energies

Article

Perspective Use of Fast Pyrolysis Bio-Oil (FPBO) in Maritime Transport: The Case of Brazil

Luís Cortez [1], Telma Teixeira Franco [1], Gustavo Valença [1] and Frank Rosillo-Calle [2,*]

[1] Núcleo Interdisciplinar de Planejamento Energético-NIPE, State University of Campinas—UNICAMP, Campinas 13083-896, Brazil; cortez@unicamp.br (L.C.) tfranco@unicamp.br (T.T.F.); gustavo@feq.unicamp.br (G.V.)
[2] Centre for Environmental Policy, Faculty of Natural Sciences, South Kensington Campus, Imperial College, London SW7 1NA, UK
* Correspondence: f.rosillo-calle@imperial.ac.uk or frc@ic.ac.uk

Abstract: The maritime transportation sector (MTS) is undertaking a major global effort to reduce emissions of greenhouse gases (GHG), e.g., sulfur oxides, nitrogen oxides, and the concentration of particulates in suspension. Substantial investment is necessary to develop alternative sustainable fuels, engines, and fuel modifications. The alternative fuels considered in this study include liquified natural gas, nuclear energy, hydrogen, electricity, and biofuels. This paper focuses on biofuels, in particular fast pyrolysis bio-oil (FPBO), a serious partial alternative in MTS. There are some drawbacks, e.g., biofuels usually require land necessary to produce the feedstock and the chemical compatibility of the resulting biofuel with current engines in MTS. The demand for sustainable feedstock production for MTS can be overcome by using cellulose-based and agroforestry residues, which do not compete with food production and can be obtained in large quantities and at a reasonably low cost. The compatibility of biofuels with either bunker fuel or diesel cycle engines can also be solved by upgrading biofuels, adjusting the refining process, or modifying the engine itself. The paper examines the possibilities presented by biofuels, focusing on FPBO in Brazil, for MTS. The key issues investigated include FPBO, production, and end use of feedstocks and the most promising alternatives; thermal conversion technologies; potential applications of FPBO in Brazil; sustainability; biofuels properties; fuels under consideration in MTS, challenges, and opportunities in a rapidly changing maritime fuel sector. Although the focus is on Brazil, the findings of this paper can be replicated in many other parts of the world.

Keywords: biofuels; fast pyrolysis; bio-oil; Brazil; marine transportation; blends; FPBO

Citation: Cortez, L.; Franco, T.T.; Valença, G.; Rosillo-Calle, F. Perspective Use of Fast Pyrolysis Bio-Oil (FPBO) in Maritime Transport: The Case of Brazil. *Energies* **2021**, *14*, 4779. https://doi.org/10.3390/en14164779

Academic Editor: José Carlos Magalhães Pires

Received: 19 June 2021
Accepted: 31 July 2021
Published: 6 August 2021

1. Introduction

The purpose of this paper is not fundamental research, but to present an overall view of current research in fuel development alternatives in the Maritime Transportation Sector (MTS), with a focus on biofuels, FPBO, and Brazil. The energy sector is undergoing a fundamental shift, and MTS is not immune to it, though each sector has its specific problems. Unlike other transport sectors, MTS is behind, given its nature, e.g., large engines for which alternatives to fossil fuels are far more difficult and limited. The transition would not be easy or short-term. However, this niche market presents unique opportunities and challenges for the use of biofuels.

Biofuels can be considered a viable partial alternative to fossil fuels in the MTS, particularly in Brazil, given their huge potential and historical experience. According to various authors [1–8], the utilization of biofuels in MTS faces several challenges, including:

- Feedstocks:
    - selection of crops, be traditional or cellulose-based
    - their sustainable production and end use competition for land

  - logistics associated with feedstocks
- Processing Technologies
  - difficulties associated with processing
  - logistics associated with processing technologies
- End Use
  - engine modifications
  - logistics associates with the change from a fossil to a biofuel-based one
  - the difficulties posed by the paradigm fuel shift

Therefore, besides the difficulties associated with the feedstocks as the conversion technologies, there is a concern about how the "business of today" heavily dependent on bunker oil will be adapted into the "business of tomorrow" in which biofuels can play a role.

In this sense, the main purpose here is to discuss the possible use of fibers as feedstock, pyrolysis as the conversion technology, and few strategies to match the biofuel and bunker oil in this transition period. This would allow a smoother transition towards a reduced emission derived from the MTS.

Biofuels are a viable partial alternative to fossil fuels in the MTS, but they face serious challenges. The paper focuses on various key issues, including production and end use of feedstocks and their most promising alternatives and sustainability; thermal conversion technologies; potential and possible engine modifications; fuel properties; fuels under consideration in MTS; potential applications of FPBO, with emphasis on Brazil; environmental sustainability, challenges, and opportunities in a rapidly changing maritime fuel sector; and policy considerations.

The emphasis on FPBO is because it offers one of the best possible alternatives to current fuel use in the MTS. It looks, in some detail, to be the pros and cons of using such technology (e.g., possible engine modification, use of blends, fuel upgrading, technical difficulties, etc.). The case for Brazil is based on the country's potential and historical experience of biofuels in the transportation sector, and strength on R&D. Although the emphasis is Brazil, the findings can be extrapolated to many other parts of the world.

2. Material and Methods

The authors have carried out an extensive literature review of all the key issues covered in the paper. They have also used personal contacts with companies working in the MTS in Brazil, other ongoing research projects, and unpublished literature. Based on this outcome, were selected the main topics discussed in this work. Some of the data remain still commercially sensitive, and hence, cannot be fully disclosed.

3. The Importance of MTS and Its GHG Emissions

The transport sector is the key user of liquid biofuels, primarily road, but other niche markets are gradually emerging, e.g., aviation and maritime transportation. While the aviation sector requires high quality fuel, the maritime sector can use lower quality fuels, such as bunker oil and marine diesel. Unfortunately, this results in higher overall emissions. Currently, more than eighty percent of goods (In 2014, the world merchandise trade was about 9.84 billion tons, and the world seaborne trade was around four-fifths (just under 8.00 bn)) are transported by ship [1].

Currently, more than eighty percent of goods are transported by ship [1]. The most utilized fuel in MTS is: Heavy fuel oil (HFO), light fuel oil (LFO), and marine gasoil (MGO). According to Rodrigue [2], maritime fuels account for about 40% of overall operating costs, and is, therefore, considered a key element in MTS. This somehow explains why MTS tends to prefer, at least until today, less expensive fuels.

However, these less expensive fuels tend also to be more pollutant. The poor quality of marine fuels is due to their high sulfur content and can be classified into two main categories; (i) lower-cost residual oil/heavy fuel oils (HFOs), mostly consumed by large low speed vessels, and (ii) distilled higher-quality oils or marine gasoil (MGO), widely used in medium and high-speed vessels and auxiliary engines of low-speed vessels. The HFO, also named bunker oil alone, is the most utilized and consumed in high quantities, 250 million tons per year [2].

Figure 1 shows global annual demand for bunker oils from 2018 and 2019 and estimates up to 2024. It is important to note a clear tendency to eliminate the use of non-scrubbed HSFO by scrubbed HSFO. It is also important the trend for cleaner fuels in the MTS, and in particular, the increase in low-sulfur fuel. Reduction in sulfur content is a global trend to promote lower environmental contamination and acid rain.

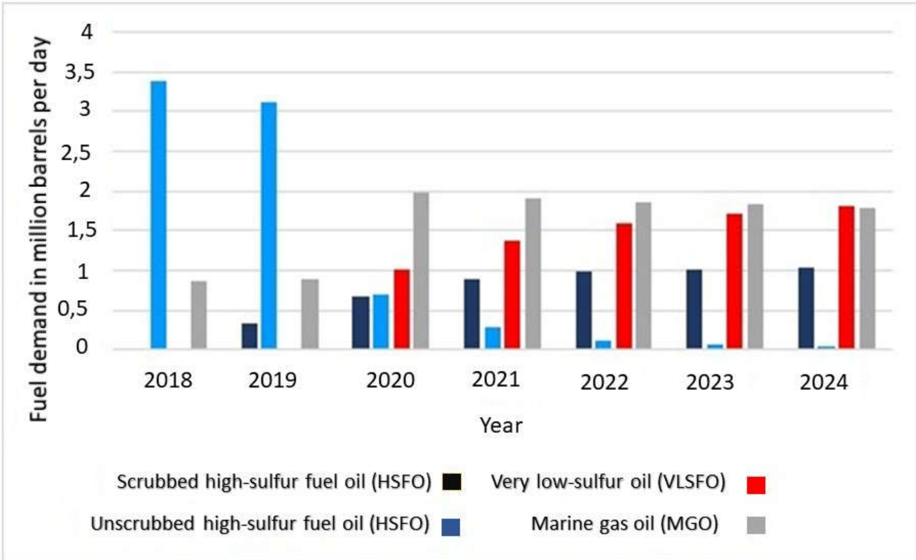

Figure 1. Daily global marine bunkers consumption. Source: [3].

Marine fuel oils have a relatively low price (~US$ 300/M metric tons) but generate a high amount of particulates in combustion. Emissions from the MTS represent 3% to 6% of CO_2, 4–9% SOx, 14% to 31% NOx. The daily global consumption is equivalent to approximately 5 million barrels of oil [4]. The International Maritime Organization (IMO), a regulatory branch of the United Nations for the navigation sector, is committed to reducing the carbon impact of shipping by 40%, relative to 2008 levels by 2030, and 70% by 2050 [9].

To mitigate these impacts, marine diesel has been mixed with fuel oil to reduce sulfur emissions and meet the SOx and NOx emission established by IMO. Under IMO legislation, restrictions on SOx and NOx have been in place, since the beginning of 2020, and 40% CO_2 emission reductions are expected by 2030. Major global health and environmental benefits are expected, particularly for populations living close to ports and coastlines [5]. Sulfur Emission Control Areas (SECAs) are the Baltic Sea, the North Sea, the North American region (containing the coastal sector of the United States and Canada), and the United States Caribbean Sea areas (around Puerto Rico and the United States Virgin Islands). Contents of 0.1% sulfur (by mass) were set in SECAs in 2015, and globally to 0.5% by 2020. According to Van et al. [10], IMO regulations will significantly impact on the MTS future marine fuel market and ship emissions. However, changes in the refinery processes will require high capital investment, e.g., the cost of desulfurized fuel is expected to go up by 50%.

New marine fuel for use in marine diesel engines and boilers, before conventional onboard treatment (settling, centrifuging, filtration), whether mixed or not, must meet the requirements established in ISO 8217: 2017, which establishes technical specifications, such as viscosity, density, cetane number, sulfur content, flash point, acidity, sediments after filtration, pour point (summer and winter), water content, ash, lubricity, among others. It also establishes seven categories of distillate fuels—one of which is for diesel engines used for emergencies and six categories of residual fuels; it also defines the terminology. For example, the term "fuels" currently includes the following: Hydrocarbons from petroleum crude oil, oil sands, and shale oil; hydrocarbons from synthetic or renewable sources, similar in composition to petroleum distillate fuels; blends of the above with a fatty acid methyl ester(s) (FAME).

3.1. Brazil as a Case Study in the MTS

Developing countries with coastlines depend heavily on maritime transportation for exports/imports. For example, Brazil strongly depends on MTS for exporting iron ore, oil products, and agricultural commodities, which represent more than 50% of its overall exports.

By volume, Petrobras, and Vale companies, are among the main bunker oil consumers, since they commercialize oil and iron ore, the main bulk goods traded by Brazil. Both companies are developing strategies for cutting sulfur and GHG emissions. This is a long and costly process but, in the long run, these companies may benefit from the image related to environmental improvement.

Vale uses large ships to transport iron ore to Asian ports, using mostly low-cost bunker oil. Low-cost iron ore requires low transport costs as competition in this sector is fierce. To make the transport more sustainable, and in compliance with IMO initiatives, Vale has implemented an Ecoshipping R&D Program in cooperation with different industrial players. The aim is to install scrubbers in the dedicated fleet and replace obsolete vessels, to reduce up to 15% of emissions by 2035. The objective is to pursue a policy to render the entire chain more sustainable, from iron ore mines to the destination harbors. For instance, Vale is studying the use of alternative, more sustainable fuels, to replace bunker oil, and biofuels are among the possibilities (see: www.vale.com accessed on 20 May 2021).

Brazil also has two other important markets for bunker or diesel oil substitution in the navigation sector. Both markets serve passenger and cargo transport linking distant locations to the main urban centers. Moreover, in both cases, the lack of adequate infrastructure is characteristic not only in ports and ships, but also in the interface with other transportation modes. Despite these difficulties, the Brazilian national navigation sector is constantly increasing its activities.

The first is the coastal transportation, since several major Brazilian cities are located alongside its more than 8000 km coastline, from Rio Grande harbor in the South of Brazil to Santana harbor near Macapá in the North of Brazil [11].

The other important market is river transportation (and other waterways), particularly in the Amazon and Paraná basins. In the Amazon region, transportation involves both passengers and cargo. It is more traditional, going back to the beginning of the Brazilian colonial period, and is vital for connecting small villages and towns to big centers like Manaus, Santarem, and Belém. Belém plays an important role as the interface/hub between the Amazon River basin and the coastal transport with the rest of Brazil.

The petroleum derivatives supply (particularly diesel) for the entire Amazon region is both energy inefficient and cost-intensive—resulting in doubling prices when compared to central-south Brazil. From an energy point of view, it is estimated that two barrels of diesel are often required to deliver one barrel, without counting its unregular supply.

Since the construction of bridges and paved roads are too expensive in the Amazon region, river transportation is likely to remain an important option both for passengers and cargo. As for the Paraná River basin, the transport was implemented in the last 40–50 years and serves almost exclusively cargo. For example, agricultural and mineral commodities, and primarily covers the states of Mato Grosso, Mato Grosso do Sul and Goiás, and then to São Paulo and Paraná states where they are moved to road transport. The Paraná basin also drains its waters through Paraguay, Argentina, and Uruguay, which could eventually be an option for export, but presently several hydroelectric dams, without locks, renders navigation more complicated.

Both markets, in the Amazon and Paraná River basins, although they are not fully exploited and present unsatisfactory infrastructure requiring important investments, are also good candidates to use sustainable biofuels. Sustainable biofuels production could benefit almost 50 million habitants scattered in more than 60% of Brazilian territory. It could help to maintain this population there, improving their quality of life. Given its enormous land size (850 Mha) and climate, Brazil has one the world's largest potential for producing vegetable and palm oils.

3.2. Biofuel Alternatives under Consideration in MTS

The MTS is committed to reducing GHG emissions and is considering several alternatives to reduce, at least partially, such emissions. Among these alternatives are: (i) Low emissions fuels, e.g., natural gas, hydrogen, methanol, and (ii) biofuels, e.g., straight vegetable oil (SVO), biodiesel (1st and 2nd generations), biogas, bio-hydrogen, and lignocellulosic-based bio-oil.

Some of the difficulties in adapting the most innovative fuel technologies to replace fossil fuels in MTS have recently been investigated by various authors. For example, Brynolft et al. [12] evaluated the environmental impacts of unconventional maritime fuels, liquified natural gas (LNG), liquified biogas (LB), methanol, and bio-methanol. The findings show that a significant impact on reducing GHG could be met, but only by replacing fossil fuels with LB and bio-methanol. Bittante and Saxen [13] have indicated that replacing conventional maritime fuels by LNG offers flexible storage and greater efficiency in fuel distribution.

Bach et al. [14], described two innovative solutions to reduce GHG emissions in the MTS, (based on experiments on the Norwegian coast), capable of meeting the Paris Agreement: Electric-battery and hydrogen energy, which can be developed more quickly to satisfy local needs. This presents the sector with both huge challenges and opportunities for large-scale implementation, e.g., regulations and standards will need to be developed, including specialized personnel. A further example of future difficulties described by the authors, in the case of battery innovation, is the fact that such batteries have been mostly adopted for light transport vehicles, while hydrogen technology is limited by the availability of large-scale sustainable supply of renewables.

The transition period will not be short-term or easy and may have to use existing mature technologies to meet demand until new renewable alternative technologies are developed, or at least are more matured.

Due to its importance, reducing emissions in the maritime sector will require a wide range of political, economic, and technological initiatives, both from the public and private sectors. A few international initiatives are already at work. A good example is Goodfuels' initiative in the Port of Rotterdam in the Netherlands. This company announced that the marine renewable biofuel sulfur-free Bio-Fuel Oil (BFO, also known as MR1-100, which is used cooking oil hydro processed by Hydroprocessed Esters and Fatty Acid (HEFA) completed 2000 running hours using 100% renewables, on the Alexander von Humboldt vessel, which is the longest trial of marine biofuel so far, with an 80% to 90% reduction of CO_2 emissions (www.goodfuels.com accessed on 20 May 2021).

Within the proposed alternatives, biofuels offer the best partial sustainable alternative to accomplish GHG reduction in the MTS. However, biofuels will need to:

(a) Guarantee environmental sustainability in the production chain, with good sustainability indicators and no competition with food production.
(b) Be produced at competitive prices; and
(c) Achieve the necessary fuel quality, and good performance in engines, comparable to fossil fuel currently in use.

3.3. Best Biofuels Alternatives for the MTS

Kesieme et al. [4] have suggested that the second generation of biofuels (G2) could be more easily implemented to satisfy fuel demand in the shipping industry. Using straight vegetable oil, biodiesel, and bio-liquefied natural gas could potentially replace the HFO for low-speed engines, the MGO for medium-size engines, and liquid natural gas in gas engines, respectively. However, other biofuels, such as bio-methane and FPBO, can also be used after some modifications. The limitations are because FPBO is an emulsion with water containing high oxygen content, high acidity and corrosiveness, low heating value, and high viscosity. Bio-methane is produced by anaerobic digestion of different types of biomass, or by thermochemical gasification, and its composition is equivalent to fossil natural gas.

Kass et al. [8] have also reported several characteristics and advantages to adopt biofuels for the navigation sector. Among the biofuels considered are biodiesel or fatty acid methyl esters (FAME), (straight vegetable oil (SVO), renewable diesel, Fischer–Tropsch (FT) (Fischer–Tropsch (FT) will be explained later in the text, is a technology that can be utilized to convert syngas to chemical, hydrocarbons or oxygenated hydrocarbons) diesel, FPBO, HTL biocrude, and upgraded FPBO or Hydrothermal liquefaction (HTL) biocrude. HFO oil was considered as a baseline for comparison. R&D recommendations are presented, for using bio-oil as a marine fuel.

Hsieh and Felby [15] published a very comprehensive report on alternative biofuels and their use in the MTS. They have also analyzed infrastructure and regulation issues.

Biofuels are already playing an important role in road transport. Solid biomass has been and remains so in many countries, one of the most important energy sources. The most important biofuels are ethanol from corn and sugarcane, and biodiesel, mainly soybean, as well as other oil-containing crops and tallow. The relatively good performance in conventional internal combustion engines was achieved by the non-drop-in type of solutions, with minor adjustments in compression ratio, and the introduction of creative solutions like the flex-fuel technology in the case of Otto cycle engines for ethanol. Although relatively good performance has allowed a large use of biofuels in road transport, it is unlikely they will continue to advance progressively on a global scale, given the disparity of available feedstocks. Their development will be geographically located in a few countries, e.g., Brazil (representing 40% of the fuel) and the USA (10%). A few other countries with significant potential, such as China, India, Australia, the EU, etc. However, many small-scale programs are possible, mostly in blends of various proportions.

In MTS, particularly in the case of large ships, there is an opportunity to introduce a non-drop-in type of solution, which can represent an enormous advantage, although the main problem would be that biofuels will have to comply specifically with additional requirements:

- Be environmentally and economically sustainable, avoid competition with food production, deforestation, and generate low GHG emissions,
- Good technical requirements, high energy value, low logistics cost, easiness to blend with the maritime bunker diesel,
- Avoid significant upgrading requirements.

Of course, it is not simple and easy to find biofuels that can simultaneously satisfy all these requirements, on a large-scale, sustainable, and environmentally, e.g., land and fuel competition, such as road transport. Therefore, the large-scale use of biofuels in the MTS will require careful consideration.

3.4. Which Feedstock for MTS?

Choosing the right feedstock is one of the most important decisions to be made when selecting an environmentally sustainable biofuel, due to many factors involved, as discussed previously, from production to technological compatibility.

Vegetable oils, although chemically the closest to combustion engine compatibility, still require a significant amount of land, unless they can use agroforestry residues and cellulose-based feedstocks. Moreover, direct burning of vegetable oils in combustion engines requires the removal of glycerol (upgrading), since when burning produces noxious gases, such as acrolein. Unlike ethanol production from sugarcane which has high productivity (around

7000 l of ethanol/ha), oil-bearing plants have far lower productivity, e.g., as low as 400 kg of oil/ha in the case of soybean. Highly productive crops, such as palm oil, with around 5000 kg/ha, are controversial for environmental and political reasons. Nonetheless, if used on a limited scale, it can be a partial solution. Tests have already been carried out successfully, particularly in European coastal areas. Another approach is the used fried Oil (UFO) used by Goodfuel, although its potential can be considered rather limited.

Therefore, to avoid direct land use and competition with food production, it is recommended to focus on cellulose-based materials, crop residues (e.g., sugarcane bagasse, and other agroforestry residues, as stated previously). Another alternative is dedicated forest energy plantations (e.g., eucalyptus, willows, etc.), which avoid direct competition with food production. A good example is sugarcane bagasse, a byproduct of sugarcane and ethanol production, with zero land use.

Gupta and Verma [6] analyzed the sustainability of bioethanol from 1st and 2nd generation yields. Although expected yields and costs are higher for G2, the main advantage is that no additional agricultural land is needed. However, it is recognized considerably more R&D is still needed.

The use of microalgae and macroalgae feedstocks have also been intensively investigated, and preliminary results show there is considerable sustainable potential for converting them to biofuels. Microalgae grown in salty water and arid areas represent a promising sustainable chain for advanced biofuel production in the future. This alternative still poses considerable challenges, due to costly scale-up and energy-intensive downstream processing [16]. Nwoba et al. [17] indicate additional reasons for using microalgae as feedstock, e.g., their high lipid contents and higher conversion of solar energy than C4 plants, rapid reproduction cycles, adaption to low-value agricultural land, hence avoiding direct competition with food-based crops, the potential use of domestic and agricultural wastewater, flue gas and waste streams. De Boer et al. [18] have concluded that a large scale and energetically feasible, wet microalgal biomass can be converted into fuel by thermochemical conversion of the whole biomass, including hydrothermal liquefaction, supercritical and catalyzed subcritical gasification. A recent work by Ramachandra et al. [19] also suggested that converting carbohydrate-rich abundant marine macroalgae (seaweeds) into biofuels, to supplement oil fuel, could be feasible. Bioprocesses of seaweeds in biorefineries would also lead to several value-added products.

Sugarcane fiber represents 2/3 of sugarcane dry matter. Thus, it is estimated that with the present global sugarcane production of about 2000 million tons per year (approximately 600 M tons/y dry matter), about 400 M tons of sugarcane fiber would be available worldwide. Therefore, the sugarcane sector represents a huge global potential (sugarcane is produced in about 100 countries) because, except for a few countries (e.g., Brazil, Australia), productivity is low, and bagasse is largely wasted. Further, in many countries' sugarcane is still burnt prior to harvesting to ease manual harvesting or simply is not harvested for various reasons. Currently, a significant part of the sugarcane bagasse is used as fuel in sugar mills and ethanol distilleries. However, in most cases, it is used very inefficiently. With high boiler pressure (Rankine systems are utilized in sugar mills. Thermodynamic efficiency depends on the pressure level utilized in these systems. Typically, when no excess bagasse is needed, lower pressures are used, resulting in less efficient systems) and more efficient systems, the potential for saving bagasse is huge, which can largely be used as biofuels. This is simply one example of just one crop. Undoubtedly, agroforestry residues should be taken as a serious alternative.

An additional possibility is dedicated forest energy plantations, such as eucalyptus, pine, and willows for fiber production. The advantage is that this option avoids direct competition with food production as they tend to occupy areas unsuitable for commercial agriculture, e.g., poor quality soils, topography, and climate.

Finally, another option is to consider using solid wastes, such as agroforestry and or municipal wastes. Agroforestry wastes tend to have a more homogeneous composition, but higher costs, due to more complex logistics. On the other hand, municipal solid wastes

(MSW) present a large spectrum of chemical composition. However, this can have negative costs to be environmentally acceptable and have good geographical distribution—all of which are highly positive factors.

3.5. Status of Promising Thermal Conversion Technologies

The thermal conversion technologies are indeed an effective way to use lignocellulosic feedstocks to produce biofuels. Among these technologies, the most promising are fast pyrolysis, although the Fischer–Tropsch (FT) process has also been tested for biomass.

Fast pyrolysis technology has shown to be promising in converting lignocellulosic materials into biofuels. In pyrolysis conversion, three fractions are obtained: Gas, liquid (bio-oil and pyroligneous acid), and solid (charcoal). The proportion and composition depend on several factors, such as raw material and operating conditions of the pyrolysis process, i.e., temperature, residence time, among others.

Extensive research has been conducted in laboratory and pilot-scale throughout the world, see [7], Aston University, in the UK, the National Renewable Energy Laboratory—NREL [20], Oak Ridge National Laboratory—OREL [21], at the Pacific Northwest National Laboratory—PNNL [22] in the USA, and at the Technical Research Centre of Finland—VTT [23]. In Brazil, see Olivares-Gomez [24], Mesa-Perez [25], and Almeida [26]; and with whole sugarcane (Some information at Ensyn website (http://www.ensyn.com/brazil.html accessed on 20 May 2021)) [27].

However, few commercial plants are currently in operation, mainly located in North America and North European countries. Nevertheless, fast pyrolysis technology has reached certain maturity to process cellulose-based feedstocks and to produce bio-oil in large-scale plants. Table 1 shows some commercial plants based in North America and Europe.

Table 1. Examples of commercial fast pyrolysis plants in operation in Europe and North America.

Company	Location	Technology	Feedstock	Feeding Rate	Bio-Oil Production	Investment
Fortum	Joensuu, Finland	Fluidized Bed	Forest residues	100,000 tons/year db	50,000 ton/year	€ 32 million
BTG-BTL	Hengelo, Holand	Rotary Cone Reactor	Wood pallets	5000 kg/h	3200 kg/h	€ 19 million
Ensyn	Port-Cartier, Canada	Circulating Fluidized Bed	Forest Residues	65,000 tons/year db	39,740 m^3/year	US$ 1 million

Also, the Canadian company Ensyn has shown interest (Some information at Ensyn website (http://www.ensyn.com/brazil.html accessed on 20 May 2021)) to install a commercial plant at Suzano (Fibria) at Aracruz, Brazil. Other companies, such as DynaMotive and Renewable Oil International, also have pyrolysis-based commercial plants.

For all its potential (technically, and economically), fast pyrolysis still faces an uphill battle because many of the current difficulties are unsolved. However, its real potential should not be underestimated either, and for this reason, this alternative is further discussed below.

4. Results and Discussion

4.1. Fast Pyrolysis Bio-Oil (FPBO) as a Substitute for Bunker Oil in MTS

As stated before, a biofuel to be considered sustainable, needs to comply with certain criteria as indicated in the introduction of this paper. Sustainability begins with how biofuel is produced. Hence, the importance of being environmentally sustainable.

Sugarcane bagasse also has an advantage, e.g., it can be obtained in sufficiently large quantities, and it is available around the world, in the tropical zones, making it a reasonably acceptable global and sustainable candidate raw material for biofuels.

These characteristics associated with pyrolysis render bio-oil obtained from sugarcane pyrolysis a very interesting biofuel option. BPBO requires relatively low capital investment. The drawback is that this bio-oil is not a "ready-to-use fuel". Bio-oil is basically a tar, with complex composition with too much water and acetic acid. For sugarcane bagasse fast pyrolysis bio-oil chemical composition, see Sohaib et al. (2017) [28].

Following is a brief description of the most promising alternatives for FPBO in large engines, such as those used in the MTS. It discusses the difficulties already identified, followed by the possible technology solutions.

4.2. Direct Use and Blending

FPBO is a complex mixture of compounds, which is much easier to transport than solid biomass because its volume is reduced substantially by conversion to a liquid biofuel of higher added value. This offers considerable advantages for storage and transport, as well as a potential source of several higher valuable chemicals than fuels. At the end of the 20th century, successful use of bio-oil was described in the literature, as boiler fuel, in diesel engines and gas turbine applications, see Czernik and Bridgwater [20] and others. Direct uses of FPBO in its pure form or blended with ethanol or methanol, or fossil fuels, were tested in engines.

As noted by Storey et al. [21], large ships require big engines. Two important features of these engines are: High efficiency (50%) and directly coupled to the propeller. Other characteristics of the 2-stroke diesel engines low rotation (22–102 rpm), uses 6–14 cylinders with more than 5 MW/cylinder weighing approximately 5.5 tons.

According to Hsieh and Felby [15], 80% of the tonnage in marine transportation takes place in large vessels. Ships sizing from 25,000 to 59,999 tons carry 35% of tonnage, and ships above 60,000 tons carry 45% of tonnage. According to the same source, the most common types of marine engines and correspondent fuels are:

(a) Compression ignition (diesel):
   - 2-stroke low speed, using HFO, MDO, and LSHFO,
   - 4-stroke medium speed, using HFO, MDO, and LSHFO,
   - Diesel electric, using HFO, MDO, and LSHFO,
   - Dual fuel using HFO, MDO, LSHFO, and LNG

(b) Spark-ignition:
   - Petrol engine, using gasoline,
   - Gas engine, using LNG and gasoline

(c) Non-reciprocating systems
   - Steam turbine engines, using HFO, MDO, LSHFO, LNG, and gasoline,
   - Gas turbines, using HFO, MDO, LSHFO, LNG, and gasoline.

(HFO, Heavy Fuel Oil; MDO, Marine Diesel Oil; LSHFO, Low Sulfur Heavy Fuel Oil; LNG, Liquified Natural Gas)

One important study using FPBO was developed by VTT Energy (Technical Research Centre of Finland) in 1996 [28]. According to this comprehensive study, wood waste pyrolysis oil was tested as diesel fuel, with the following results:

- Pyrolysis oil was found to be an attractive alternative fuel for diesel engine operation;
- The use of pyrolysis oil, however, involves several challenges and problems, requiring further attention, such as low heating value and corrosion. This suggests the need for a new injection system;
- Additional problems are that pyrolysis oil contains solid particles which can clog filters and cause abrasive wear.
- Pyrolysis oil has bad ignition properties.

The study also concludes that a new injection system can be developed, rendering pyrolysis oil technically feasible.

Combustion of FPBO in stationary diesel engines is also an approach for combined heat and power (CHP) applications. Even at a relatively small scale (<1 MWe), high electrical efficiencies of over 40% are achievable. However, some properties of FPBO make the direct application in diesel engines challenging, due to acidity, water content, high viscosity (compared to diesel), sensitivity to polymerization, and that it is difficult to ignite. Standard fuel injectors and fuel pumps are not corrosion-resistant; however, stainless steel can withstand corrosion, but is often not hard enough to withstand abrasive wear and high impact.

Emulsified mixtures of FPBO have been developed, applying to diesel engines. Increased proportions of added bio-oil showed a reduction of NOx emissions, but increase smoke density, increased ignition delays, and erosion of engine parts and piping. Model-based formulations of biofuel blends have been developed to estimate the combustion performance as suggested by Dahmen and Marquard [29]. They identified the best performing blends to maximize the energy of fuel produced given a fixed amount of biomass. Different blends of twelve biobased intermediates (acetic acid, butyric acid, butanediol, furfural, hydroxymethyl furfural, bioethanol, lactic acid, isobutanol, succinic acid, propanediol, butanol, and furfural) were considered. Blends of FPBO with butanol and marine fuels have been identified by Chong and Bridgwater [7] as short- to medium-term solutions to mitigate emissions from the MTS. However, other reviewers have highlighted that modification of the fast pyrolysis bio-oil processed by chemical/physical reactions (upgrading), may be needed to meet marine fuel requirements.

Laesecke et al. [30] investigated blends of FPBO from softwood pellets with biodiesel by using initial mixtures of 80:20 and 60:40 biodiesel-FPBO (*v*/*v*), prepared using neat biodiesel and FPBO. However, as the two mixtures gave rise to phase separations, the performance of the separated liquid phases was characterized based on a thermogravimetric analysis, heating value, acidity, water content, pH, viscosity, and elemental composition before combustion tests. Thermodynamic performance and exhaust emissions of the biodiesel-FPBO were compared with those for neat biodiesel and diesel. It was found that a better understanding of the performance of FPBO-biodiesel blends would still be required, since the concentrations of the most important components of biodiesel and FPBO were unknown in each tested liquid biofuel.

Li et al. [31] studied the stability of ternary systems of FPBO and a series of mixed solvents (solvent mixture was 33.3% acetic acid, 33.3% hydro acetone, 13.3% phenol, 13.3% furfural, and 6.8% methanol, *w*/*w*). This methodology was useful to determine the solubility regions of mixing FPBO with solvents and to predict the storage and aging stability of those mixtures.

Ternary phase diagrams are powerful for predicting phase separation of mixtures of FPBO-bioethanol and marine diesel. Galindo et al. [5] investigated blends of FPBO from two different feedstocks (one from energy cane and the other from *Eucalyptus*) mixed with bioethanol and marine diesel. They looked at how much GHG emissions could be reduced by replacing pure marine diesel by bioethanol and by FPBO—to find economically feasible renewable homogenous blends. Bioethanol is considered an advanced biofuel with low environmental impact, according to the U.S. Environmental Protection Agency on GHG emissions, and has a higher potential to reduce such emissions than conventional gasoline, according to Life Cycle Assessment (LCA) techniques. Figure 2 represents a phase diagram of the blends of bioethanol, marine diesel, and FPBO. The homogenous region at the left side of the triangle diagram indicates all possible mixtures that can potentially be injected into an engine, due to phase stability. These homogenous blends contain marine diesel concentrations below 40% (*w/w*), and are complemented with any ratio of bioethanol/FPBO, mixed at 25 °C. The properties of all homogeneous blends did not meet the marine fossil fuel specifications, or the most important fuel requirements (low and high heating values [32–35], acidity, viscosity, flash point) after detailed experimental essays. It was observed that the blends which exhibited properties closer to those of marine fuel, achieving the highest low heating value (LHV), lowest water content, lowest acidity, and suitable viscosity, are made of low FPBO concentration and high ethanol concentration, corresponding to the upper homogenous region of the phase diagram. When only FPBO and bioethanol, without any marine diesel, were mixed, complete solubilization of the systems was observed, which is represented by the left side of the triangle, soluble at any ratio. However, binary systems made of marine diesel and bioethanol (right side of the triangle) are completely heterogeneous; the same happens for mixtures of marine diesel and FPBO (bottom side of the triangle). The environmental impacts of the homogenous blends were compared with pure sugarcane ethanol, pure corn ethanol, plain FPBO, municipal solid waste FPBO, and marine diesel. LCA of the ternary systems identified that the impacts followed the mass ratio of the three components. Climate change, water acidification (expressed by kg SO_2eq), and eutrophication and human toxicity impacts were estimated and expressed as a response of the functional unit of 1 kg of fuel. Their work also indicated the need to add an upgrading step to the fast pyrolysis technology to substantially improve marine fuel requirements.

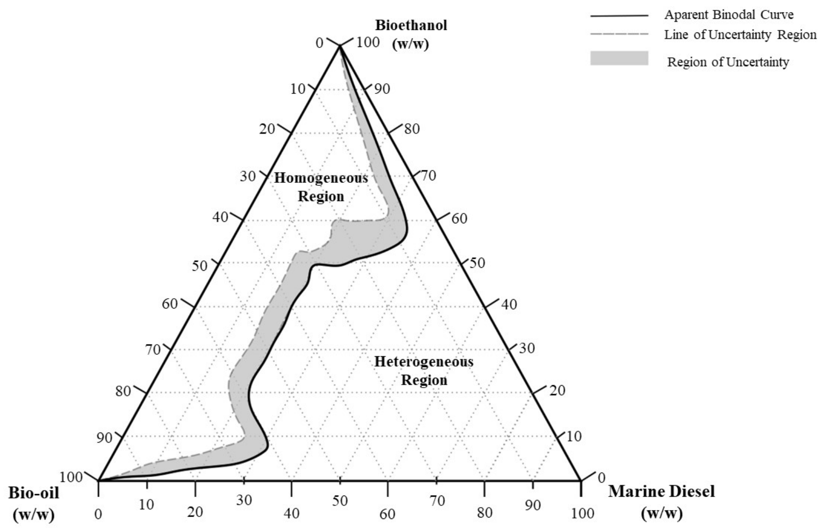

Figure 2. Phase Diagram of FPBO—sugarcane ethanol—Marine Diesel ternary system (25 °C). Adapted from Galindo et al. [5].

Van de Beld et al. [36] used FPBO in diesel engines for combined heat and power applications. The addition of 10–20% ethanol (*w/w*) to FPBO improved the atomization properties used in two modified diesel engines. Volumetric fuel consumption was higher in the case of FPBO, but the electrical efficiency was similar to diesel performance in the available engines located at the company BTG in the Netherlands.

4.3. Improving Strategies for Sustainable Bio-Oil Production

Chemical treatments may be used to improve the bio-oil quality as fuel [37]. Several authors have studied bio-oil catalytic deoxygenation [38–42]. Several reactions take place in the catalytic processes of biomass pyrolysis bio-oil, such as decarbonization, decarboxylation, dehydration, oligomerization, isomerization, and dehydrogenation reactions. The goal of the post catalytic process of bio-oil is to remove oxygen from the molecules, usually as small molecules, such as CO, CO_2, or H_2O [43]. The post catalytic process of bio-oil is an attempt to improve the bio-oil properties by chemically removing the oxygen atoms (hydrotreatment) from bio-oil still in the pyrolysis phase, with its several environmental and economic impacts.

One way to achieve an efficient post catalytic process of bio-oil is by adding a piece of extra equipment to the bio-oil production rig. Different mixtures of oxygenated and non-oxygenated hydrocarbons with sizes between C4 to C18 have been obtained from catalytic reactions resulting in a heating value around 41.3 MJ kg^{-1} [44]. Several studies have also looked at deoxygenation of bio-oil [44,45] or deoxygenation followed by Aldol condensation of ethanol [43,44]. Besides deoxygenation, these studies include condensing large molecules with higher heating values [32,44–46].

In addition to improving fuel properties, stabilization, and standardization of bio-oil some problems remain. In the case of stabilization, the problem is the polymerization of free radicals, also called the "aging" process. Both stabilization and standardization remain major R&D challenges.

Within the first strategy of bio-oil mixtures, it will be necessary to investigate their aging or stability, to avoid problems in the mixtures.

As mentioned before, the Fischer–Tropsch (FT) technology is another route for producing fuels, converting syngas—a mixture of CO and H_2—to chemical, hydrocarbons, or oxygenated hydrocarbons depending on the catalyst used [33,34]. Among the many advantages of FT fuels compared to crude oil is that they are sulfur-free, nitrogen-free, metal-free, and with a low content of aromatics [35]. However, to obtain the syngas mixture—that can use coal, natural gas, biomass, or any carbon source—the energy demand is high. In general, the reactors used to produce syngas operate at 900 °C, a temperature that requires special materials for the construction of the reactors and high consumption of fuel to achieve the required temperature [47]. In general, FT solutions for fuels are feasible only when there is a high abundance of high-density fuel—natural gas or methane—and a competitive market price for fuels. Thus, using biomass as a carbon source for FT synthesis of maritime fuel will be feasible only if the price for bunker oil is high or if there is an abundant source of carbon, such as biogas or charcoal near or at the harbor [48–50]. Or simply, for political and environmental pressures.

Finally, another strategy could be the production of a "green marine diesel", similar to HBio/Petrobras technology (bio-oil in the oil refinery [51]). Different proprietary technologies are available in the market, ranging from coprocessing only vegetable oil with gasoil in FCC units, as in the case of Petrobras in Brazil, to tall oil in the UPM Technology (Finland), to HydroFlex technology (Haldor-Topsøe) or UOP Ecofining technology. In all cases, the raw material—some form of vegetable oil—is processed with hydrogen with a catalyst to produce a green diesel. The processing can be carried out together with gasoil (as in the case of Petrobras) or with pure vegetable oil as in the case of UOP or UPM technologies.

The technology known as H-Bio, developed by Petrobras, Brazil, consists of processing vegetable oil together with gasoil in an FCC unit. Petrobras concluded in 2020 pilot-plant scale tests in a 208,000 barrels per day unit operating up to 30% vegetable oil. Different vegetable oils, such as soy and castor oil, were tested, under different operating conditions, showing the advantages of the process in terms of flexibility of raw material and the high efficiency, of at least 95% *v/v*, to diesel without generating waste and a small production of propane. For every 100 L of soybean oil processed, 96 L of diesel oil and 2.2 Nm^3 of propane are produced [51].

The technical feasibility of integrated coprocessing, which integrates bio-oil with a fluidized catalytic cracking unit (FCC), is not yet a proven concept, but it is promising, with large demonstration plants in operation in various countries. No changes are foreseen in the process, but using the existing infrastructure is foreseen, thus minimizing operating and capital costs. Coprocessing consists of a mixture of up to 10% of the product with oil, at the process entrance [52,53].

Ensyn corporation has developed a product named biocrude, produced with bio-oil obtained from forests and agricultural residues. Ensyn's biocrude can be considered a renewable feedstock for refineries to produce renewable gasoline and diesel (http://www.ensyn.com/ accessed on 20 May 2021). The same strategy used by Ensyn could be applied to develop marine fuels from biomass.

Other methods to evaluate the potential of FPBO use techno-economic analysis, life cycle assessment, and technology readiness. The combination and integration analysis of these methods better predict the maturity of a technology. For example, Soronmu et al. [54] have evaluated the potential of FPBO upgrading and concluded that the production costs, scalability, and yields, still need to be optimized to replace conventional fossil fuels at the present stage of the existing technology.

5. Where and How Can Sustainable Biofuels Be Produced?

The bio-oil production locations will depend primarily on the selected feedstocks. Three potentially major feedstocks, e.g., sugarcane, forest biomass ad solid wastes (agro-forestry residues), are discussed.

For example, sugarcane, a very promising feedstock, could be a good starting point for producing marine fuels. Sugarcane has a huge potential for expansion, has a well-developed infrastructure, and produces a large number of residues—largely underutilized or simply wasted.

In the case of forest biomass, there are even more possibilities, including areas located in colder regions of the world, such as Canada and North of Europe and Asia, although it needs to be recognized that there is an important limiting factor, such as:

(a) In cold climates, with high latitudes, biomass production from the forest is not as good as in tropical climates (lower productivity),
(b) In tropical climates, most of the existing forests are natural and should be preserved,
(c) Planted forests are a small fraction of existing forests worldwide and are dedicated primarily to pulp and paper production. The use of these residues may be foreseen for biofuels production. There are some dedicated energy plantations, e.g., eucalyptus in Brazil, used in the production of charcoal, which is in turn used to produce pig iron, used in special steels.

On the other hand, MSW is very abundant worldwide and is currently mostly wasted. Roughly, it can be estimated the average production of around 1 kg of municipal solid waste per person per day, totaling around 2.5 billion tons per year as the global MSW annual production.

To produce biofuels on a large scale and in an environmentally sustainable way is a major challenge. For example, a politically sensitive issue is the perceived competition with food production, which, despite many studies demonstrating it is a misconception [55], remains a challenge. Thus, avoiding direct land use for food production, needs to be at the core of large-scale biofuel production. The feedstocks can be produced on a large scale without affecting food production in many ways, just by using agroforestry residues, waste currently underused or wasted, together with co-products.

Finally, it is important to recall that the volumes of biofuels required for maritime transport can be considered relatively small compared to road transport. As stated previously, the total demand for marine fuels is about six times smaller when compared with road transportation (see Table 1). Therefore, if biofuels are to be considered partial substitutes of fossil fuels in the MTS, it is a feasible alternative if the lignocellulosic type of biomass is used as feedstock.

6. Conclusions

Due to the nature of MTS, e.g., big engines and perceived less direct environmental impacts, the search for sustainable transport alternatives is far behind other transportation sectors.

The use of biofuels in light and heavy vehicles required some engine modifications. The MTS has important similarities, but with much bigger engines, with the logistics associated playing a much greater role. Replacing current heavy fuels with biofuels, be it partially, will require important R&D efforts, particularly in fuel quality, diesel engine adaptation/modifications.

The sustainability of feedstock production, together with the potential competition with food production and other uses of biofuels, is often regarded as a major problem. However, this is not necessarily the case. This is because there are large amounts of biomass-based feedstocks, e.g., lignocellulosic, agroforestry residues, or sugarcane bagasse, widely available in many regions of the world. Bagasse is of particular interest because it is readily available from existing sugar and ethanol mills.

Many of the technologies/processes are partly or close to commercialization. Significant advances have been made in the past decades. What is needed is a clear strategy in the MTS to select the most appropriate technologies, processes, and feedstocks to speed up their implementation.

FPBO is one of the most promising alternatives to convert cellulose-based low-cost materials into concentrate liquid, easy to transport. However, a remaining obstacle is that pyrolysis bio-oil is not a ready-to-use fuel, requiring further refinement (upgrading) for large-scale production, to meet potential demand for marine engines. This could incur some additional costs.

The future use of biofuel in the marine sector will depend on a combination of political, feedstock availability, environmental, technological, and socio-economic considerations, and choices. The maritime sector will not make fundamental changes unless there is strong pressure to do so. Large companies involved in maritime transport must accept Business-as-Usual Scenario is no longer acceptable and must be at the center of the fuel shifting.

The MTS needs to modernize quickly to catch up with the rest of the transport systems and seriously considers all possible alternatives. Given the stage of R&D of biofuels in Brazil, it's potential, and accumulated historical experience, the country should play a leading role in this paradigm shift. Brazil should focus on developing FPBO, lignocellulose-based sustainable feedstocks; engine and fuel modifications, so that biofuels can be a serious alternative in MTS, as is the case for other transport uses. As in other biofuels-related activities, where the country successfully put in place a clear policy framework, this principle should also apply to MTS.

This paper has highlighted the main issues affecting the MTS with regards to biofuels, with reference to Brazil. Some technical details are omitted because they are still regarded as commercially sensitive. There are still huge challenges ahead, but also great opportunities.

Author Contributions: Conceptualization, L.C. and F.R.-C.; Data curation, T.T.F.; Investigation, L.C.; Methodology, T.T.F.; Project administration, L.C.; Writing—original draft, L.C. and T.T.F.; Writing—review & editing, F.R.-C. and G.V. All authors have read and agreed to the published version of the manuscript.

Funding: This research work was financially supported by the State of Sao Paulo Research Foundation-FAPESP (No. 2015/50612-8) and by the Office of Naval Research Global through Grant No. N62909-17-1-2008.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Acknowledgments: We sully acknowledge Carolina Silveira Bueno for kindly helping the revision of the last version of this manuscript.

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

References

1. UNCTAD. *Review of Maritime Transport 2015*; United Nations: Geneva, Switzerland, 2015; Available online: https://unctad.org/system/files/official-document/rmt2015_en.pdf (accessed on 14 May 2020).
2. Rodrigue, J.P. *The Geography of Transport Systems*, 5th ed.; Routledge: New York, NY, USA, 2020.
3. Statista. Available online: https://www.statista.com/statistics/1098994/marine-bunkers-product-demand-by-fuel/ (accessed on 5 May 2020).
4. Kesieme, U.; Pazouki, K.; Murphy, A.; Chrysanthou, A. Biofuel as alternative shipping fuel: Technological, environmental and socioeconomic assessment. *Sustain. Energy Fuels* **2019**, *3*, 899–909. [CrossRef]
5. Galindo, R.F.; Cortez, L.A.B.; Franco, T.T. Ternary blends of renewable fast pyrolysis bio-oil, advanced bioethanol and marine gasoil as potential marine biofuel. *Chem. Eng. Technol.* **2020**, *43*, 1–9. [CrossRef]
6. Gupta, A.; Verma, J.P. Sustainable bio-ethanol production from agro-residues: A review. *Renew. Sustain. Energy Rev.* **2015**, *41*, 550–567. [CrossRef]

7. Chong, K.J.; Bridgwater, A.V. Fast pyrolysis oil fuel blend for marine vessels. *Environ. Prog. Sustain. Energy* **2016**, *36*, 677–684. [CrossRef]
8. Kass, M.; Abdullah, Z.; Biddy, M.; Drennan, C.; Hawkins, T.; Jones, S.; Holladay, J.; Longman, D.; Newes, E.; Theiss, T.; et al. *Understanding the Opportunities of Biofuels for Marine Shipping*; Oak Ridge Laboratory: Oak Ridge, TN, USA, 2018. [CrossRef]
9. International Maritime Organization (IMO). Available online: https://www.imo.org/en/MediaCentre/HotTopics/Pages/Reducing-greenhouse-gas-emissions-from-ships.aspx (accessed on 5 May 2020).
10. Van, T.C.; Ramirez, J.; Rainey, T.; Ristovski, Z.; Brown, R.J. Global impacts of recent IMO regulations on marine fuel oil refining processes and ship emissions. *Transp. Res. Part D Transp. Environ.* **2019**, *70*, 123–134. [CrossRef]
11. Terra, R.B. Cenários de Longo Prazo para Demanda de Combustíveis Marítimos do Setor de Transporte Aquaviário Brasileiro. Master Dissertation, UFRJ, Rio de Janeiro, Brazil, 2015.
12. Brynolf, S.; Fridell, E.; Andersson, K. Environmental assessment of marine fuels: Liquefied natural gas, liquefied biogas, methanol, and bio-methanol. *J. Clean. Prod.* **2014**, *74*, 86–95. [CrossRef]
13. Bittante, A.; Saxen, H. Design of small LNG supply chain by multi-period optimization. *Energies* **2020**, *13*, 6704. [CrossRef]
14. Bach, H.; Bergek, A.; Bjørgum, O.; Hansen, T.; Kenzhegaliyeva, A.; Steen, M. Implementing maritime battery-electric and hydrogen solutions: A technological innovation systems analysis. *Transp. Res. Part D* **2020**, *87*, 102492. [CrossRef]
15. Hsieh, C.-W.C.; Felby, C. *Biofuels for the Marine Shipping Sector: An Overview and Analysis of Sector Infrastructure, Fuel Technologies and Regulations*; IEA Bioenergy: Paris, France, 2017.
16. Chiaramonti, D.; Prussi, M.; Buffi, M.; Rizzo, A.M.; Pari, L. Review and experimental study on pyrolysis and hydrothermal liquefaction of microalgae for biofuel production. *Appl. Energy* **2017**, *185*, 963–972. [CrossRef]
17. Nwoba, E.G.; Parlevliet, D.A.; Laird, D.W.; Alameh, K.; Moheimani, N.R. Pilot-scale self-cooling microalgal closed photobioreactor for biomass production and electricity generation. *Algal Res.* **2020**, *45*, 101731. [CrossRef]
18. De Boer, K.; Moheimani, N.R.; Borowitzka, M.A.; Bahri, P.A. Extraction and conversion pathways for microalgae to biodiesel: A review focused on energy consumption. *J. Appl. Phycol.* **2012**, *24*, 1681–1698. [CrossRef]
19. Ramachandra, T.V.; Hebbale, D. Bioethanol from macroalgae: Prospects and challenges. *Renew. Sustain. Energy Rev.* **2020**, *117*, 109479. [CrossRef]
20. Czernik, S.; Bridgwater, A.V. Overview of applications of biomass fast pyrolysis oil. *Energy Fuels* **2004**, *18*, 590–598. [CrossRef]
21. Storey, J.; Kass, M.; Theiss, T.; Kaul, B.; Nafziger, E. Bio-oil use in marine engines. In Proceedings of the 5th ICCT Workshop on Marine Black Carbon Emissions, San Francisco, CA, USA, 19–20 September 2018.
22. Zacher, A. Prospects of pyrolysis of lignocellulosic biomass to produce marine biofuels. In Proceedings of the IEA Bioenergy ExCo78 Workshop, Rotorua, New Zealand, 9 November 2016.
23. Lehto, J.; Oasmaa, A.; Kyto, M.; Chiaramonti, D. *Fuel Oil Quality and Combustion of Fast Pyrolysis Bio-Oils*; VTT Technical Research Centre of Finland: Espoo, Finland, 2013; ISBN 978-951-38-7929-7.
24. Olivares-Gomez, E. Study of Elephant Grass Fast Pyrolysis in a Bubbling Fluidized Bed Reactor through the Fine Charcoal Characterization. Ph.D. Thesis, Unicamp, Campinas, Brazil, 2002.
25. Mesa-Perez, J.M. Experimental Tests of Biomass Fast Pyrolysis in Fluidized Bed Reactor Criteria To System Optimization. Ph.D. Thesis, Unicamp, Campinas, Brazil, 2004.
26. Almeida, M.B.B. Bio-óleo a Partir da Pirólise Rápida, Térmica ou Catalítica, da Palha da Cana-de-Açúcar e seu Co-processamento com Gasóleo em Craqueamento Catalítico. Master Dissertation, UFRJ, Rio de Janeiro, Brazil, 2008.
27. Baldassin, R., Jr. Fast Pyrolysis of Whole Sugarcane in Pilot-Scale Fluidized Bed Reactor. Ph.D. Thesis, Unicamp, Campinas, Brazil, 2015.
28. Sohaib, Q.; Muhammad, A.; Younas, M. Fast pyrolysis of sugarcane bagasse: Effect of pyrolysis conditions on final product distribution and properties. *Energy Sources Part A Recovery Util. Environ. Eff.* **2017**, *39*, 184–190. [CrossRef]
29. Sipila, K.; Korhonen, M. (Eds.) *Power Production from Biomass II with Special Emphasis on Gasification and Pyrolysis R&DD*; Technical Research Centre of Finland: Espoo, Finland, 1996; ISBN 951-38-4555-9.
30. Dahmen, M.; Marquardt, W. Model-based formulation of biofuel blends by simultaneous product and pathway design. *Energy Fuels* **2017**, *31*, 4096–4121. [CrossRef]
31. Laesecke, J.; Ellis, N.; Kirchen, P. Production, analysis and combustion characterization of biomass fast pyrolysis oil–Biodiesel blends for use in diesel engines. *Fuel* **2017**, *199*, 346–357. [CrossRef]
32. Nugraha, R.E.; Prasetyoko, D.; Bahruji, H.; Suprapto, S.; Asikin-Mijan, N.; Oetami, Y.P.; Jalil, A.A.; Vohi, D.V.N.; Taufiq-Yap, Y.H. Lewis acid Ni/Al-MCM-41 catalysts for H2-free deoxygenation of reutealis trisperma oil to biofuels. *RSC Adv.* **2021**, *11*, 21885. [CrossRef]
33. Anderson, J.R.; Boudart, M.; Dry, M.E. The fischer-tropsch technology. In *Catalysis: Science and Technology*; Springer-Verlag: Berlin, Germany, 1981; Volume 1, p. 159.
34. Gholami, Z.; Tišler, Z.; Rubáš, V. Recent advances in Fischer-Tropsch synthesis using cobalt-based catalysts: A review on supports, promoters, and reactors. *Catal. Rev. Sci. Eng.* **2020**, *62*, 1–84. [CrossRef]
35. Steynberg, A.P. Studies in surface science and catalysis. In *Fischer-Tropsch Technology*; Steynberg, A.P., Dry, M., Eds.; Elsevier Science: Amsterdam, The Netherlands, 2004; Volume 152, p. 1.
36. Li, M.; Zhang, M.; Yu, Y.; Wu, H. Ternary system of pyrolytic lignin, mixed solvent and water: Phase diagram and implications. *Energy Fuels* **2018**, *32*, 465–474. [CrossRef]

37. Van de Beld, B.; Holle, E.; Florijn, J. The use of a fast pyrolysis oil–Ethanol blend in diesel engines for CHP applications. *Biomass Bioenergy* **2018**, *110*, 114–122. [CrossRef]
38. Bulushev, D.A.; Ross, J.R.H. Catalysis for conversion of biomass to fuels via pyrolysis and gasification: A review. *Catal. Today* **2011**, *171*, 1–13. [CrossRef]
39. Eibner, S.; Margeriat, A.; Broust, F.; Laurenti, D.; Geantet, C.; Julbe, A.; Blin, J. Catalytic deoxygenation of model compounds from flash pyrolysis of lignocellulosic biomass over activated charcoal-based catalysts. *Appl. Catal. B Environ.* **2017**, *219*, 517–525. [CrossRef]
40. Rogers, K.A.; Zheng, Y. Selective deoxygenation of biomass-derived bio-oils within hydrogen-modest environments: A review and new insights. *ChemSusChem* **2016**, *9*, 1750–1772. [CrossRef]
41. Sanna, A.; Andresen, J.M. Bio-oil deoxygenation by catalytic pyrolysis: New catalysts for the conversion of biomass into densified and deoxygenated bio-oil. *ChemSusChem* **2012**, *5*, 1944–1957. [CrossRef]
42. Xiao, X.; Bergstrom, H.; Saenger, R.; Johnson, B.; Sun, R.; Peterson, A. The role of oxygen vacancies in biomass deoxygenation by reducible zinc/zinc oxide catalysts. *Catal. Sci. Technol.* **2018**, *8*, 1819–1827. [CrossRef]
43. Rezaei, P.S.; Shafaghat, H.; Daud, W.M.A.W. Production of green aromatics and olefins by catalytic cracking of oxygenate compounds derived from biomass pyrolysis: A review. *Appl. Catal. A Gen.* **2014**, *469*, 490–511. [CrossRef]
44. Lovón-Quintana, J.J.; Rodriguez-Guerrero, J.K.; Valença, G.P. Carbonate hydroxyapatite as a catalyst for ethanol conversion to hydrocarbon fuels. *Appl. Catal. A Gen.* **2017**, *542*, 136–145. [CrossRef]
45. Tsuchida, T.; Kubo, J.; Yoshioka, T.; Sakuma, S.; Takeguchi, T.; Ueda, W. Reaction of ethanol over hydroxyapatite affected by Ca/P ratio of catalyst. *J. Catal.* **2008**, *259*, 183–189. [CrossRef]
46. Hernández-Giménez, A.M.; de Kort, L.M.; Whiting, G.T.; Hernando, H.; Puértolas, B.; Pérez-Ramírez, J.; Serrano, D.P.; Bruijnincx, P.C.A.; Weckhuysen, B.M. Upscaling effects on alkali metal-grafted ultrastable y zeolite extrudates for modeled catalytic deoxygenation of Bio-oils. *ChemCatChem* **2021**, *13*, 1961–1965. [CrossRef]
47. Martinelli, M.; Gnanamani, M.K.; LeViness, S.; Jacobs, G.; Wilson, D.; Shafer, W.D. An overview of Fischer-Tropsch synthesis: XtL processes, catalysts and reactors. *Appl. Catal. A Gen.* **2020**, *608*, 117740. [CrossRef]
48. Rostrup-Nielsen, J.R. Making fuels from biomass. *Science* **2005**, *308*, 1421–1422. [CrossRef] [PubMed]
49. Santos, R.G.; Alencar, A.C. Biomass-derived syngas production via gasification process and its catalytic conversion into fuels by Fischer Tropsch synthesis: A review. *Int. J. Hydrog. Energy* **2020**, *45*, 18114–18132. [CrossRef]
50. Gupta, P.K.; Kumarb, V.; Maitya, S. Renewable fuels from different carbonaceous feedstocks: A sustainable route through Fischer–Tropsch synthesis. *J. Chem. Technol. Biotechnol.* **2020**, *98*, 853–868. [CrossRef]
51. Talmadge, M.; Kinchin, C.; Chum, H.L.; Pinho, A.R.; Biddy, M.; de Almeida, M.B.B.; Casavechia, L.C. Techno-economic analysis for co-processing fast pyrolysis liquid with vacuum gasoil in FCC units for second-generation biofuel production. *Fuel* **2021**, *293*, 119960. [CrossRef]
52. Graça, I.; Ramôa Ribeiro, F.; Cerqueira, H.S.; Lam, Y.L.; Almeida, M.B.B. Catalytic cracking of mixtures of model bio-oil compounds and gasoil. *Appl. Catal. B Environ.* **2009**, *90*, 556–563. [CrossRef]
53. Bertero, M.; Sedran, U. Coprocessing of bio-oil in fluid catalytic cracking. In *Recent Advances in Thermo-Chemical Conversion of Biomass*; Pandey, A., Bhaskar, T., Stöcker, M., Sukumaran, R., Eds.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 355–381.
54. Soronmu, Y.; Billen, P. A review of thermochemical upgrading of pyrolysis bio-oil: Techno-economic analysis, life cycle assessment and technology readiness. *GCB Bioenergy* **2019**, *12*, 4–18. [CrossRef]
55. Brelsford, R. Petrobras's REPAR Completes Renewable Diesel Production Testing. Oil Gas. 2020. Available online: https://www.ogj.com/refining-processing/article/14179720/petrobrass-repar-completes-renewable-diesel-production-testing (accessed on 21 May 2021).