

Review

# Methanol, a Plugin Marine Fuel for Green House Gas Reduction—A Review

Dimitrios Parris <sup>1,\*</sup> , Konstantinos Spinthiropoulos <sup>1</sup> , Konstantina Ragazou <sup>2,3</sup> , Anna Giovou <sup>4</sup>  
and Constantinos Tsanaktsidis <sup>5</sup>

<sup>1</sup> Department of Management Science and Technology, University of Western Macedonia, 50100 Kozani, Greece; kspinthiropoulos@uowm.gr

<sup>2</sup> Department of Accounting and Finance, University of Western Macedonia, 50100 Kozani, Greece; koragazo@uth.gr

<sup>3</sup> Department of Business Administration, Neapolis University Pafos, Pafos 8042, Cyprus

<sup>4</sup> Customs Control Service of Thessaloniki, 57001 DrosiaThermis, Thessaloniki, Greece; agiovou@hotmail.com

<sup>5</sup> Department of Chemical Engineering, University of Western Macedonia, 50100 Kozani, Greece; ktsanaktsidis@uowm.gr

\* Correspondence: dimit.parris@gmail.com

**Abstract:** The escalating global demand for goods transport via shipping has heightened energy consumption, impacting worldwide health and the environment. To mitigate this, international organizations aim to achieve complete fuel desulphurization and decarbonization by 50% by 2050. Investigating eco-friendly fuels is crucial, particularly those with a reduced carbon and zero sulfur content. Methanol derived mainly from renewable sources and produced by carbon dioxide's hydrogenation method, stands out as an effective solution for GHG reduction. Leveraging its favorable properties, global scalability, and compatibility with the existing infrastructure, especially LNGs, methanol proves to be a cost-efficient and minimally disruptive alternative. This review explores methanol's role as a hybrid maritime fuel, emphasizing its ecological production methods, advantages, and challenges in the shipping industry's green transition. It discusses the environmental impacts of methanol use and analyzes economic factors, positioning methanol not only as an eco-friendly option, but also as a financially prudent choice for global shipping. Methanol is efficient and cost-effective and excels over MGO, especially in new ships. It is economically advantageous, with decreasing investment costs compared to LNG, while providing flexibility without specialized pressure tanks. Global marine fuel trends prioritize fuel traits, accessibility, and environmental considerations, incorporating factors like policies, emissions, bunkering, and engine adaptability during transitions.

**Keywords:** methanol; shipping; environmental protection; renewable energy; marine fuel



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## 1. Introduction

Economic and demographic growth have emerged as pivotal drivers of the global energy demand, precipitating a substantial expansion in the international maritime trade and an upswing in the global fleet of ships [1]. The maritime industry shoulders the responsibility for transporting roughly 80–90% of the world's trade [2], facilitating the movement of more than 10 billion tons of solid and liquid bulk cargo in containers every year across the planet's oceans [3]. By the close of 2019, global trade had witnessed an 18% upswing in comparison to 2016 [4], a trajectory that is poised to result in a 50% escalation in the consumption of shipping fuel from 2012 to 2040 [5]. In this sector, fossil fuels, primarily Heavy Fuel Oil (HFO), maintain their dominance, notorious for their elevated sulfur content. Emissions stemming from a vessel operating on fuel with a sulfur content of 3.5% equate to the emissions generated by a staggering 210,000 trucks [6]. The year 2018 witnessed global shipping being accountable for over one million tons of greenhouse gases (GHG)

and carbon dioxide (CO<sub>2</sub>) emissions, signifying a 9.6% and 9.3% expansion compared to levels recorded in 2012, respectively [7]. Additionally, as indicated by the United Nations, the collective greenhouse gas emissions from the global fleet experienced a 4.7% increase in 2022. Concurrently, data from the United Nations revealed that in April 2022, carbon dioxide (CO<sub>2</sub>) emissions amounted to 847 million tons, reflecting a noteworthy 23% escalation over the preceding 10 years [2]. Consequently, the maritime sector's contribution to global anthropogenic emissions has ascended to 3.0% [8]. Disturbingly, nearly 70% of ship emissions occur within 400 km of coastlines [9,10], posing a significant hazard to the global environment and human well-being, attributable to the discharge of GHGs [11], carbon dioxide (CO<sub>2</sub>), carbon monoxide (CO), methane (CH<sub>4</sub>), sulfur oxides (SO<sub>x</sub>) [12–14], nitrogen oxides (NO<sub>x</sub>) [13–15], and particulate matter (PM) [13,14,16–19]. The International Maritime Organization (IMO), during its third GHG study in 2014, forecasted that the growth in global trade could lead to a surge in shipping emissions ranging from 50% to 250% by 2050 [20]. Furthermore, they projected that shipping transport would be responsible for approximately 15% of global CO<sub>2</sub> emissions during the same period [18].

This emissions scenario within the maritime transport sector poses a severe challenge to vital global emission reduction commitments, including the Paris Agreement and the Kyoto Protocol. Consequently, the IMO and the entire shipping industry play a pivotal role in mitigating their emissions. The IMO has introduced and proposed more stringent regulations for vessel operators and owners in the maritime sector to confront these challenges [18,21].

The International Maritime Organization's (IMO) efforts to address emissions began in September 1997 with the inception of Annex VI under the International Convention for the Prevention of Pollution from Ships (MARPOL). Annex VI was officially enforced on 19 May 2005 with a primary focus on regulating ship emissions and their environmental impact [22]. Following a three-year assessment period, the NO<sub>x</sub> Technical Code was unveiled in October 2008 during the MEPC 58 meeting, and it became effective on 1 July 2010. This code aimed to limit the release of nitrogen oxide (NO<sub>x</sub>) emissions from ships equipped with engines of 130 kW and above [23]. Subsequently, at the MEPC 59 meeting on 17 July 2009, Regulation 14 was introduced to reduce emissions of sulfur oxide (SO<sub>x</sub>) and particulate matter (PM). Until 1 January 2020, sulfur emissions from ships were capped at 3.50%, after which the limit was lowered to 0.50%.

In addition, the Energy Efficiency Design Index (EEDI) regulation was established during the MEPC 62 meeting in 2011, and it became enforceable on 1 January 2013. EEDI is obligatory for newly constructed ships exceeding 400 gross tonnages (GT) and is aimed at encouraging the utilization of energy-efficient technologies and materials. In the same year, the Ship Energy Efficiency Management Plan (SEEMP) was put into effect to enhance the energy efficiency of ship operations. Another regulation, the Data Collection System (DCS), was implemented in March 2018, applying to ships exceeding 5000 GT [22]. Currently, under the DCS rule, fuel consumption, CO<sub>2</sub> emissions, distance traveled, and cargo quantity are monitored and reported annually.

Furthermore, during the MEPC 75 meeting in November 2020, the Energy Efficiency Existing Ship Index (EEXI) and the Carbon Intensity Indicator (CII) were introduced, becoming effective from 1 January 2023 [24]. EEXI is mandatory for ships exceeding 400 GT, with the initial limit set and unalterable unless vessel modifications occur. Meanwhile, CII is obligatory for ships exceeding 5000 GT, and these vessels are graded annually from A to E based on their carbon intensity performance [25].

The ultimate objective of the IMO, is the complete decarbonization of the marine transportation sector [26]. The IMO has established objectives to reduce CO<sub>2</sub> intensity by 40% by 2030 and lower total GHGs emissions by at least 50% by 2050, in relation to 2008 levels [27]. Consequently, it is estimated that at least 70% of the current marine fuels will need to be altered or substituted to meet these IMO regulations [18,28].

In assessing the global shipping community's responsiveness and adherence to the specified requirements, a recent investigation conducted by Parris et al. (2023) [29], uti-

lizing the Dynamic Slack-Based assessment non-oriented Data Envelopment Analysis methodology, revealed that highly dynamic shipping sectors worldwide, exemplified by the Marshall Islands, exhibit the least eco-efficient levels due to their role as tax havens for shipowners. Additionally, well-established maritime economies such as China demonstrate a notable upswing in eco-efficiency scores. This increase is attributed to the strategies employed by shipping companies headquartered in the region, involving investments and the adoption of Environmental, Social, and Governance principles, leading to commendable eco-efficiency ratings. Lastly, nations with smaller fleets, register the highest eco-efficiency scores, as local governments have actively participated in sustainable initiatives and endeavors over the past four to five years, fostering the growth and dominance of their maritime sector in the market.

Bio-based marine fuels and exhaust gas cleaning systems, known as scrubbers, have emerged as the most practical and efficient near-term solutions for reducing greenhouse gas emissions from ships [30]. These measures hold significant potential and can pave the way for the eventual adoption of hydrogen-related fuels in the long run. In the medium term, the goal is to evaluate the commercial and operational feasibility of effectively integrating alternative low-carbon and zero-carbon fuels, with a special focus on updating national action plans to accommodate these marine fuels. Furthermore, the most substantial and immediate opportunities for mitigating CO<sub>2</sub> emissions in the maritime sector, are closely linked to improving the energy efficiency of existing vessels [18,31].

In the pursuit of environmentally friendly shipping and the overarching goal of reducing carbon emissions in the maritime industry, the adoption of alternative fuels is imperative. This approach aims to address carbon emissions originating from shipping, as opposed to solely relying on fossil fuels that might require post-combustion treatment systems. This strategy is recognized for its enduring impact on carbon reduction, as emphasized by DNV in 2020, and complements the implementation of carbon taxes [32].

The engine's manufacturers are compelled to shift their focus towards exploring and advancing technologies, as well as innovative fuel options that do not necessitate engine modification. This shift is driven by the increasing energy demands and stringent emission regulations imposed by governments [33]. Essentially, the aim is to develop alternative fuels capable of meeting the high energy requirements while mitigating environmental issues globally. The significance of utilizing fuel types that do not require engine modifications in diesel engines cannot be overstated. This approach has the potential to reduce costs and present readily acceptable alternatives. Within this context, lower-order alcohols like methanol (CH<sub>3</sub>OH) emerge as promising candidates for unmodified internal combustion engines, considering the preferred specifications mentioned earlier [34,35]. Oxygenated fuels are widely favored among alternative fuel options due to their high oxygen content which enhances combustion within the engine cylinder and enables the reduction of emissions at the source [36–40].

Methanol stands out as a hydrogen-rich, solitary molecule liquid compound that maintains stability under normal environmental conditions. Its hydrogen content, when measured in terms of volumetric density, surpasses that of liquid hydrogen (LH<sub>2</sub>) at extremely low temperatures, specifically at 20 K. When considered alongside ammonia, methanol boasts one of the highest hydrogen storage densities in terms of both volume and weight, especially when compared to other storage mediums. Furthermore, it is worth noting that methanol production is a well-developed technology with a firmly established supporting infrastructure [41,42].

In 2019, Ammar [43] demonstrated the potential of using methanol in a dual-fuel engine, combined with a slow steaming technique to significantly reduce exhaust emissions by up to 90% and comply with IMO emission regulations. However, safety concerns regarding methanol storage due to its lower flash point [44], invisible flame, and its life cycle assessment compared to other fuels should not be overlooked [32,45].

The increasing utilization of intermittent sustainable energy sources, such as solar and wind power, has made the potential production of methanol from renewable electricity

(e-methanol) and captured carbon dioxide increasingly attractive [46]. Its appeal lies in its elevated octane rating, the utilization of renewable electricity in its manufacturing, and its low sulfur and aromatic content [47]. However, the current production process is costly and demands substantial energy input, serving as constraining factors. Furthermore, the widespread adoption of e-methanol as a fuel necessitates significant infrastructure development and investment [48].

## 2. Methanol as a Marine Fuel

There is a growing interest in utilizing methanol as an alternative fuel within the maritime industry, primarily spurred by increasingly stringent emission regulations. The International Maritime Organization (IMO), has implemented Tier 3 NO<sub>x</sub> emission regulations for ocean-going vessels, particularly in Emission Control Areas (ECAs), encompassing densely populated coastal zones. Concurrently, there is a reduction in the permissible sulfur content of marine fuels. To meet these more demanding regulations, diverse technologies have been introduced, including those facilitating the continued use of heavy fuel oils (HFO), such as aftertreatment systems. In addition, alternative fuels are gaining traction, with initial emphasis on liquefied natural gas (LNG). However, integrating a liquefied gas storage system, significantly impacts ship design or retrofitting. Methanol, being in liquid form at atmospheric conditions, is often deemed a more manageable fuel for various applications. It is also produced from natural gas. According to a recent technical report from the EU's Joint Research Center, LNG and methanol stand out as the most promising alternative fuels for shipping currently, partially owing to methanol's widespread availability in most major ports [49].

Methanol's viability as a marine fuel is tied to its safety features, its superior emissions profile compared to bunker fuel or heavy fuel oils commonly used by large ships, and its complete miscibility in water. This miscibility allows existing vessels with double hulls to be modified for methanol storage, unlike hydrocarbons that necessitate double hulls due to their inability to mix with water. The infinite miscibility of methanol enables its storage in these voids, as any tank breach would result in the fuel dissolving. A study conducted by Malcolm Pirnie Inc. (Verbena, AL, USA) [50] determined that in the event of a methanol spill, rapid dilution occurs, preventing the attainment of dangerous concentrations. The swift dilution is further attributed to methanol's lethal concentrations (for marine life), which are 240 times higher than diesel and 1900 times higher than gasoline. Consequently, the likelihood of reaching such concentrations is deemed highly improbable.

In general, these large marine engines operate as dual-fuel diesel engines, directly comparable to dual-fuel marine engines designed for liquefied natural gas (LNG) applications, such as those found in LNG tankers. However, methanol presents distinct safety advantages over LNG due to its liquid form. Despite having a (net) volumetric Lower Heating Value (LHV), approximately 23% lower than LNG (15.9 vs. 20.5 MJ/L), methanol offers easier storage on vessels without the complexities associated with cryogenic gas storage. An important safety aspect is the considerably lower flash point of methanol compared to LNG. In fact, the flammability index of methanol, is much more akin to that of diesel. In the event of a pool fire, methanol proves significantly safer than both gases and liquid hydrocarbons [51–53]. According to Oloruntobi et al. (2023) [53], a rising trend in the maritime field involves the adoption of liquid low-flashpoint fuels such as methanol, for marine engines. As indicated by Ampah et al. (2021) [18], MAN's ME-LGI system, initially integrated into Dual Fuel (DF) engines for methanol combustion in various vessels, employs high-pressure pumping and functions with a low fuel supply pressure, but it is limited within the injector [54].

Methanol represents a liquid fuel characterized by a low flashpoint, an absence of sulfur content, and ease of storage. Furthermore, it generates reduced emissions, and boasts a smaller carbon footprint when compared to traditional marine fuels. Methanol is a viable option for marine propulsion, with at least one dual-fuel marine engine available in the market that has the capability to utilize methanol [55]. As supported by research, methanol

stands out as the “optimal alternative fuel” due to its “rapid availability”, utilization of existing infrastructure, cost-effectiveness, and the simplicity of both engine design and maritime technology [56]. As of now, there are 11 operational methanol-powered ships [57]. In contrast to heavy fuel oil or marine gasoline oil, the combustion of methanol in marine engines results in only a marginal reduction in carbon dioxide emissions, but significantly lowers emissions of other pollutants [58]. Methanol has the potential to be distributed to significant port terminals globally, thanks to its extensive worldwide production network. Investigating the possible applications of methanol as a marine fuel in the short, medium, and long term is a valuable pursuit given the consistent availability and broad distribution of methanol [59].

Methyl alcohol, characterized as a clear, easily flammable organic compound devoid of impurities in suspension, exhibits water miscibility at any rate. Conforming to Machiele (1987) [51,53], when not addressed, fatal quantities typically fall within the range of 1 to 2 milliliters per kilogram of body weight. This equates to 60–240 milliliters for individuals within a typical weight range. In contrast, Yaman et al. (2024) [35] support that even minimal methanol quantities prove toxic to living organisms, with a lethal dose ranging from 11.5 g to 160 g. [34]. According to Tian et al. (2022) [60], exposure to a methanol concentration between  $3.913 \times 10^3$  and  $6.515 \times 10^3$  g/m<sup>3</sup> for 30–60 min poses a significant danger, surpassing the Chinese occupational health standard PC-STEL [61] of 50 mg/m<sup>3</sup> by 768–1310 times. Notably, in the aftermath of a methanol leak, emergency repairs were carried out without protective measures, resulting in symptoms like headaches, dizziness, and fainting emerging two hours later. Furthermore, prolonged exposure to a methanol environment, ranging from  $1.2 \times 10^3$  to  $8.3 \times 10^3$  ppm (equivalent to  $1.56 \times 10^3$ – $1.079 \times 10^4$  mg/m<sup>3</sup>) has been reported to cause visual impairment [60,62,63].

Methanol, widely recognized as CH<sub>3</sub>OH and commonly denoted as MeOH [64], plays a pivotal role in the chemical and pharmaceutical sectors [65] as well as in the synthesis of artificial hydrocarbons. It is noted that global methanol production has reached approximately 90 million tons per year, with approximately 65% originating from natural gas through steam methane reforming and the remaining 35% derived from coal via gasification procedures [46,66,67]. This versatile compound is acknowledged as a sustainable and eco-friendly energy source, with significant potential for reducing emissions in internal combustion engines [63,68].

In the context of maritime applications, methanol bears similarities to LNG, with the advantage of it being in liquid form at a standard temperature and pressure, making it more manageable [32,69]. As reported by Tian et al. (2022) [60], vaporizing methanol poses challenges, but its ability to be stored in plastic containers adds convenience to transportation, filling, storage, and utilization. In any case, the findings of a 2015 study, executed by Ellis and Tanneberger, suggest that methanol holds an edge over LNG when it comes to onboard containment because of its liquid form. However, incorporating it into marine fuel systems demands modifications to existing setups and an infrastructure upgrade to facilitate regular bunkering [54,70]. Additionally, due to its non-static nature, methanol easily dissolves in water and can be extinguished using water in the event of a fire [63].

Methanol’s appeal as an alternative fuel stems from its clean-burning qualities, characterized by the absence of sulfur and carbon-to-carbon bonds. This trait contributes to a reduction in SO<sub>x</sub> and PM emissions, while its lower adiabatic flame temperature has the potential to restrict NO<sub>x</sub> formation during combustion, as highlighted by Glaude et al. (2010) [70]. Aabo (2020) [71] and Korberg et al. (2021) [72] underscore findings from MAN Energy Solutions research, indicating that the introduction of water to methanol can effectively control NO<sub>x</sub> formation in combustion [72,73]. This outcome enables the engine to comply with Tier III NO<sub>x</sub> regulations, negating the need for Selective Catalytic Reduction (SCR) or Exhaust Gas Recirculation (EGR) systems [54]. It has demonstrated the potential for lower emissions of sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), and particulate matter (PM) in marine engines, further underscoring its environmental advantages. For instance,

NO<sub>x</sub> emissions were significantly reduced when using methanol as fuel compared to marine gas oil (MGO) [74]. Moreover, PM, SO<sub>x</sub>, and carbon dioxide (CO<sub>2</sub>) emissions were substantially lower with methanol use, making it compliant with Emission Control Area regulations [18]. However, it is important to note that greenhouse gas (GHG) emissions from non-renewable methanol sourced from natural gas are slightly higher than those from heavy fuel oil (HFO) and marine diesel oil (MDO) [69]. Conversely, the utilization of renewable methanol derived from biomass feedstock can lead to a GHG impact approximately 56% lower than HFO [18,74].

As reported by the Methanol Institute (2023) [75], compared to conventional fuels, the use of renewable methanol leads to a remarkable reduction in carbon dioxide emissions by as much as 95%, significantly lowers nitrogen oxide emissions by up to 80%, and completely eliminates emissions of sulfur oxide and particulate matter [76].

Methanol as a fuel offers notable advantages in terms of economy, safety, environmental friendliness, reliability, and versatility, positioning it as an excellent alternative to conventional internal combustion (IC) engines for energy needs [68]. In comparison to traditional gasoline and diesel fuels, methanol fuel, with its single carbon atom composition, is less prone to soot formation post-combustion. Owing to its elevated oxygen content, methanol proves well-suited for lean combustion, leading to a reduction in cylinder combustion temperatures, thereby impeding the generation of NO<sub>x</sub>. If methods can be devised to enable the compression ignition of methanol in diesel engines, the potential elimination of the need for diesel particulate filters (DPF) and selective catalytic reduction (SCR) becomes feasible. This, in turn, would curtail operational costs and exhaust emissions, thereby fostering the global IC engine industry's progression towards low carbon and environmental sustainability [63,68].

Reviewing the literature that explores the application of methanol in diesel engines [77], the analyses regarding how methanol's application leads to a decrease in particulate matter (PM) emissions can be classified into three distinct categories: (1) Methanol's lower carbon fraction helps prevent the generation of aromatics, thereby minimizing soot formation [78,79]. (2) The presence of the -OH group and the low cetane number of methanol result in an extended ignition delay [80,81], fostering greater premixed fuel vaporization and consequently reducing local rich combustion zones, ultimately lowering soot formation [77,82]. (3) The oxygenated nature of methanol provides an additional oxygen supply, facilitating combustion promotion [80] and carbon oxidation [83,84].

According to Wang et al. (2023) [42], methanol as a Liquid Hydrogen Carrier (LHC) can be transported using standard methods, without requiring compression or cryogenic conversion, utilizing existing energy infrastructure. Upon reaching the delivery sites, hydrogen (H<sub>2</sub>) is extracted from these carriers for utilization. The liquid carriers are subsequently recycled and ready for another delivery [76].

Additionally, certain characteristics specific to methanol, could enhance its practicality. For instance, methanol has the potential to directly fuel a fuel cell, resulting in CO<sub>2</sub> production that is comparatively easier to capture and store [85,86].

Several demonstration projects have been actively exploring the implementation of methanol as a fuel for shipping, with two prominent examples being the conversion of the Stena Germanica 1500 passenger ferry which occurred in 2015 [87,88], and the operation of Waterfront Shipping's 50,000 deadweight tonnage methanol tanker vessels [89]. These initiatives involve the practical use of methanol in these vessels [53].

Ampah et al. (2021) [18] agree with this, stating that over the last two decades, various projects have explored methanol utilization in marine vessels; among others, they included the METHAPU project from 2006 to 2009 [74], the SUMMETH project in 2018 [70,90], and the launch of the world's first methanol-powered ferry, the Stena Germanica, by Stena Line in 2015 [49]. By 2018, seven methanol-fueled vessels were operational worldwide [91]. Xing et al. (2021) recommend considering methanol as a potential energy source for marine fuel cells, even in the absence of established international maritime regulations for fuel cell

power systems [90]. Additionally, Ni et al. (2020) suggest using methanol in waste heat recovery systems, offering potential fuel savings of up to 9% [18,44].

For the Stena Germanica project, Wärtsilä enhanced medium-speed four-stroke marine diesel engines with specialized injectors, enabling the separate direct injection of methanol and pilot fuel (marine gasoil, MGO). In the case of the Waterfront Shipping tankers, MAN low-speed two-stroke engines are utilized, featuring a separate direct injection system for methanol and pilot fuel (MGO or HFO). However, detailed measurement data for these engines are currently limited, with only a few results provided by the manufacturers. Despite the limited data, the available information suggests that the engines comply with emission regulations and exhibit efficiencies comparable to those achieved with diesel fuel [53].

### 2.1. Use of Methanol in Diesel Engines

However, the majority of internal combustion engines have used methanol as an additional fuel and not as the main fuel, until this moment.

Diesel engines are widely recognized for their attributes such as high thermal efficiency, substantial torque, low pollution emissions, and high reliability, making them prevalent in both commercial and passenger vehicles. The utilization of methanol fuel in diesel engines is particularly meaningful for reducing diesel consumption and curbing pollutant emissions. Presently, the primary approaches to integrate methanol fuel into diesel engines involve direct mixing, port injection, and in-cylinder direct injection, as detailed in reference [63,92].

### 2.2. Blending Diesel and Methanol Directly

The direct mixing method combines methanol and diesel, but requires costly co-solvents due to their incompatible properties. Conversely, Methanol-to-Diesel (MTD), synthesized from methanol, is a liquid mixture blended with diesel. Guo et al.'s study [92] found that a 20–30% MTD blend with diesel, showed comparable power but a 14% increase in fuel consumption and significantly reduced exhaust emissions, establishing MTD as a cost-effective, environmentally friendly diesel additive.

Soni and Gupta (2021) [93] and Soni and Gupta (2021) [94] found that increasing methanol in diesel from 10% to 30 significantly reduced NO, CO, and HC emissions by 65%, 68%, and 56%, respectively. They also advocated for adding water to the fuel to further decrease emissions [93,94].

In experiments by Jamrozik, up to 30% methanol positively affected the engine thermal efficiency without significant IMEP changes. However, exceeding 30% resulted in reduced CO emissions, but caused significant CO<sub>2</sub> and THC emission changes, alongside a notable drop in cylinder pressure, leading to engine instability [95].

Huang (2004) [96] demonstrated that higher methanol fractions enhance combustion characteristics, such as engine thermal increases and BSFC decreases with greater oxygen or methanol fractions. CO and smog in exhaust gas are substantially reduced, but NO<sub>x</sub> increases, particularly at high loads. The NO<sub>x</sub>–soot balance curve remains relatively flat during diesel–methanol mixed fuel operations [96].

Despite direct application benefits, challenges persist due to methanol and diesel immiscibility, requiring costly co-solvents. Blending ratios are limited due to cold start issues and oil separation, restricting the full potential of methanol fuel in direct mixing methods [63,97–100].

### 2.3. Methanol Injection through the Port, Coupled with Direct Injection of Diesel

In the port injection method, methanol is injected into the intake port during the intake process, forming a combustible mixture with fresh air. Diesel is then directly injected into the cylinder near the top dead center, leading to the ignition of the methanol/air mixture through the spontaneous combustion of diesel. However, the considerable latent heat released during methanol evaporation, when sprayed into the inlet, absorbs a substantial amount of heat, resulting in a significant reduction in the inlet temperature. This phe-

nomenon can pose challenges such as engine cold start difficulties or idle misfires [101]. To overcome this issue, Professor Yao from Tianjin University introduced the diesel/methanol combined combustion (DMCC) concept. Under the DMCC system, diesel engines operate in two combustion modes: diesel diffusion combustion and diesel pilot air/methanol mixed combustion. Pure diesel combustion is employed during an idling speed and low load, while the DMCC combustion mode is activated when the engine load, cooling water temperature, and engine speed meet the specified values [102].

According to Yao et al. (2008) [103], DMCC combustion in a direct-injection diesel engine reduces soot and NO<sub>x</sub> emissions, but increases HC and CO emissions, compared to the original diesel engine. Combining DMCC with an oxidation catalyst mitigates CO, HC, NO<sub>x</sub>, and soot emissions [103].

Cheng et al.'s study on methanol fumigation revealed that increasing fumigated methanol decreases the brake thermal efficiency (BTE) at low loads, but increases it at high loads. Methanol fumigation increases HC, CO, and NO<sub>2</sub> emissions but reduces the NO<sub>x</sub> concentration, smoke opacity, and particulate matter mass concentration. Combining fumigated methanol with a diesel oxidation catalyst, reduces CO, HC, NO<sub>2</sub>, particulate matter mass, and numbers [77].

Geng et al. (2014) [104] observed that, under low and medium loads, DMDF combustion significantly reduces dry soot emissions before the diesel oxidation catalyst (DOC), with a slight increase under high loads. DOC significantly reduces the particulate matter mass and number concentration under all engine loads. An increased methanol injection decreases the intake air temperature, leading to a lower particulate matter mass and number concentration in the DMDF mode [104].

Wei et al. (2015), found that a high premixed ratio of methanol (PRm) in a dual-fuel diesel engine leads to prolonged ignition delay, shortened combustion duration and altered emissions, disrupting the traditional NO<sub>x</sub>-soot trade-off [105]. Diesel oxidation catalyst (DOC) application post-PRm combustion effectively reduces HC, CO, and formaldehyde emissions. Liu et al. (2015) observed that in the Dual Fuel-Diesel Methanol Fumigation (DMDF) mode, a low injection pressure yields a lower indicated mean effective pressure (IMEP) than pure diesel combustion [102]. Higher injection pressures in the DMDF mode enhance combustion characteristics and reduce brake-specific fuel consumption (BSFC), with NO<sub>x</sub> and smoke emissions lowered, but HC, CO, and NO<sub>2</sub> emissions increased compared to pure diesel combustion. The port injection of methanol is favored over direct mixing for its flexibility in controlling methanol ratios, achieving higher substitution rates, and improving fuel economy and emissions [63,102,105].

#### 2.4. Injecting Methanol and Diesel Directly

In agreement with the literature review, both methanol and diesel utilize in-cylinder direct injection, enhancing the replacement rate to improve fuel efficiency and decrease emissions, thereby expanding methanol's usage in compression ignition engines [63,106]. In a heavy-duty diesel engine, separate injections of diesel and methanol effectively overcome the NO<sub>x</sub>-soot trade-off, showcasing the successful integration of methanol into high-pressure diesel injection systems [106]. Research by Jia and Denbratt (2018) indicates that a direct methanol injection efficiently reduces total hydrocarbon (THC) and CO emissions in a heavy-duty diesel/methanol engine [107].

Two primary in-cylinder direct injection approaches involve adding a separate fuel injection system for methanol in larger engines or using a single injector for both fuels, addressing spatial constraints, but presenting developmental challenges [108–110].

### 3. E-Methanol's Production and Infrastructure

Methanol is predominantly generated from natural gas and coal, but alternative sources like wood, agricultural and domestic wastes, renewable sources, and even CO<sub>2</sub> can serve as viable inputs, as highlighted in multiple references [69,110–113].

Nevertheless, the utilization of fossil fuels accompanied by the release of pollutants and CO<sub>2</sub> stands as an obstacle to addressing global climate change and constructing a sustainable, low-carbon society [63].

Hence, the practical significance of advancing renewable alternative fuels is paramount. Utilizing CO<sub>2</sub> for methanol synthesis not only mitigates the greenhouse effect associated with CO<sub>2</sub>, but also yields a diverse range of chemical products and clean fuels. This approach represents a pioneering strategy that accomplishes multiple goals simultaneously, as emphasized in references of Nguyen and Zondervan (2019) and Battaglia et al. (2021) [63,114,115].

According to Tian et al. (2022) [60], methanol holds significance as a fundamental chemical raw material and a crucial fuel source. Currently, its primary production involves the synthesis of natural gas or coal-derived synthesis gas, comprising hydrogen (H<sub>2</sub>) and carbon monoxide (CO) [63], while in accordance with studies that were carried out by Cocco, Pettinau and Cau. (2006) and Araya et al. (2020), methanol is predominantly manufactured from synthesis gas with the utilization of heterogeneous catalysts of the Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> type, necessitating an elevated temperature (200–300 °C) and pressure (50–100 bar) [46,116,117]. Nevertheless, when producing methanol from coal or coke oven gas, the process generates wastewater and waste gas, leading to significant ecological and environmental pollution challenges. Additionally, the preparation procedure releases a substantial quantity of CO<sub>2</sub>, contributing to the greenhouse effect.

In recent times, there has been a growing emphasis on the concept of carbon neutrality, leading to increased interest in the technical approach, involving the hydrogenation of CO<sub>2</sub> to produce methanol [46]. Conforming to Guil-López et al. (2019), CO<sub>2</sub> serves as the fundamental raw material for the production of methanol, urea, formic acid, salicylic acid, cyclic carbonates, ethylene carbonate, dimethyl carbamate, formaldehyde, and co-polymers [118]. Notably, the industrial synthesis of methanol and urea from CO<sub>2</sub> is economically feasible, leading to the consumption of approximately 110 million metric tons of CO<sub>2</sub> annually [119].

Additionally, Ma et al. (2009) supports e-methanol's generation through the catalytic hydrogenation of CO<sub>2</sub> in an adiabatic fixed-bed catalytic reactor [120]. The catalyst primarily comprises Cu and Zn, supplemented with various additives such as Al, Zr, Cr, Si, B, Ga, etc. [46]. This pathway is recognized as a pivotal means of achieving carbon neutrality in the long term. The process of converting CO<sub>2</sub> into high-value fuels or chemicals is regarded as a sustainable method of transforming waste into valuable resources. In accordance with Zhang et al. (2017) [121], the synthesis of methanol from CO<sub>2</sub> not only addresses the greenhouse effect associated with CO<sub>2</sub> emissions, but also yields a diverse range of chemical products and clean fuels. Methanol, known for its efficacy as a fuel, can be further transformed into high-value chemicals such as olefins and aromatics [121]. The widespread adoption and application of CO<sub>2</sub> hydrogenation to methanol necessitates realization through technologies like photocatalysis [63,119,122–124], photo electrocatalysis, or water electrolysis, with a reliance on renewable energy sources such as solar energy [63,124].

Typically, the technology for the hydrogenation of CO<sub>2</sub> to methanol involves the utilization of CO<sub>2</sub> and H<sub>2</sub> through a heterogeneous catalyst, catalyzing a reduction reaction to produce methanol—a process also known as direct hydrogenation. This method has evolved primarily from the CO hydrogenation process and boasts a certain level of industrial development. However, the direct hydrogenation approach is associated with relatively harsh reaction conditions and low methanol selectivity. In response, researchers have introduced a homogeneous catalyst based on the direct hydrogenation method to enhance the efficiency of CO<sub>2</sub> hydrogenation to methanol. Kothandaraman et al. (2016) [125] employed a Ru-based homogeneous catalyst to achieve the hydrogenation of CO<sub>2</sub> to methanol. The resulting methanol can be easily separated from the product through simple distillation. The experimental evidence has demonstrated that even trace amounts of CO<sub>2</sub> in the air can serve as a carbon source, leading to a methanol yield of up to 79% [125]. Riduan, Zhang, and Ying (2009) utilized N-heterocyclic olefin catalysts for the conversion

of CO<sub>2</sub> to methanol at room temperature [126]. In comparison to heterogeneous metal catalysts, homogeneous organic catalysts offer milder reaction conditions and the catalytic conversion of CO<sub>2</sub> into methanol at ambient temperatures. This technology, capable of directly utilizing atmospheric CO<sub>2</sub>, presents a novel approach to achieving carbon neutrality and reducing energy consumption [125,126].

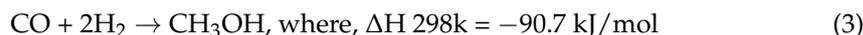
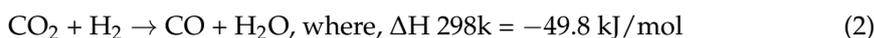
The electrocatalytic reduction method, conducted at a regular temperature and pressure, has gained attention for its streamlined operation and precise control of reaction conditions [127,128]. However, studies suggest that deploying the CO<sub>2</sub> electrocatalytic reduction method for methanol production often yields diverse by-products, such as CO, methane (CH<sub>4</sub>), formaldehyde (HCHO), and methanoic acid (HCOOH), underscoring the critical role of choosing the appropriate electrode and catalyst [129]. In a study employing cyclic voltammetry, Portenkirchner et al. (2014) directly compared pyridazine and pyridine as catalysts, revealing higher methanol selectivity for both despite distinct reaction paths [130]. Nevertheless, it is important to note that the CO<sub>2</sub> electrocatalytic method for methanol production tends to have a higher energy consumption [127–129].

In keeping with Na et al. (2012), the photocatalytic reduction use, harnessing sunlight for methanol synthesis, is an environmentally promising method explored by researchers [131]. Li et al. (2012) synthesized TiO<sub>2</sub> nanotubes (TNTs) photocatalysts through a hydrothermal process and CdS (or Bi<sub>2</sub>S<sub>3</sub>)/TiO<sub>2</sub> nanotubes photocatalysts through direct precipitation [132]. They investigated the photocatalytic activity for reducing CO<sub>2</sub> to CH<sub>3</sub>OH under visible light and the CO<sub>2</sub> adsorption performance. The results revealed that, under 1 atm pressure and 298 K, TNTs exhibited a CO<sub>2</sub> adsorption capacity of 0.269 mmol/g, surpassing the other two heterostructure photocatalysts. Modification with Bi<sub>2</sub>S<sub>3</sub> or CdS enhanced visible light absorption and the photocatalytic performance of TNTs photocatalysts. The Bi<sub>2</sub>S<sub>3</sub>-modified TNTs photocatalyst demonstrated superior photocatalytic activity, CO<sub>2</sub> adsorption capacity, and visible light absorption compared to the CdS-modified counterpart. Particularly, after 5 h of visible light exposure, the Bi<sub>2</sub>S<sub>3</sub>-modified TNTs photocatalyst achieved a maximum methanol yield of 224.6 μmol/g, approximately 2.2 times that of TNTs [131,132].

As per Zhang (2015), in the biocatalytic reduction process for converting CO<sub>2</sub> to methanol, the absence of a requirement for high-temperature and high-pressure conditions, as well as the exclusion of heavy metals, results in a low energy consumption and minimal environmental pollution [133]. This feature enhances the method's practical significance. The pivotal factor in the efficacy of this approach lies in cultivating bacterial microorganisms with superior catalytic performance. Cui et al. (2004) identified *Methylophilus thermophilus* IMV 3011 as a catalyst capable of bioconverting carbon dioxide to methanol. Since the CO<sub>2</sub>-to-methanol conversion process consumes energy, the periodic regeneration of methane is necessary to restore reducing equivalents in the cell [134]. Xin et al. (2007) similarly observed IMV3011's ability to catalyze the bioconversion of CO<sub>2</sub> to methanol [135]. However, the capacity for methanol synthesis is constrained by the availability of reducing equivalents in the cell. They discovered that poly-β-hydroxybutyrate (PHB) stored in cells can generate reducing equivalents upon decomposition, thereby enhancing the methanol production capacity. The accumulation of PHB in the cell can be adjusted by manipulating the concentration of nitrogen and copper in the medium. When PHB accumulation reaches 38.6%, the ability of CO<sub>2</sub> to be reduced to methanol is maximized.

According to Biswal et al. (2022), the hydrogenation of CO<sub>2</sub> to methanol is an exothermic process facilitated by hydrogen, but without a catalyst it becomes challenging and produces undesired by-products [119]. Optimal conditions involve a suitable catalyst, low temperatures (<150 °C), and pressures of 5–10 mPa to maximize the CH<sub>3</sub>OH yield and avoid by-product formation. Temperatures above 240 °C activate CO<sub>2</sub>, and at high temperatures, H<sub>2</sub> consumption increases, causing a reverse water–gas shift reaction and decreasing CH<sub>3</sub>OH yield. Olah (2005), Bataglia et al. (2021), Meesatham and Kim-Lohsoontorn (2022), and Kaiser et al. (2022) agree with this, saying that the conventional procedure typically functions at temperatures ranging from 250 to 300 °C and pressures between 50 and 100 bar,

commonly employing catalysts based on Cu/Zn/Al [115,136–139]. This ratio ensures the most efficient utilization of resources in the process. In accordance with Sun et al. (2015) and Zou et al. (2020), CO<sub>2</sub> hydrogenation results in CH<sub>3</sub>OH, as per Equations (1)–(3) [21,140]. The overall hydrogenation reaction (Equation (1)) requires 3 mol of H<sub>2</sub> for 1 mol of CO<sub>2</sub> to produce methanol and water. When 1 mol of CO<sub>2</sub> reacts with 1 mol of H<sub>2</sub> (Equation (2)) it forms CO and H<sub>2</sub>O in the water–gas shifting reaction. Additionally, 1 mol of CO reacts with 2 mol of H<sub>2</sub>, producing 1 mol of CH<sub>3</sub>OH (Equation (3)).



As defined by C.A del Pozo et al. (2022) [63], the optimal stoichiometric ratio for maximizing the conversion efficiency in the reaction is  $M = 2$  [46,64].

$$M = \frac{[\text{H}_2] - [\text{CO}_2]}{[\text{CO}] + [\text{CO}_2]} \quad (4)$$

In any case, regardless of the chosen method for methanol production from CO<sub>2</sub>, the overarching objective is to simplify the CO<sub>2</sub>-to-methanol process, reduce production costs and CO<sub>2</sub> emissions, and ultimately achieve zero carbon emissions [63].

### 3.1. Methanol's Infrastructure

As reported by Verhelst et al. (2019) [52], methanol's prominence in the chemical landscape stems from its existing substantial production capacity and well-established infrastructure. The sheer magnitude of its global production is underscored by the production of approximately 70 million metric tons in 2015, with the worldwide capacity reaching approximately 110 million metric tons, as referenced in the methanol Institute (2017) [75]. This figure is noteworthy, especially when compared to the roughly one billion metric tons of global gasoline production in 2012. Methanol, a versatile compound, plays a pivotal role in the petrochemical industry, contributing to the synthesis of various chemicals through processes such as methanol-to-olefins, resulting in the production of more plastics and related materials [52,136,141].

The far-reaching impact of methanol is evident in its widespread international shipping, driven not only by its application in chemical processes, but also by its use as a fuel. The demand for large-volume methanol shipments has spurred advancements in marine engine technology to accommodate its usage efficiently. China stands out as a major player in methanol production, with regional coal mining permits paving the way for the construction of extensive production facilities. China's current installed capacity is sufficient to meet half of its road transport fuel requirements [141]. In contrast, the United States witnessed a significant surge in methanol capacity in 2015, more than doubling its production. This increase was facilitated by the accessibility of affordable natural gas from shale rock, resulting in the U.S. surpassing China as the world's leading low-cost methanol producer [52,142].

Putting these numbers into perspective, while a large oil refinery typically processes around 500,000 barrels of crude oil per day, a contemporary methanol production facility can produce approximately 20,000 barrels of methanol per day. This highlights the scale and impact of methanol production in comparison to traditional oil refining processes.

According to Bilgili (2023) [113] and Zincir, Deniz, and Tunér (2019) [22], despite its higher specific fuel consumption due to a lower calorific value, methanol remains more cost-effective than MGO, with a balanced relationship between fuel system simplicity and cost, even when its crude price exceeds LNG, as stated in a 2022 study produced by McGill, Remy, and Winther [22,143]. Additionally, as reported by Ammar (2019), although methanol is 38.6% cheaper per metric ton than diesel, the annual fuel cost rises by 28.16%, requiring

a 28% reduction in the ship speed to maintain consistent fuel costs [43,113]. Concerning the new ship construction, as Svanberg (2018) says, a methanol propulsion system offers economic advantages with lower investment costs compared to LNG [12,69], and these costs are expected to decrease with growing experience in utilizing this innovative fuel [110]. Andersson, Lundgren, and Marklund (2014) [144] employed a techno-economic model to assess methanol production. Their study explored a stand-alone unit and integration with a pulp and paper mill. The economic analysis showed a substantial 11–18 EUR/MWh cost reduction in methanol production, along with a notable 7% increase in plant efficiency through integration with existing industries [110,144].

### 3.1.1. Substantial Ships Engaged in Global Commerce

To ensure the widespread acceptance of marine fuel among globally trading ships, the establishment of an extensive network of bunkering facilities for the fuel is essential. As per Svanberg et al. (2018), certain alternative marine fuels such as methanol and LNG require onboard fuel and safety systems' adaptation [143]. Specialized storage tanks and fuel piping are necessary for LNG. Methanol necessitates modifications, albeit to a lesser extent due to its liquid state at an ambient temperature. The technology readiness assessment for methanol as a fuel emphasizes its utilization of well-established, mature technology components widely used in the maritime industry, with innovation lying in the nuanced interaction among these components. Regarding fuel storage, methanol offers flexibility, being a liquid at ambient shipboard conditions, eliminating the need for specialized pressure tanks. Existing tanks can be modified with methanol-compatible coatings, and their non-classification as a marine pollutant by IMO allows for their placement next to the hull, following IMO regulations for ships carrying hazardous chemicals [97]. In contrast, conventional oil uses double-bottom tanks, gaseous fuels require pressure tanks, and LNG, a cryogenic liquid, needs independent pressure tanks, potentially challenging volume-critical ships [110,145].

McGill, Remley, and Winther (2013) highlighted that this requirement, in relation to LNG's attractiveness as a fuel for a majority of ships [143], is similarly emphasized by Chryssakis et al. (2018) who note that the absence of bunkering facilities and uncertainties about long-term fuel availability act as obstacles to the introduction of any new fuel [146]. The considerable fuel demands of ocean-going vessels are underscored by Florentinus et al. (2012), who report that the largest container ships engaged in global trade can possess fuel capacities ranging from 10 to 14 thousand metric tons [147].

In considering methanol as a potential fuel for this maritime sector, as discussed earlier in this paper and acknowledged by Andersson and Salazar (2015), it is crucial to recognize that methanol derived from fossil feedstock, particularly natural gas, is globally accessible [148]. While renewable methanol availability is currently limited, produced in few locations and in small quantities, methanol sourced from fossil feedstock can serve as an interim or pathway fuel. This provides a practical solution until the production and availability of renewable methanol can be significantly scaled up [110].

Ellis and Tanneberger (2015) support that the existing infrastructure for methanol storage and distribution to the chemical industry is already in place at many ports worldwide, such as Rotterdam and Antwerp in Europe [69], in agreement with Andersson and Salazar (2015), transforming this infrastructure to provide methanol as a marine fuel which requires only minor adjustments, especially when compared to the substantial modifications needed for the implementation of LNG infrastructure [148]. Storage tanks originally designed for gasoline can be easily and promptly adapted for methanol storage [149]. Hence, when compared to some other alternative fuels, the development of infrastructure poses a relatively minor obstacle for the utilization of methanol as a marine fuel [110].

### 3.1.2. Ships Involved in Short-Distance, Coastal, and Domestic Trade

In the domain of smaller vessels navigating confined areas like short sea shipping and coastal routes, bunkering opportunities are limited.

Skold and Styhre (2017) say that, using the provision of conventional oil bunker fuel in Sweden as an example, this service is primarily provided by a few major companies [150]. Vessels like ferries, often operating between just two ports, typically rely on bunkering services at one port, as seen with the Stena Germanica ferry bunkering methanol in Gothenburg every four to six days [151].

A report by Ford (2012) supports that bunkering operations, whether conducted offshore, at anchor, or alongside, entail the transfer of fuel from sources like road tankers, bunker barges, or other vessels [152]. Despite the diverse providers, the procedural steps involved remain consistent. It is crucial to recognize bunkering as a high-risk activity, where mistakes have the potential to cause pollution, incur significant financial penalties, or even result in imprisonment. Despite the absence of dedicated bunker barges for methanol, converting to an existing one is cost-effective at EUR 1.5 million [148]. In Sweden, smaller vessels like road ferries are bunkered by trucks using existing transportation systems for methanol [153].

### 3.1.3. The Availability of Fuel and the Competition from Other Consumers

Conforming to Svanberg et al. (2018), ship owners must have a degree of assurance regarding the long-term availability of fuel before committing to a fuel switch that necessitates additional investments in adapting fuel systems and engines [110]. According to Chryssakis et al. (2018), ship owners carefully evaluate the decision to retrofit a vessel for alternative fuels, taking into account factors such as the availability and cost of fuels. An analysis of anticipated global marine fuel trends for 2030, based on a 2014 Lloyd's report [154], underscores how imperative it is for a fuel to exhibit traits of accessibility, cost-effectiveness, compatibility with current and emerging technologies, and conformity with extant and forthcoming environmental mandates. Ship operators, in contemplating a transition to environmentally superior fuels such as methanol, may also factor in considerations like environmental policies, customer expectations, and corporate branding. Adherence to emissions reduction regulations, encompassing both regulated and unregulated environmental impacts, necessitates careful consideration. An operational study should primarily focus on the bunkering process and associated infrastructures, evaluating their adequacy for fulfilling both individual and market-wide fuel requirements in relation to existing quantities. Furthermore, the financial aspect must extend beyond infrastructure modification costs, encompassing potential disparities in the cost of the new fuel compared to conventional alternatives and additional operational expenses in the fossil fueling process. The decision-making process is also contingent on the adaptability of ship engines to the new fuel, entailing potential retrofitting or replacement costs. Simultaneously, the feasibility of storing and managing the new fuel on ships should be assessed, accounting for tank construction capabilities and risk behavior [110]. In cases where a ship operator aims to reduce greenhouse gas (GHG) emissions by utilizing renewable methanol, the consideration of future availability becomes crucial [146]. This outlook is influenced by both the production of renewable methanol and the demand from other users. Currently, the limited quantity of renewable methanol produced is primarily employed in fuel blending to fulfill objectives like those outlined by the European Commission concerning the use of renewable energy in transportation.

Svanberg et al. (2018) also support that methanol fuel utilized in a diesel combustion engine may exhibit a lower purity than the Methanol Consumers and Producers Association (IMPCA)-quality methanol typically used by consumers in fuel blending and the chemical industry [110]. Tests conducted by Ryan et al. (1994) have shown that methanol with a purity as low as 90% performs well as fuel, as described in detail by Stenhede (2013) [155,156].

Seddon (2011) outlines a fuel-quality methanol with a specified purity exceeding 95% and a water content of less than 1% [157]. While this high-purity methanol is not traded, it has been produced for alternative fuel demonstration projects. The availability of fuel-grade methanol would be suitable for marine use, reducing competition from other

users. Additionally, the environmental impact of fuel methanol production would be lower than that of IMPCA grade, as it requires less distillation.

### 3.2. Comparison of Bunkering Cost between Methanol, E-Methanol, and Conventional Fuels

The existing infrastructure adaptability and cost-effective bunkering operations position methanol favorably against conventional fuels [12,98,148]. Despite a higher specific fuel consumption, methanol proves cost-effective compared to MGO and diesel, offering economic advantages in new ship construction with lower investment costs [22,43,69,111].

As per Helgason et al. (2020) [158], methanol production encompasses various feedstocks such as carbon dioxide sourced from carbon capture and utilization processes (CCUs), as well as fossil fuels and biomass [159,160]. CCUs involve capturing and reusing effluent carbon dioxide emissions [161]. Although methanol is predominantly derived from fossil fuel pathways, particularly coal, natural gas presently stands out as the predominant feedstock, constituting 90% of global methanol production through the catalytic conversion of pressurized syngas [162]. These fossil fuel pathways have a commercial history spanning approximately 80 years, demonstrating maturity compared to newer methods employed in CCU processes [163].

With a wide array of potential feedstocks, methanol presents a considerable potential for production capacity. However, it is crucial to recognize that its energy density, represented by the lower heating value (LHV), stands at 15.6 MJ/L. This value is notably lower than conventional maritime fuels, such as Heavy Fuel Oil (HFO), which boasts an LHV of approximately 38.4 MJ/L [164,165]. Consequently, in the absence of efficiency improvements, engines with a comparable power output would necessitate approximately twice the volumetric fuel content when using methanol instead of HFO [158].

In accordance with a Bilgili (2023) [113] study, the investment in methanol production yields a notable return within three years [110], with an initial cost favorable in comparison to exhaust gas treatment technologies and below LNG investments [69]. Despite concerns about the relatively high production expense [1,166], the production cost of methanol is indicated as 69 EUR/MWh [167]. Operating costs are estimated at USD 3–4.5/kWh [69] or USD 2.5/kWh [168], with dual-fuel engines' conversion cost reported at USD 285/kW [148]. Methanol, despite its high specific fuel consumption, proves more cost-effective than MGO due to its low calorific value [22]. While its crude price surpasses that of LNG, the balance in favor of methanol results from the interplay between fuel system complexity and cost [143]. Despite being 38.6% cheaper than diesel fuel, a 28.16% annual fuel cost increase requires a 28% reduction in ship speed to maintain cost parity [43,113]. Additionally, Svanberg et al. (2018) [110] say that Bio-methanol production costs vary significantly based on feedstock, conversion processes, and production capacity. Capital cost (CAPEX) and feedstock acquisition contribute 75–90% to the total production cost [167]. Biomass-based methanol production costs range from 71–91 EUR/MWh [167], with potential reductions to 50–66 EUR/MWh by adjusting capital and feedstock costs.

For black liquor gasification in a pulp mill, the total production cost is 69 EUR/MWh, with contributions from capital, feedstock, auxiliary power, and other O&M costs [167]. Adjustments similar to those in biomass gasification lead to a reduction in total production costs to 58 EUR/MWh.

Integration or co-location with other industries can lower production costs, as demonstrated by Andersson et al. [144], showcasing an 11–18 EUR/MWh cost reduction and a 7% increase in plant efficiency through integration. Utilizing residual heat for methanol production can further decrease costs by 10–12% in case studies [110,169,170].

Environmental externalities were evaluated for HFO, Natural Gas (NG) methanol, and ReNewable (RN) methanol from 2018 to 2050 under various fuel price and externality scenarios. RN methanol may not be cost-competitive with HFO until the 2040s, while NG methanol emerges as a more cost-competitive option, exhibiting the lowest total cost under high external cost scenarios throughout 2018–2050. NG methanol also outperforms HFO under medium external cost scenarios and a high fuel price.

Presently, NG methanol proves cost-competitive with HFO for cargo ships, fishing vessels, and cruise ships, provided externalities are considered in fuel purchase costs. Accounting for environmental externalities is crucial in maritime fuel pricing. Policymakers must urgently address maritime emissions, instituting incentives and comprehensive pollutant assessments, and considering spatial distribution, ecological, and public health impacts, to justify effective mitigation strategies for enhanced marine sustainability [158].

### 3.3. The EU ETS and Fuel EU Regulations

The measures initially implemented by the aforementioned organizations such as IMO and the E.P.A. about the gradual reduction of greenhouse gas emissions have been gradually adopted by the European Union as well. Through the issuance of regulations, the EU now defines and requires the reduction, and ultimately, the neutralization, of fuels by 2050.

Until now, the monitoring–record–verifying (MRV) system has been implemented with European Regulation EU 757/2015 [171]. As stated in this regulation, all ships moving within European ports or traveling to and from European ports, must record and annually report to the European Maritime Safety Agency the quantity of fuel consumed and the amount of carbon dioxide emitted. Consequently, the recording and database creation for ship emissions are in progress and have not yet been completed.

Additionally, the European Union has introduced two more regulations, the EU Emission Trading System (EU ETS) and the Fuel EU Regulation, encoded by Regulation EU 2023/1805.

#### 3.3.1. EU ETS Regulation

The EU ETS employs a ‘cap and trade’ system, limiting greenhouse gas emissions annually. Since 2005, it has reduced emissions by 37%. Emissions are quantified in allowances, tradable on the EU carbon market. Companies must surrender enough allowances each year, facing fines if they fall short. The declining cap ensures market value, incentivizing cost-effective emission reductions. Revenues, exceeding EUR 152 billion since 2013, primarily support national budgets for renewable energy, energy efficiency, and low-carbon technologies. Allowance sales also fund the Innovation Fund and the Modernization Fund for low-carbon initiatives.

The main goals of the EU ETS regulation is to charge emitters for their greenhouse gas releases, contribute to emission reductions, and generate funds for the EU’s environmental shift. This encompasses all EU nations, including Iceland, Liechtenstein, and Norway (EEA-EFTA states). In addition, it applies to approximately 10,000 facilities in energy and manufacturing, plus aircraft operators within the EU and those departing to Switzerland and the UK, constituting around 40% of EU emissions. Starting in 2024, it will extend to emissions from maritime transport [172,173].

Ships that do not comply with the EU MRV requirements for two or more consecutive periods, may be expelled and prohibited from engaging in trade within the EU. Companies that fail to submit allowances may incur an excess emissions penalty of EUR 100 per ton of CO<sub>2</sub> and are still responsible for fulfilling the required allowance surrender. Furthermore, companies that persistently fail to comply for two or more consecutive periods may be at risk of being denied entry into the EU for all ships under their jurisdiction [172,173].

#### 3.3.2. Fuel EU Regulation (EU 2023/1805)

The Fuel EU Maritime Regulation, complementing the EU ETS, gradually reduces shipping sector fuel emissions. It was adopted on 13 September 2023 and with take effect by 1 January 2025. This regulation will cover CO<sub>2</sub> emissions from large ships until 1 January 2024 and promote cleaner fuels, setting ambitious targets from a 2% decrease in 2025 to 80% by 2050. The regulation includes methane and nitrous oxide emissions, follows the Well to Wake principle, and mandates zero-emission measures at berth to reduce air pollution in ports.

Adopting a flexible, technology-neutral approach, it introduces voluntary pooling and applies to vessels above a 5000 gross tonnage at EEA ports. Reporting through THETIS MRV from 2025, it aligns with the EU's goals of a 55% net emissions reduction by 2023 and climate neutrality by 2050 [171–173].

### *3.4. Methanol and E-Methanol Affection by the International Regulations*

Renewable methanol derived from biomass exhibits a 56% lower GHG impact than heavy fuel oil [18,74]. Adopting renewable methanol results in significant reductions, including a 95% cut in CO<sub>2</sub> emissions and an 80% decrease in nitrogen oxide emissions [75,76]. Innovative synthesis approaches using CO<sub>2</sub> not only counteract the greenhouse effect, but also offer diverse chemical products and clean fuels [63,114,115]. Despite challenges like wastewater, hydrogenating CO<sub>2</sub> for methanol aligns with carbon neutrality goals [46]. Industrial synthesis consumes about 110 million metric tons of CO<sub>2</sub> annually [119], addressing the greenhouse effect and producing chemical products [119]. Experimental evidence supports using trace CO<sub>2</sub> for an up to 79% methanol yield [125]. Catalyst technologies like N-heterocyclic olefin catalysts contribute to carbon neutrality [125,126]. In essence, renewable methanol, especially from innovative sources, stands out for substantial GHG reduction and sustainable energy practices [75,76,114].

It is premature to draw conclusions about how methanol will be affected by the implementation of international regulations. However, its properties such as CO<sub>2</sub> sequestration during production—especially when derived from renewable sources and carbon dioxide hydrogenation—as well as its low emissions compared to conventional fuels make it an environmentally friendly fuel. It seems likely to meet the conditions for achieving greenhouse gas emission reduction goals. Considering additional measures outlined in the regulations to propel shipping into the new era of fuels, such as carbon taxation on conventional fuels, investments in methanol infrastructure, and strict penalties for non-compliant vessels [174,175], we can assume that this particular fuel will likely be positively impacted by the European Union's new regulations. Future research will confirm these assumptions.

## **4. Challenges of Using Methanol as a Marine Fuel**

All the literature sources surveyed consistently highlighted methanol's utilization as a marine fuel, albeit not without complications. The primary challenges encompass supply, infrastructure, and bunkering processes. Researchers such as Svanberg et al. (2018) and Vredeveltdt et al. (2020) underscored the critical evaluation needed in bunkering facilities, fuel supply systems, onboard containment systems, and vessel engines [110,176]. It was emphasized that proper ventilation and an open deck location are indispensable for bunkering stations. The liquid state of methanol facilitates easy storage and availability for bunkering purposes. Insights from Van Hoecke et al. (2021) indicated that the existing infrastructure developed for the chemical industry could ensure the sufficient availability of methanol [177]. However, the study also suggested that additional terminals might be necessary to accommodate the widespread use of methanol in maritime vessels. In contrast, Brynolf (2014) [16] proposed an alternative perspective, suggesting that methanol could be stored in conventional fuel tanks for onboard storage. This method offers ease of use as a liquid low-flashpoint fuel under ambient conditions, presenting a convenient storage solution [53].

As per findings by Ellis and Tanneberger (2015), methanol, distinguished by its non-cryogenic nature, stands out for its simplicity in both handling and transportation, surpassing other fuels and aligning with the familiar procedures of conventional bunker vessels [69]. Drawing from the operational experiences of Platform Supply Vessel (PSV) and Offshore Support Vessel (OSV) fleets in the offshore industry, extensively reported by Le Fevre (2018) and Rousseau and Tomdio (2023), these instances can be regarded as a valuable guide for the widespread adoption of methanol as a bunkering fuel [178,179].

Highlighting the importance of considering fuel characteristics, especially in the context of risk assessment analyses, remains a key takeaway from this body of research.

Ellis and Tanneberger's insights, along with the practical knowledge shared by Le Fevre, Rousseau, and Tomdio, underscore the potential of methanol as a feasible and efficient option within bunkering processes [53].

Methanol emerges on the maritime horizon as a beacon of promise for ship bunker fuel, owing to its global ubiquity and efficient distribution.

According to Ghorbani et al. (2022), methanol is a compact energy storage solution, showcasing remarkable efficiency by volume despite its energy content lagging behind that of alternative fuels [180]. The allure of methanol becomes particularly pronounced for short-sea vessels, navigating the intricate interplay of limited trade distances and regulatory landscapes. Given methanol's requirement for more frequent bunkering, short-sea freight vessels can seamlessly pivot to accommodate this need, aligning operational demands with fuel dynamics.

Navigating the seas of carbon neutrality and low-carbon fuel adoption proves more intricate for larger vessels. Gray et al. (2021) contend that the incorporation of low-energy-content fuels such as methanol demands the substantial redesigning of ships [181]. This is essential to augment fuel tank capacities, ensuring sufficient energy stores for extended voyages. Despite methanol's inherent versatility and its relative ease of integration into ship designs compared to other low-flashpoint fuels, industry studies exemplified by Pundir et al. (2021) and Ellis and Bomanson (2018) raise concerns about compliance with MSC.1/Circ.1621 regulations, specifically regarding methanol's placement below the lowest possible waterline [88,182].

These studies collectively illuminate methanol's potential to curtail CO<sub>2</sub> emissions by around 10% when positioned as the primary marine fuel. Gray et al. (2021) underscore the pivotal role of sustainable production methods, such as biomass, biogas, or renewable electricity, in propelling methanol toward the promising realm of carbon-neutral fuels [181].

#### 4.1. Advantages of Using Methanol

In consonance with Oberg (2013) and Ellis and Tanneberger (2015), methanol is recognized for its properties as a light, colorless, and flammable liquid which holds the potential for utilization in the transportation sector, a feasibility attributed to its substantial production capacity on a large scale [52,69,112,113].

Additionally, as reported by Verhelst et al. (2019), employing methanol as a fuel brings forth various advantages, encompassing a significant evaporation temperature, a diminished stoichiometric air/fuel ratio, an increased specific energy ratio, a swift flame speed, a notable molar expansion ratio, a moderate flame temperature, and a substantial H/C ratio [52]. Furthermore, methanol maintains its liquid state under typical ambient temperature and pressure conditions.

As stated by Sayin (2010), methanol exhibits traits such as reduced viscosity, facilitating effortless injection, atomization, and seamless mixing processes [183]. Brynolf (2014), in his book, supports that methanol finds applicability in Otto engines or diesel engines, particularly when incorporating glow plugs or pilot fuel, but also in fuel-cell use [16].

According to Bilgili (2023), the current infrastructure, but also gas tanks for LNG, can easily be used so as to accept methanol ready for use by the shipping industry, with a few easy conversions [113].

Ancic, Percic, and Vladimir (2020) support that the current infrastructure and storage facilities can be seamlessly adjusted to incorporate the alternative fuels mentioned [166]. However, a significant drawback is the substantial production costs involved. While utilizing these alternative fuels in the shipping industry could lead to decreased or even zero greenhouse gas emissions, the considerable expenses associated with investment, maintenance, and production create a notable economic barrier, hindering their widespread adoption in shipping [166].

As reported by Svanberg et al. (2018), the existing infrastructure for methanol storage and supply to the chemical industry is already in place at numerous ports worldwide, such as Rotterdam and Antwerp in Europe [69,110]. The adaptation of this infrastructure to

support methanol as a marine fuel requires only minimal modifications, particularly when contrasted with the challenges associated with implementing LNG infrastructure [148]. Tanks initially designed for storing gasoline can be swiftly and easily repurposed for methanol storage [149]. Thus, in contrast to certain other alternative fuels, the establishment of infrastructure does not emerge as a substantial barrier for methanol, as documented in the cited references [110]. Bunkering methanol is an easy procedure, as methanol is in a liquid form [43,69].

The efficiency of methanol engines either matches or exceeds that of traditional fuels [137,148,184]. Additionally, methanol demonstrates higher efficiency, particularly at low loads [52]. The primary factor contributing to this efficiency is the elevated oxygen content, a characteristic associated with methanol's high-octane number [22]. Another significant factor is the high evaporative cooling feature, which enhances the volumetric efficiency [183]. Research studies also support the idea that the utilization of methanol contributes to an improved engine performance [185,186]. Despite the need for adjustments in storage tanks, piping, and safety systems, these modifications are deemed acceptable, given that methanol is available in liquid form at ambient temperatures [110]. Methanol shares combustion characteristics with diesel fuel, surpasses gasoline in advantages, and is considered a more fitting fuel for Otto engines due to its high resistance to auto-ignition [22,52,113].

#### 4.2. Disadvantages of Using Methanol

Despite the peculiarities that make methanol a promising future clean fuel and the possibility of its production, distribution, and storage on a large scale in the supply chain, there are still some disadvantages of its use. These disadvantages are mainly due to the physicochemical elements of methanol and its toxicity as a chemical compound. The main areas in which the negative factors find a direct response are human health, therefore, by extension, affecting the health of ship crews, and the ability of methanol to create the uptake of certain materials, which has a negative impact when used in internal combustion engines' combustion, but also in the initiation and treatment of fires.

#### 4.3. Potential Hazards and Factors to Take into Account When Bunkering Methanol

Pearson and Turner (2012) and Bromberg (2010) provided safety assessments of methanol and ethanol, establishing that although these alcohols are hazardous and toxic substances, such risks are inherent to all considered alternatives to gasoline and diesel [187,188]. Notably, studies by Machiele (1987) and Machiele (1990) for the US Environmental Protection Agency [50,51] also reached the conclusion that in many respects, alcohols, including methanol, can be deemed safer than gasoline [52].

Methanol, with the chemical formula  $\text{CH}_3\text{OH}$ , is a colorless liquid fuel characterized by a low flash point. Numerous "Environmental Toxicology" studies highlight its toxicity and corrosiveness to materials.

According to Van Hoecke et al. (2021), ingesting methanol poses severe health risks, including threats to the central nervous system, coma, death, or blindness. In addition, the inhalation of methanol vapor, denser than air, can lead to asphyxiation, particularly in confined spaces on board [177].

Gerba (2019) stresses the need for cautious handling, especially in the case of spills or leaks [174].

Elsaid et al. (2021) specifies an Immediately Dangerous to Life or Health Concentrations (IDLH) value of 6000 ppm, and a Permissible Exposure Limit (PEL) of 200 ppm [175]. Methanol vapor tends to accumulate in lower regions, necessitating the implementation of detection and ventilation systems in leak-prone areas [53].

As reported by Verhelst et al. (2019), the primary challenge confronting alcohols, particularly methanol, pertains to their toxicity, whether through ingestion, skin or eye contact, or inhalation. Small amounts of methanol are easily metabolized by the human body due to its natural presence in fruits and vegetables [52]. However, an excessive intake

overwhelms the digestive system, leading to dangerously high concentrations of toxic intermediary products, namely formaldehyde and formic acid.

According to Machiele (1987), fatal doses, if left untreated, are documented to fall within the range of 1 to 2 mL per kg of body weight [50]. This translates to approximately 60–240 mL for individuals with typical body weights.

Gable (2004) stated that the lethal dosage of ethanol is roughly double that of methanol (ranging from 350–577 mL for ethanol, depending on body mass and metabolism, compared to 115–470 mL for methanol) [189].

#### Danger of Fire Onboard End ICE's Corrosion Using Methanol as Bunker

The significant risk lies in the near invisibility of methanol flames in sunlight, which is associated with its low flash point [52,113] compared with HFO and other marine fuels. The difficulty in detecting methanol flames is attributed to their low light emission, low temperature, and absence of soot [53,88].

Moreover, due to its non-conductive nature, methanol readily dissolves in water and can be extinguished using water in the event of a fire [52,63].

According to Hughes (2021), the evaporation of methanol liquid is slower than that of liquefied gas under typical temperature and pressure conditions [190].

Additionally, in accordance with a study by Shamsul et al. (2014), flammability in methanol occurs when methanol vapor concentrations fall within the range of 6.5% to 36.5% and are exposed to an ignition source [191].

As per Verhelst et al. (2019), to avert sparks or ignition sources, precautions must be taken in the methanol manifold, pressure/vacuum (P/V) relief valve, and ventilation system [52,53].

Electrical equipment exposed to methanol gas, with an autoignition temperature of 450–470 °C, should be shielded with a T2 surface temperature class. Ellis and Tanneberger (2015) recommend the use of inert gas to prevent explosive behavior in the methanol tank vapor space [53,69].

Referring to corrosion caused by methanol, the investigation highlighted its potential when methanol interacts with CO<sub>2</sub>, wet, or salty conditions, emphasizing the need to avoid inert gases containing carbon dioxide [53,88].

Engine modifications prompted by methanol's corrosive nature and high auto-ignition temperature are essential [148,192]. Its unsuitability for diesel engines stems from issues such as low viscosity, high auto-ignition characteristics, a low cetane number, and a high latent heat of vaporization [69,193]. Furthermore, the low flash point (10–11 °C) falls below SOLAS limits, necessitating extra safety measures during operation [52,110,113,185].

#### 4.4. Environmental Impact of Using Methanol

The central environmental factor essential for appraising alternative marine fuels lies in ensuring that the use of the fuel complies with both present and anticipated future environmental regulations. This emphasizes the critical importance of evaluating marine fuel options in light of evolving environmental standards.

In the evaluation of greenhouse gas (GHG) emissions throughout the life cycle of a fuel, the selection of feedstock and production methods for methanol fuel emerges as a pivotal consideration [110].

Brynolf et al. (2014) conducted an analysis indicating that, when utilized as a ship fuel, methanol derived from natural gas was estimated to have a GHG life cycle impact equivalent to that of Heavy Fuel Oil (HFO) [17]. Conversely, in agreement with assessments by DNV GL, the life cycle GHG emissions from methanol produced from natural gas were found to be slightly higher than those associated with conventional fuel oils. Notably, methanol derived from biomass demonstrated significantly lower GHG life cycle emissions, as evidenced by both DNV GL and Brynolf et al. (2014) [24,68]. These findings underscore the importance of considering both feedstock and production methods when assessing the environmental impact of methanol as a marine fuel [110].

According to Shahhosseini et al. (2018), Tuner (2015), and Tuner et al. (2018), methanol is renowned for its low greenhouse gas (GHG) and emission levels and owes this attribute to its high hydrogen-to-carbon (H/C) ratio and lack of sulfur [43,52,194–196]. In a dual-fuel system study, increasing the methanol percentage correlated with decreased emission rates. Using only Marine Diesel Oil (MDO) resulted in NO<sub>x</sub>, SO<sub>x</sub>, PM, CO<sub>2</sub>, and CO rates of 9.06, 0.192, 0.101, 367.1, and 0.746 kg/min. Contrastingly, an 89% methanol-11% MDO blend yielded lower rates: 2.02, 0.021, 0.011, 300.4, and 0.338 kg/min [43]. These findings highlight methanol's favorable emissions profile and its potential to mitigate environmental impacts in fuel usage.

As reported in a study by Yao et al. (2012), the NO<sub>x</sub> formation and emissions are reduced by 30% when methanol is used [197]. In agreement with Verhelst et al. (2019), Yao et al. (2008) and Cheung et al. (2009) found that utilizing methanol results in a reduction of NO<sub>x</sub> levels by 6–50%, contingent on the engine load. However, it concurrently elevates the NO<sub>2</sub>/NO ratio [52,103,198]. According to Fox and Storwold (2011) and Riaz, Zaheldi, and Klemes (2013), the information given above is correct [199,200].

In accordance with (Ellis and Tanneberger, 2015) data collected from the sibling engine of the *Stena Germanica*, the NO<sub>x</sub> emissions are reported to be in the range of 3 to 5 g/kWh [69].

According to Zincir, Deniz, and Tuner (2019), low NO<sub>x</sub> production when using methanol is attributed to its low evaporation temperature and reduced flame temperature from the dense fuel injection into the cylinder [22]. In agreement with Brynolf (2014), Brynolf et al. (2014), and Zincir et al. (2019), there are studies that support methanol's compliance with IMO Tier III restrictions, conflicting with existing views [17,22,68].

On the other hand, Svanberg et al. (2018) and Fridell, Salberg, and Salo (2021) argue the opposite by refuting the above view [110,201].

Ellis and Tanneberger (2015) support that employing methanol results in a 7% reduction in the CO<sub>2</sub> generated during operation when compared to Marine Gas Oil (MGO). This underscores the environmental benefits associated with methanol use in comparison to traditional fuels [69].

However, a study by Zincir et al. (2019) indicates a 10–25% reduction in CO<sub>2</sub> per ton-nautical mile at lower engine loads [22]. Verhelst et al. (2019) supports that methanol use was found to elevate CO and HC emissions [52]. Notably, CO formation significantly increased at low loads (10%—22.7 g/kWh, 15%—4 g/kWh, 25%—2.7 g/kWh) due to larger rich fuel regions and incomplete combustion from a shorter combustion delay [22].

Conforming to Rachow et al. (2018), methanol application was associated with a potential 46% rise in the Specific Fuel Oil Consumption (SFOC), with a higher SFOC at lower loads [22], and an increase in formaldehyde formation [48,68,69,113,202].

Referring to the ocean's protection, Moirangthem and Baxter (2016) and Ellis and Tanneberger (2015) support that in the case of leakage, methanol swiftly disperses in water, preventing the attainment of hazardous concentrations and thereby avoiding toxic effects on aquatic organisms [48,69]. However, it is crucial to note that on a regional scale, potential harm may persist until the adequate dilution to low concentrations is achieved [68,113].

## 5. Conclusions

In summary, this exploration underscores the pivotal role of methanol as a transformative solution in the maritime energy landscape, particularly amid the maritime industry's critical juncture in meeting emission reduction targets. The intensification of global shipping demands necessitates a paradigm shift towards sustainable fuels to mitigate significant environmental and health implications. The emphasis on 50% decarbonization by 2050 aligns with methanol's attributes such as a high hydrogen storage density and global production capacity. While IMO's regulatory framework guides the imperative for sustainable maritime energy solutions, methanol's liquid form at standard conditions, advantageous properties, and existing infrastructures in key ports position it favorably.

However, persisting challenges such as safety concerns, lower flash points, and health risks associated with methanol need careful consideration. Despite these limitations, leveraging intermittent sustainable energy sources for methanol production offers promising avenues. Advancements in synthesis methods and existing infrastructure in key ports amplify methanol's economic viability, environmental benefits, and technological adaptability.

In moving forward, research endeavors should delve deeper into operational studies, considering bunkering processes, more infrastructures, and financial implications to navigate the transition towards cleaner and more efficient maritime energy solutions. The multifaceted nature of these considerations necessitates global collaboration and innovation, highlighting the significance of a holistic approach to ensure the successful integration of methanol as a sustainable alternative fuel in the evolving energy landscape.

As we believe in this new green fuel, the limit is whether the industry can respond to the universal demand.

The implementation of the ESG criteria across maritime companies will provide a greater impetus for the adoption of the new fuel, more investments, and increased funding for research, resulting in corresponding positive environmental impacts, including a reduction in the carbon footprint of fuels, almost zero emissions of SO<sub>x</sub>, as well as reduced emissions of NO<sub>x</sub> and PMs.

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