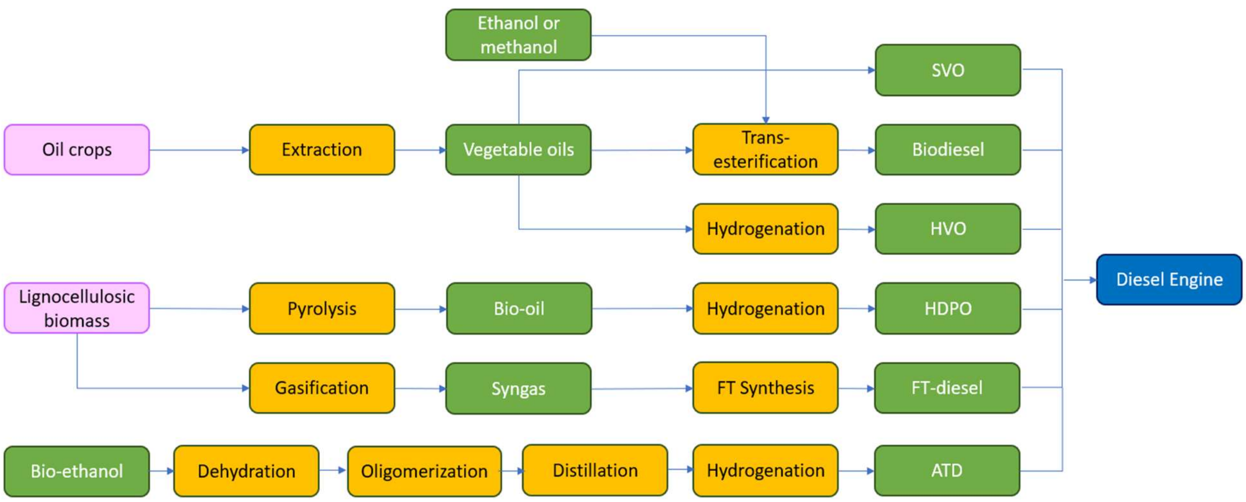
To better describe the technological possibilities, this study divided the fuels into three groups (Table 1 and Figure 1). Group 1 encompasses distillate fuels suitable for diesel (compression ignition) engines. Group 2 comprises alcohols and liquefied gases suitable

[2] Naturally, the major part of the energy demand of a ship is associated to its propulsion. However, energy is also required to the production of heat and electricity onboard. Today, this demand is also met by oil products.

for spark ignition or dual-fuel engines. Finally, group 3 includes hydrogen, ammonia and hydrogen-based synthetic fuels (e-fuels).

Table 1: Groups of fuels considered in the analysis

	Fuel pathways	
Group 1 Liquid distilled biofuels	SVO	Straight vegetable oil
	Biodiesel	Biodiesel produced using FAME/FAEE
	HVO	Hydrotreated vegetable oil
	HDPO	Hydrotreated pyrolysis oil
	FT-diesel	Biomass-derived diesel
	ATD	Alcohol-based diesel (Alcohol-to-Diesel)
Group 2 Alcohol and liquefied gases	Bio-LNG	Liquefied bio-methane
	Bio-CH_3OH	Biomass-derived methanol (bio-methanol)
	Bio-C_2H_5OH	Biomass-derived ethanol (bio-ethanol)
Group 3 Hydrogen, ammonia and e-fuels	Green H_2	Renewable-based hydrogen
	Green NH_3	Renewable hydrogen-based ammonia
	e-diesel	Renewable hydrogen-based diesel (electrodiesel)
	e-LNG	Renewable hydrogen-based methane (electromethane)
	e-CH_3OH	Renewable hydrogen-based methanol (electromethanol)



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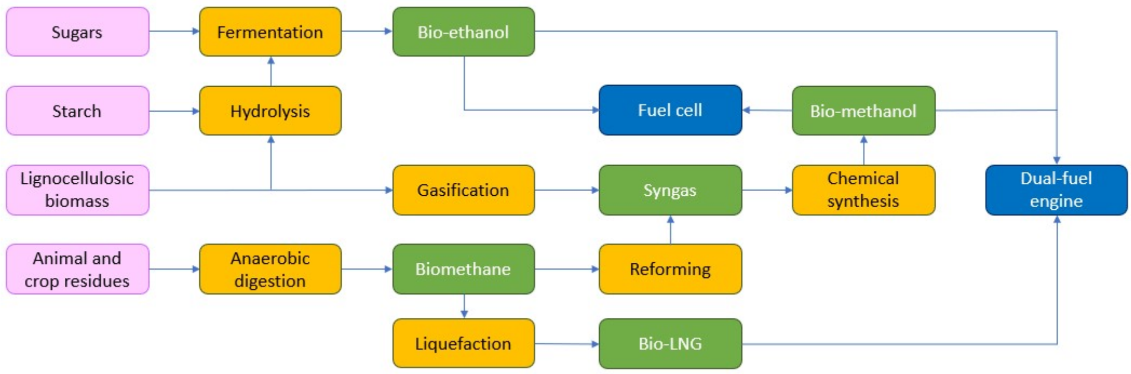

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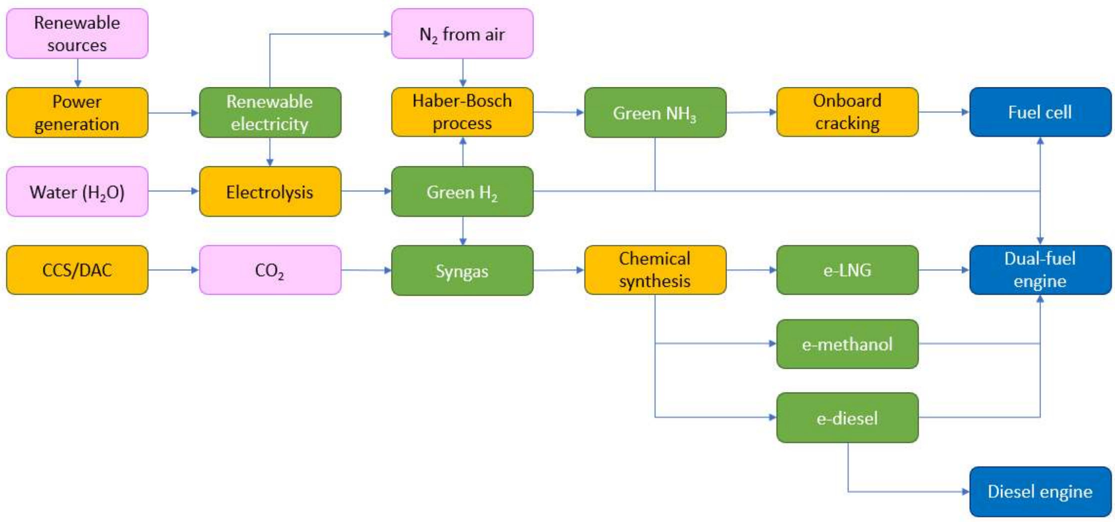

(c)

Figure 1: Potentially carbon-neutral fuels. 1a: Group 1 - distilled biofuels[3], 1b: Group 2 - alcohol and liquefied gases; 1c: Group 3 – hydrogen, ammonia and electrofuels.

The categorization is based on the similarities between the fuel-motorization systems of the different alternatives. Group 1 is composed of almost, if not completely, drop-in fuels, derived from biomass feedstocks and routes that produce or co-produce distillates. Although biodiesel has stability problems [16] and SVO has viscosity problems [17–20], they are more compatible with the existing motorization of the Brazilian fleet, even to be blended with diesel used in the 4-stroke auxiliary motors. Group 2 is composed of fuels from biomass feedstocks that require more severe adjustments in logistics, bunkering, storage and motorization to be used. Finally, group 3 includes fuels associated to the renewable hydrogen chain. Notwithstanding, such categorization is

[3] For biodiesel to be a carbon-neutral alternative, renewable methanol or ethanol (not FAME, but FAEE, in this case) must be used in the transesterification process.

limited by the interrelationships between these groups, given the complexity of fuel pathways. For example, e-diesel is analyzed from the perspective of hydrogen, although, in terms of chemical composition, it is identical to FT-diesel. The description of relevant physical-chemical properties for maritime fuels and their values for each fuel evaluated in this study are presented in the Supplementary Material.

3. Methods

The aim of this work is to compare the fuels described in section 2 based on a review of the literature with special attention to the particularities of the Brazilian case. Figure 2 shows the steps of the adopted methodology.

First, a set of nine criteria, involving technical, economic and environmental aspects, was defined (Table 2). A qualitative analysis was developed for each fuel from the viewpoint of this theoretical framework. Then, these criteria were turned into quantitative indicators through the attribution of notes from 1 (Very Bad) to 5 (Very Good). Finally, based on criteria weights (Table 2), the final score was calculated for each fuel, establishing a ranking of the alternatives. Given the quantity (nine) and weights (1, 2 or 3) of the indicators, the maximum score of the scale would be 85. For the sake of a better understanding, the ratings were normalized to fit a decimal scale. Thus, the score x of a particular fuel is given by equation (1), in which w_i and p_i stand for the weight and the note of the fuel in the criteria of index i.

$x = \sum_{i=1}^{9} w_i \, p_i \, /0.80$ (1)

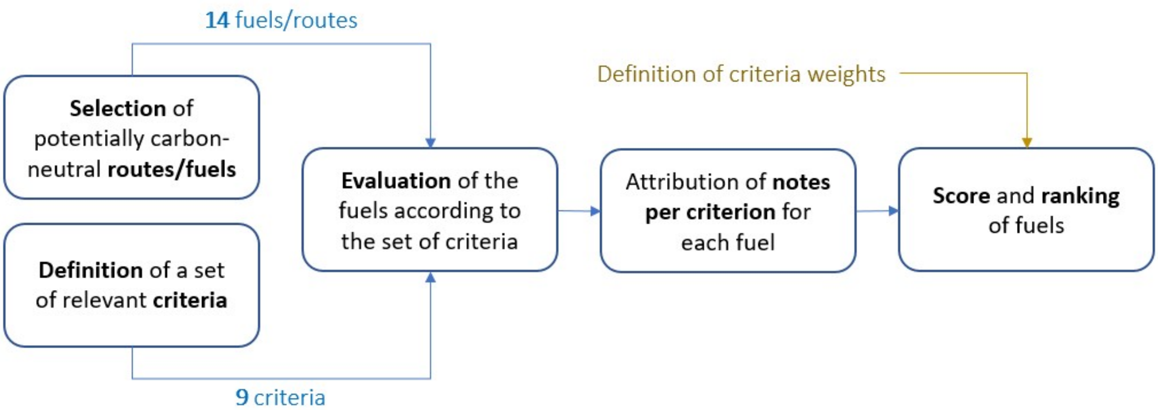

Figure 2: Overview of the methodology for comparison of alternative fuels.

In order to rank the most promising alternatives, weights were attributed to the different criteria. Weight 3 was attributed to global sustainability, as this study focus on IMO's goals. On the other hand, weight 2 was attributed to technical criteria (availability, applicability, energy density and technological maturity) and safety criteria, as they indicate the need to adapt logistic systems, bunkering, motorization and tanking in ships, being prerequisites for potential use of these fuels. The other criteria (economy, local sustainability and standardization) received weight 1. Their lower weight does not mean that these aspects are not important for the development of alternative fuels, but they have lower relative relevance compared to the other criteria, considering the scope of the study. Furthermore, it is worth noting that, despite the relevance of the economic criterion from a practical point of view, technological costs can be significantly reduced over time. In addition, the mandate to reduce GHG emissions may induce, in the short to medium term, a niche market for alternative fuels, as long as they have scale and applicability. Regarding local sustainability, a lower weight was chosen given that the IMO's have already set regulations on fuel's sulphur content [21,22]. In this sense, it is implicit that any alternative fuel used for maritime transportation must address local sustainability issues. Also, for the ratings of criteria 4 (energy density) and 5 (economic), for which there are very straightforward quantifications, a normalization of the indicators is required to keep the analysis consistent.

Table 2: Criteria/indicators considered in the comparative analysis.

Index	Criteria	Description	Weight
1	**Availability**	Availability of feedstock and infrastructure facilities	2
2	**Applicability**	Compatibility of the fuel with the operating fleet and current infrastructure for transportation, storage and bunkering	2
3	**Technological maturity**	Readiness level of the production and utilization technologies	2
4	**Energy density**	Volumetric energy density, reflecting the need for space related to fuel storage onboard	2
5	**Economic**	Levelized costs, comprising fuel production, bunkering infrastructure and ship modifications (engines and tanks)	1
6	**Safety**	Safety in operation, fuel handling and toxicity.	2
7	**Standards**	Existence of fuel standards and/or certifications that prove renewable origin	1
8	**Global sustainability**	GHG emissions related to the fuel use and production and distribution chain	3

9	**Local sustainability**	Air pollutant emissions (AP)[4], impacts on biodiversity and water resources	1

In the case of the energy density indicator, the normalization is based on the volumetric energy content of the fuels, as shown in Figure 3.

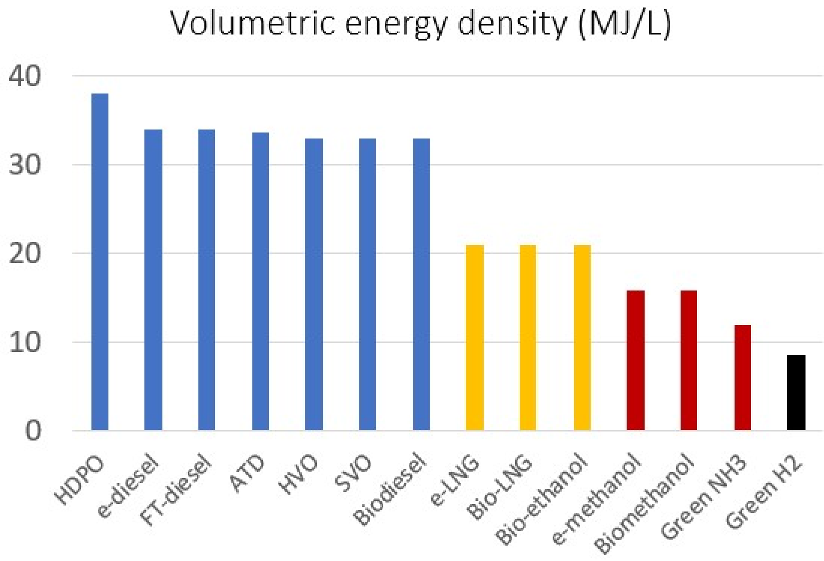

Figure 3: Volumetric energy density scale. Based on [12,20,23–28].

For the economic indicator, the normalization is based on average costs of energy, using the bunker (HFO) price as a reference (Figure 4**Erro! Fonte de referência não encontrada.**).

[4] In this study, we included SO_x, Particulate Matter (PM) and NO_x. In high concentrations, nitrogen oxides (NO_x) are highly toxic and cause health problems. They participate in various atmospheric reactions, producing tropospheric ozone and PM. NO_x is a precursor of acid rain, diminishes air visibility and contributes to nutrient pollution in coastal waters [69]. Emission of high SO_2 concentrations lead to formation of other sulfur oxides (SO_x) which, when react with various atmospheric components, increase the levels of PM in the atmosphere. These are harmful to human health (respiratory diseases) and precursors of acid rain [70,71]. Particulate matter (PM) emissions occur by the agglomeration of small particles of partially burned fuel, by the ash content of the fuel and lubricating oil and the presence of sulfates, water and hydrocarbons in the partially burned fuel [72].

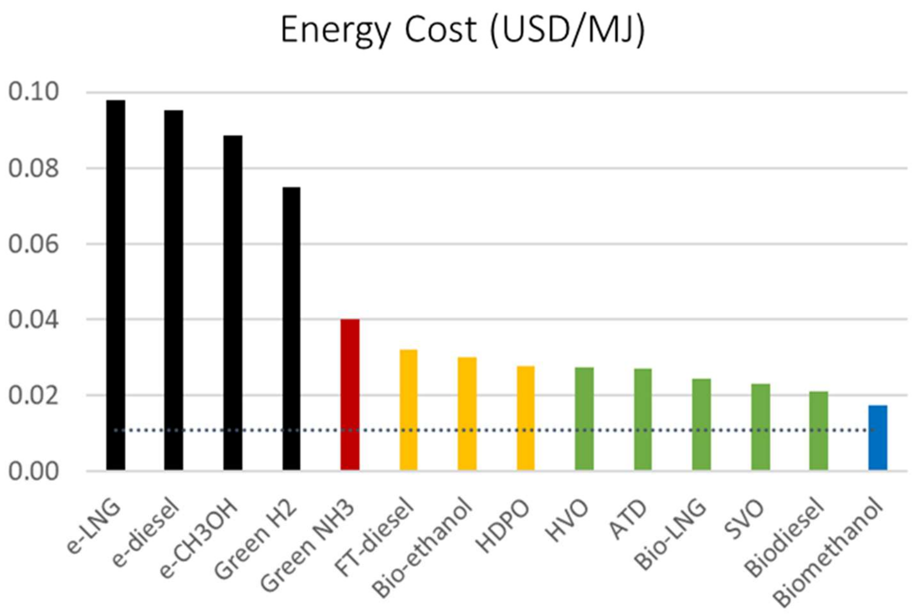

Figure 4: Cost normalization to compare the different fuel alternatives (dashed line represents HFO energy costs). Ratings based on the ratio fuel cost/bunker cost (5: until 200%, 4: 200-250%, 3: 250-300%, 2: 300-400%, 1: above 400%). Elaborated with data from [4,25,37–42,29–36].

Table 3 summarizes safety aspects regarding some of the assessed fuels and represents a guide to evaluate them in the safety indicator. Table 4 presents a summary of the existing regulations for using alcohols as fuels for bunkering procedures and identifies areas where additional regulation is required.

Table 3: Safety and environmental risks of selected fuels. Based on [42].

	MGO	LNG	CH_3OH	H_2 (liq.)	NH_3 (liq.)
Flammability	Liquid and flammable vapor	Extremely flammable gas	Highly flammable liquid and vapor	Extremely flammable gas	Flammable gas
Pressurized gas	-	Chilled gas: cryogenic burn risks	-	Chilled gas: cryogenic burn risks	Pressurized gas: risk of explosion if heated
High toxicity	Harmful if inhaled	-	Toxic if inhaled, ingested or in contact with skin		Toxic, if inhaled
Inhalation risks	May be fatal if inhaled or ingested	-	-		-
Skin corrosion	Skin irritation/burns	-	-		Several damage to skin and eyes
Marine environment	Toxic for marine life (long lasting effect)	-	-		Very toxic for marine life (long lasting effect)

Table 4: Regulations for use alcohols as fuels. Based on [7]

Item	Methanol	Ethanol
	Use as marine fuel	
IMO	IGF	IGF
Class Rules	DNV, LR	DNV
	Rules for cargo transportation	
IMO – Rules for bulk chemicals transport	MARPOL Annex II and Code IBC	MARPOL Annex II
IMO – Rules for dangerous cargo transport	Code IMDG	Code IMDG
	Rules for cargo transport in internal waterways	
European rules for dangerous cargo transport	ADN	ADN
	Bunkering	
Ships bunkering	MARPOL Annex II e Code IBC	MARPOL Annex II
Trucks bunkering	ADR	ADR
Port operations	ISM	ISM
	Fuel standards	
Fuel quality standards	IMPCA – Reference specifications for methanol and/or ASTM D-1152/97	EM 15376 or ASTM D 4806 specifications for ethanol as blend fuel

4. Results

Table 5 presents the scores (in color and number scale) of the 14 fuels according to Brazilian context. After evaluating the alternatives, the final score was determined according to the weights defined for the different criteria (Table 6). The complete evaluation of fuels and justification for the scores given can be accessed in the Supplementary Material.

Table 5: Evaluation of fuels in the defined criteria

	SVO	Biodiesel	HVO	HDPO	FT-diesel	ATD	Bio-LNG	Biomethanol	Bioethanol	Green H_2	Green NH_3	e-diesel	e-LNG	e-methanol
Availability	2	2	2	3	4	3	2	4	3	3	3	1	1	1
Applicability	4	3	5	5	5	5	3	4	2	1	2	5	3	4
Technology Readiness	5	5	5	2	3	4	5	4	3	3	2	3	2	2
Energy Density	5	5	5	5	5	4	3	2	3	1	2	5	3	2
Economic	4	4	4	3	3	4	4	5	3	1	2	1	1	1
Safety	5	5	5	3	5	4	3	3	4	2	2	5	3	3
Standards	3	3	4	4	4	4	4	5	5	1	1	4	4	5
Local Sustainability	4	4	4	4	5	4	5	4	4	3	3	3	3	3
Global Sustainability	3	3	3	4	5	4	3	4	2	5	5	5	4	5

Table 6: Final score of fuels evaluation

Ranking	Score	Fuel
1	89	FT-diesel
2	81	HVO
3	80	ATD
4	78	SVO
5	76	e-diesel
6	75	Biodiesel
7	75	Biometanol
8	74	HDPO
9	68	Bio-LNG
10	60	Bioetanol
11	60	e-methanol
12	55	e-LNG
13	54	Green NH3
14	50	Green H2

SVO

Besides being a drop-in alternative, SVO has the advantages of high technological maturity and good energy density to replace heavy fuel oil (HFO). Depending on operational conditions, SVO should be pre-heated prior to the injection in diesel engines [18,19]. However, its current utilization in the food industry and for biodiesel production may affect its availability. Also, sustainability issues may hamper its utilization as a maritime fuel, especially if produced from oil crops such as soybeans and palm [43].

Biodiesel

Biodiesel's energy density and technological maturity comprise its largest advantages as a marine fuel. Also, its consolidated market and distribution chain enhance its economic feasibility, at least in the near-term. To produce a totally renewable biodiesel, renewable alcohols should be used in the transesterification process, which may increase fuel costs. Notwithstanding, the fuel's low stability and the possibility of water contamination hinder its utilization as a drop-in alternative [44,45]. Furthermore, biodiesel's current utilization in road transport and some of its sustainability issues reduce its attractiveness to the shipping sector [43]. Sustainability concerns are related to oil crops production, as the fuel is produced from SVO, and to the use of fossil methanol in the current conversion process.

HVO

HVO represents a drop-in alternative to replace fossil maritime fuels. Its high energy density, its current production at commercial scales and the growth forecast for the upcoming years make it an interesting alternative to replace fossil fuels [46]. However, sustainability issues regarding oil crop-based biofuels may compromise its availability. Further, the high quality of HVO may make it a more suitable alternative for use in the aviation sector [43].

HDPO

HDPO is also a drop-in alternative produced from lignocellulosic biomass, which is a largely available resource throughout the world and especially in Brazil. The high energy density of HDPO makes it a suitable option to replace fossil fuels in ocean-going vessels. Although the technology is not mature yet, new conversion facilities are under construction [44,47,48]. Finally, concerns regarding its low flash point and high costs may become a barrier for its use as a maritime fuel.

FT-diesel

FT-diesel is another drop-in alternative that uses residual biomass as feedstock, which may be an advantage for Brazil. The fuel's high energy density and mitigation potential makes it an interesting alternative to replace fossil fuels in long-distance shipping. Also, the high value co-products (road diesel, naphtha, jet fuel etc.) may enhance FT plants feasibility. However, up until now at least, the technology has been demonstrated at a pilot-scale but is not commercially available yet [49–51]. Moreover, as a high-quality and costly alternative (around 0,03 USD/MJ), it may be better suited for the aviation sector, whose fuel is highly priced.

ATD

ATD is also a drop-in alternative that uses bio-based alcohols to produce distillate fuels. The fuel has the advantages of high applicability, technological maturity and energy density. As for FT-diesel, the high value co-products may encourage the development of alcohol-based biorefineries and, therefore, enhance fuel competitiveness. However, as biomass-based alcohols has been widely used in the road transportation sector, it may not be available to produce maritime biofuels, at least in the medium term. Notwithstanding, the utilization of residual biomass to produce second generation alcohols and the prospects of road transport electrification may increase its availability significantly in the medium to long term.

Bio-LNG

Bio-LNG represents a biofuel alternative that is not suitable for diesel engines, that comprise the major part of the world shipping fleet. Some LNG-fueled vessels, equipped with dual-fuel engines, are already in operation [9,52]. Bio-LNG's development is mostly limited by the availability of bunkering facilities around the World. Also, the technological processes to produce the fuel are fully developed. However, the fuel has lower volumetric energy density in comparison to distillate fuels (about 20 MJ/L), which means that it requires 80% more storage space in ships [12]. Also, bunkering costs represent an economic challenge for its use as maritime fuel [53]. Nonetheless, the existence of standards for gaseous maritime fuels and the potential reduction in GHG and air pollutant emissions make bio-LNG a potentially attractive alternative.

Biomethanol (Bio-CH3OH)

Biomethanol is a liquid fuel under ambient temperature and pressure. It can be produced from several feedstocks and relies on a solid existing infrastructure, especially if produced from biomethane. It has also a good economic performance, with reasonable production costs in comparison to other low-carbon options[6] [54]. Despite not being a drop-in fuel, methanol has good applicability on the global fleet, since its use requires minor modifications on dual-fuel engines and bunkering infrastructure, with the possibility of flex-fuel operation. Moreover, biomethanol provides significant air pollution and GHG emissions cutbacks [27,54]. The main inconvenient related to the use of biomethanol as a maritime fuel is its low energy density, as it requires approximately twice as much space as distillate fuels. Also, in the case of the biodigestion route, bio-CH3OH depends on geographically dispersed feedstock.

Bioethanol (Bio-C2H5OH)

Ethanol is the most used biofuel in transport sector, with the US being the largest producer followed by Brazil. Given its high availability, bioethanol prices are low compared to other carbon-neutral fuels [55]. However, ethanol has not been used as a fuel in large maritime engines. In order to make it a drop-in alternative for diesel engines, it is necessary to increase its cetane number and lubricating power, which could substantially raise its production cost [56]. For the long term, ethanol fuel cells may become an option, though [57–60]. Moreover, bioethanol has about half the energy density of diesel, which implies in additional fuel storage space. In terms of safety, it can be corrosive to some materials, but it easily dissolves

[6] Reasonable production costs in the case of the biodigestion + reforming route.

in water and is biodegradable. At the same time, bioethanol can contribute to local and global impacts, considering its aldehydes and CO2 emissions and, depending on engine characteristics, nitrogen oxides (NOx) as well [55].

Green Hydrogen

Hydrogen (H2) use in fuel cells is the main alternative for its utilization for ship propulsion, but the adaptation of internal combustion engines (ICEs) can also be considered. Its use as a fuel does not generate direct GHG emissions or air pollution. Nevertheless, green H2 has relevant disadvantages to be used as a maritime fuel. In addition to being highly flammable, producing an invisible flame and having a very low volumetric energy density, the fuel also has high production, transport and bunkering costs (total costs ≈ 0,03 USD/MJ) [9,12,61]. Technological readiness is also an issue, especially when produced from intermittent renewable energy sources. Moreover, the existing infrastructure is completely based on non-renewable energy and the production via electrolysis puts extra pressure on water resources, indicating its current lack of feedstock and infrastructure for its production and use [37]. On the other hand, remaining global solar and wind energy potentials are vast, which would be a plus for green hydrogen production and use in the future [62].

Green Ammonia

Green ammonia is potentially a carbon-neutral fuel (reduction of at least 95% in lifecycle GHG emissions) that also leads to significant reductions in air pollutants (except for NOx). It could be used as a maritime fuel in internal combustion engines or in fuel cells (either directly or as an energy carrier for H2) and both pathways face technological and technical challenges. The use of pure NH3 in ICEs, for instance, is hindered by its combustion properties[7]. Alternatively, it could be used as a support fuel, such as green H2, biomethanol or biogas [63]. In the case of fuel cells, an onboard plant would be required to crack the NH3 molecules and produce H2. To this end, high-temperature fuel cells, which are not fully developed, would be required. Thus, NH3 is not a fully mature technology yet (especially in terms of its use as a fuel) and has low applicability to the existing fleet. Energy density is also a problem given that NH3 requires a volume three times higher than conventional bunker fuel [12,42]. Due to the high cost of electrolysis, green ammonia's economic performance is also weak (≈ 0.04 USD/MJ), with levelized energy costs around two times those of distilled

[7] Narrow flammability range and low flame speed.

biofuels. Finally, although NH3 is safe from a flammability perspective, it is corrosive and highly toxic, harnessing its operational safety [42,63]. This is particularly important for releases into the sea (spills), as shown by [64]. A possible pathway for NH3 as a fuel in long-distance travel ships could be, firstly, based on the least-cost fossil derived-NH3. This would allow converting harbors and fleet. Then, a green NH3 industry could be deployed in large scale. However, as of today, Brazil is already highly dependent on ammonia/urea imports as fertilizer, and the country´s existing ammonia plants have been recently closed [65].

Electrodiesel (e-diesel)

Electrodiesel is the same fuel as FT-diesel in terms of chemical composition. Thus, it has very good energy density, applicability and safety ratings. Also, from a global sustainability perspective, the e-diesel is a promising fuel, presenting very low or nearly zero lifecycle GHG emissions. Its main drawback is the economic aspect, with production costs around 0,1 USD/MJ [38]. The production of H2 from intermittent energy sources implies high costs and several technical challenges. Besides, there is another relevant issue regarding feedstock availability, given the fact that CO2 must come from CCS[8] or DAC[9], which are currently not available in large scales [66].

Electromethane (e-LNG)

Electromethane is chemically identical to biomethane. Therefore, many of the bio-LNG ratings also apply to e-LNG. Furthermore, similarly to e-diesel, e-LNG has a weak performance in terms of costs (≈ 0,1 USD/MJ) and feedstock availability (again, CO2 from CCS or DAC) [38].

Electromethanol (e-CH3OH)

Electromethanol shares many of the biomethanol ratings because they are equivalent fuels in terms of molecular composition. Similarly to the other e-fuels, e-methanol faces challenges regarding feedstock availability (once again, CO2 from CCS or DAC) and technology readiness level. However, its production costs tend to be slightly lower than those of e-diesel and e-LNG, which could be an advantage [38].

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[8] Carbon Capture and Storage (CCS) is the process of capture, transport and storage of waste CO_2 from different sources (industries, refining, and biomass conversion plants, for example).

[9] Direct Air Capture (DAC) represents the capture of CO_2 directly from the atmosphere to produce a concentrated stream of CO_2.

5. Discussion

FT synthetic diesel occupies the first position in the ranking followed by HVO and ATD. The potential for reducing GHG emissions of FT-diesel favors its evaluation and the drop-in characteristic of FT-diesel, HVO and ATD that indicates low or negligible/zero need for engines, bunkering and logistics modifications, contributes for their high scores. SVO, e-diesel and biodiesel figure in fourth, fifth and sixth positions. Even though SVO has the advantages of high availability, technology maturity and almost drop-in characteristics, sustainability concerns threat its utilization as marine fuel. The same applies to biodiesel, whose utilization in marine diesel engines is limited by up to 7% mass basis [67,68]. E-diesel has the best score among the e-fuels given its drop-in characteristic, despite its high cost and availability challenges.

In an intermediate range figures biomethanol, HDPO, bio-LNG and bioethanol. Biomethanol has advantages in terms of bunkering but is penalized by its low energy density. In case of HDPO, the fuel has the advantage of being a drop-in alternative that uses residual biomass as feedstock, while the technological maturity represents its major drawback. For bio-LNG, the lack of infrastructure, safety concerns and methane fugitive emissions, hamper its utilization as marine fuel. Regarding bioethanol, even though the fuel is largely produced in Brazil, issues regarding its applicability and energy density undermine its use as marine fuel in the short term.

Electromethanol, electromethane, green ammonia and green hydrogen occupy the worst positions in the ranking. Electromethanol has similar evaluation to biomethanol, with the additional challenges regarding, feedstock availability, technology readiness and high costs. Electromethane's high costs and low technology readiness and availability penalize its evaluation in addition to biomethanol's. Finally, even though green ammonia and green hydrogen have high potential to reduce GHG emissions, their low energy density, high cots, safety and applicability issues hamper their utilization in the short term. In the case of ammonia, it is worth mentioning that, even though some studies enhance its use as an alternative fuel, they highlight its applicability only for short-distance transportation [42].

Besides the evaluation of the fuels in each criterion, the choice of criteria weights may impact the results. Hence, a sensitivity analysis was conducted to evaluate differences in the ranking according to different criteria weights. First, it was considered weight 1 for all criteria (case S1). Then, weight 2 was attributed to economic criterion (case S2) and the same weight as in the baseline case (Table 2) for the others. Table 7 summarizes the attributed weights in sensitivity analysis cases in comparison with the baseline.

Table 7: Sensitivity analysis cases

Sensitivity analysis - Criteria weights	Baseline	S1	S2
Availability	2	1	2
Applicability	2	1	2
Technology Readiness	2	1	2
Energy Density	2	1	2
Economic	1	1	2
Safety	2	1	2
Standards	1	1	1
Local Sustainability	1	1	1
Global Sustainability	3	1	3

Table 8 compares the final ranking for each sensitivity case with the baseline (as shown in Table 6). These results show that modifications in criteria weights have minor impact the ranking, as most of the fuels remains in nearly position. FT-diesel, HVO, ATD and SVO registered the same performance in all cases, occupying the fourth first positions.

E-diesel was the only fuel whose performance varies considerably in each of the sensitivity cases. In the baseline scenario, e-diesel occupies the fifth position while in cases S1 and S2, it occupies the nineth and eighth positions, respectively. Such difference is justified by e-diesel's high potential to reduce GHG emissions, which favors its evaluation in the baseline scenario and its high costs, which undermines its performance in case S2.

Biomethanol, biodiesel, HDPO, Bio-LNG remain in intermediary positions, while ethanol occupies the same position in all cases. E-methanol, e-LNG, green NH3 and green H2 registered the lowest scores in all cases, mostly due to their high costs, low technological maturity, availability and energy density.

Table 8: Fuel ranking in the sensitivity analysis cases

		Results			
Baseline		S1		S2	
FT-diesel	89	FT-diesel	87	FT-diesel	87
HVO	81	HVO	82	HVO	81
ATD	80	ATD	80	ATD	80
SVO	78	SVO	78	SVO	78
e-diesel	76	Biomethanol	78	Biomethanol	76
Biodiesel	75	Biodiesel	76	Biodiesel	75
Biomethanol	75	HDPO	73	HDPO	73

HDPO	74	Bio-LNG	71	e-diesel	73
Bio-LNG	68	e-diesel	71	Bio-LNG	68
Bioethanol	60	Bioethanol	64	Bioethanol	60
e-methanol	60	e-methanol	58	e-methanol	58
e-LNG	55	e-LNG	53	Green NH_3	53
Green NH_3	54	Green NH_3	49	e-LNG	53
Green H_2	50	Green H_2	44	Green H_2	48

6. Final Remarks

The evaluation and comparison of the different fuel alternatives carried out in this study aimed to identify the main advantages, disadvantages and application possibilities of these alternatives in the Brazilian long-distance maritime transport sector. Results indicate that distilled biofuels are the most promising alternative, at least in the short term, given their high energy density and their compatibility with the existing infrastructure. This is particularly relevant in the case of Brazil, whose international trade profile is characterized by long-distance transportation of low added value products. However, the availability of sustainable biomass and competition with other sectors may hinder its application in the production of biofuels for the maritime transport sector.

In this sense, the use of biomass residues that are currently not used reduces the concerns associated with sustainability and allows the production of bioenergy on a large scale. Also, some technological pathways produce high value products, such as biojet fuel and naphtha, that may stimulate the construction of novel biorefineries in which bio-based bunker fuels are considered as residual products and, therefore, have lower production costs.

However, logistical issues associated with the dispersed location of resources and large-scale production plants can increase the costs and emissions of biofuels. Bio-LNG represents a medium and long-term alternative that may not be suitable for long-distance maritime transport, given the lack of supply infrastructure and its low energy density.

Biomethanol is also shown to be a favorable alternative as it presents technological maturity and a consolidated transport and distribution infrastructure. It has good applicability in the current fleet of ships, but has low energy density, which makes it demand twice as much space on the vessels when compared to distillate fuels. The use of bioethanol as a marine fuel is particularly interesting for Brazil, one of its main world producers. However, its low energy density, the need for additives, the risk of corrosion and its current use in road transport reduce its competitiveness for navigation.

Green hydrogen seems to be a distant alternative for the Brazilian case, mainly due to its low performance in terms of costs, energy density and applicability. Green ammonia, which has slightly better ratings in these criteria, may be an option for a hydrogen carrier or an alternative for Brazilian cabotage transport. On the other hand, e-fuels are an interesting option from both a technical and a sustainability perspective, but still face significant challenges in terms of cost and technological maturity in the medium term.

Finally, despite the efforts to conduct a preliminary assessment for Brazilian potential to produce carbon-neutral fuels for maritime transportation, some limitations should be addressed in future studies to investigate in further details the implications of fuel replacements to comply with IMO goals 2050. For instance, site-specific life-cycle assessments and georeferenced analysis would determine the mitigation potential and logistic challenges regarding novel fuels production and utilization. Also, an economic evaluation of fuel technology pathways and their inclusion in integrated assessment models (IAMs) would provide a better understanding of the impacts in energy and land-use by replacing conventional maritime fuels for carbon-neutral alternatives.

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