

Methanol as a marine fuel

Advantages and limitations

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Abstract

E-Methanol is prominently discussed as a potential candidate to decarbonise deep-sea shipping. This study assesses whether the potential benefits and risks of e-methanol are sufficiently reflected in the current discussion and whether methanol is preferable to current fossil marine fuels and other RFNBOs. Methanol has many advantages but also some disadvantages compared to other marine fuels. In comparison, methanol is easy to handle and combust. E-methanol can offer reductions in GHG and air pollutant emissions. To be carbon-neutral, it is of upmost importance that the fuel is produced with renewable energy and a sustainable CO₂ source. However, e-methanol is likely to be more expensive than other fuels, like e-ammonia in the decades ahead and a significant upscaling of its production would be necessary to meet the fuel demand of shipping. Overall, e-methanol could play an important role in a future fuel mix that is more diverse. Its share in the fuel mix will be determined by several factors: upscaling of green methanol production, decrease in fuel cost, and acceptance of ammonia in the maritime sector. The years up to around 2030 will likely be key as this decade will be decisive for where investments will be made. Policy makers, therefore, should implement the right incentives as soon as possible. This includes taking a well-to-wake approach for measuring and regulating GHG emissions and considering all potential harmful pollutants that might occur due the use of future fuels like e-methanol.

Kurzbeschreibung

E-Methanol wird als möglicher Kandidat für die Dekarbonisierung der Hochseeschifffahrt diskutiert. In dieser Studie wird untersucht, ob die potenziellen Vorteile und Risiken von Methanol in der aktuellen Diskussion ausreichend berücksichtigt werden und ob Methanol den derzeitigen fossilen Schiffskraftstoffen und anderen RFNBOs vorzuziehen ist. Methanol hat viele Vorteile, aber auch Nachteile im Vergleich zu anderen Schiffskraftstoffen. Methanol ist vergleichsweise leicht zu handhaben und zu verbrennen. E-Methanol kann zur Verringerung von Treibhausgas- und Luftschadstoffemissionen beitragen. Um klimaneutral zu sein, ist es von größter Bedeutung, dass der Kraftstoff mit erneuerbarer Energie und einer nachhaltigen CO₂-Quelle hergestellt wird. E-Methanol wird in den nächsten Jahrzehnten wahrscheinlich teurer sein als andere Kraftstoffe, wie z.B. E-Ammoniak. Eine erhebliche Ausweitung der Produktion wäre notwendig, um den Kraftstoffbedarf der Schifffahrt zu decken. Insgesamt könnte E-Methanol eine wichtige Rolle im künftigen Kraftstoffmix spielen. Sein genauer Anteil am Kraftstoffmix wird von mehreren Faktoren abhängen: Hochskalierung der Produktion von grünem Methanol, Senkung der Kosten und Akzeptanz von Ammoniak im maritimen Sektor. Die Jahre bis etwa 2030 werden wahrscheinlich entscheidend sein, denn in diesem Jahrzehnt wird entschieden, wo Investitionen getätigt werden. Die politischen Entscheidungsträger sollten daher so bald wie möglich die richtigen Anreize setzen. die Dazu gehört ein Lebenszyklusansatz für Messung und Regulierung von Treibhausgasemissionen und die Berücksichtigung aller potenziellen Schadstoffe, die durch die Verwendung künftiger Kraftstoffe wie E-Methanol entstehen könnten.

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List of Abbreviations

AFIR	Alternative Fuels Infrastructure Regulation
CCfD	Carbon Contracts for Difference
DAC	Direct Air Capture
DF	Dual Fuel
BECCS	Bioenergy with Carbon Capture and Storage
ECHA	European Chemicals Agency
ETS	Emission Trading System
GHG	Greenhouse Gas
GHS	Globally Harmonized System of Classification and Labelling of Chemicals
НСНО	Formaldehyde
HFO	Heavy Fuel Oil
ICE	Internal Combustion Engine
IMO	International Maritime Organization
LNG	Liquefied Natural Gas
MGO	Marine Gas Oil
Mt	Million tonnes
PM	Particulate Matter
RFNBOs	Renewable Fuels of Non-Biological Origin
TtW	Tank-to-Wake
WGSR	Water-Gas Shift Reaction
WtT	Well-to-Tank
WtW	Well-to-Wake

Summary

The use of Renewable Fuels from Non-Biological Origin (RFNBOs) will be the main emission mitigation measure for deep-sea shipping. Upscaling the production and supply of RNFBOs to shipping will become crucial in the decades ahead in order to decarbonise the sector. To date, little experience has been gathered with using hydrogen, e-methanol or e-ammonia as a fuel in shipping. Further, it is not yet clear which RFNBO is the most appropriate for use in deep-sea shipping and which option will gain the highest share in the fuel mix by 2050.

This study assesses whether the potential benefits and risks of e-methanol are sufficiently reflected in the current discussion about future marine fuels and whether methanol is preferable to current fossil marine fuels and other RFNBOs.

There are many aspects to consider for the suitability of a future marine fuel. E-methanol and e-ammonia are both discussed as promising candidates for the decarbonisation of deep-sea shipping, and both fuels have advantages and disadvantages. The characteristics of methanol make it easier to handle and combust than, for example, ammonia and hydrogen. While further research on the level of formaldehyde emissions from marine engines is necessary, e-methanol can offer reductions in various GHG and air pollutant emission species. To be carbon-neutral, it is of upmost importance that the fuel is produced with renewable energy and a sustainable CO₂ source. Carbon-free RFNBOs (like ammonia) have the advantage of not needing CO₂ as an input and of having higher efficiency in the production process. However, methanol is primarily produced with natural gas today. Green hydrogen production and the DAC technology need to be scaled up significantly in order to provide substantial amounts of e-methanol for shipping. However, this is unlikely to happen in a significant volume before 2030. –Thus, a more rapid increase in the rate of uptake in the 20-year period up to 2050 will be required to ensure maritime transport can be decarbonised.

In comparison to other fuels, methanol's future will not only be decided by the upscaling of the production but also by its availability in different ports and by future fuel costs. The storage of methanol at ports for use as a marine fuel is already taking place, albeit at low volumes, to supply the current global demand mainly from initial pilot projects. However, the potential for storage has already been quantified globally at approx. 25 Mt with a further considerable potential to scale up this capacity by converting the existing storage infrastructure for petroleum-based products in the case of sufficient demand. Projections for demand could exceed 200 Mt annually based on ambitious pathways to decarbonising maritime transport by 2050. This would require additional investment in new storage capacity for methanol. Some long-term cost scenarios indicate that ammonia-fuelled vessels will be less expensive than methanol-fuelled vessels. Fuel cost decreases will be subject to upscaling of DAC and green hydrogen as well as decreases in renewable electricity prices. However, the acceptance of ammonia's toxicity and the implementation of international safety guidelines could influence the preference of shipowners for one fuel or the other. Methanol is toxic to humans, especially when ingested orally. For aquatic organisms, however, it is hardly toxic. In case of spillages, methanol dissolves very quickly in the sea water. Vapours that get into the air are also dispersed very quickly. Safety guidelines for methanol in the shipping sector are already in place and ships exist that are running on methanol.

Table 1 compares e-methanol with other fuels when used in ICEs based on key criteria from a wellto-wake perspective. The comparison is made horizontally across fuels. The higher the given number, the better the performance of the fuel.

Table 1:Comparison of RFNBOs with the status quo of fossil HFO/MGO based on
key criteria

Criterium	E-Methanol	Hydrogen	E-Ammonia	HFO
GHG reduction potential (lifecycle)	5	5	4*	1
Air pollutants (incl. exhaust gas aftertreatment)	4	5	5	1
Aquatic ecotoxicity	5	5	2	1
Human toxicity	3	5	2	3
Flammability	2	1	2	5
Explosion risks	5	2	4	5
Infrastructure (plants, bunkering)	4	1	3	5
TRL production/engine, retrofits	3	1	2	5

Notes: Ranking: 1= high risk/ low performance to 5=low risk/ high performance, assuming fuel use in ICE with exhaust gas aftertreatment system; *uncertainty about N_2O emissions, TRL=technology readiness level. Source: Authors' own compilation

In conclusion, e-methanol has low environmental risks compared to other future fuels (except hydrogen), can offer sufficient energy density for most voyages, is easy to handle, and enables a ship to be operated in a climate-neutral way from well to wake. It is clear that the future fuel mix will be more diverse than the current 97 % dominance of petroleum-based fuels across all segments of the shipping market. E-methanol could play an important role in this. Its exact share in the fuel mix will be determined by several factors: upscaling of green methanol production, decrease in fuel cost, and the acceptance of ammonia as a fuel in the maritime sector. The years up to around 2030 will likely be key as this decade will be decisive for where investments will be made. Policy makers should therefore implement the right incentives as soon as possible. On the one hand, it will be important to ensure the supply of e-methanol to the sector. This could include support for investments in green methanol infrastructure (incl. in ports) or the use of CCfDs. On the demand side, on the other hand, strong incentives for RFNBOs including a RFNBO sub-quota as for aviation would be required.

1 Introduction

Reaching the goals of the Paris Agreement requires extensive greenhouse gas (GHG) emission reductions in all sectors. Emissions from the maritime transport sector have been increasing, strongly coupled with increasing globalisation and economic growth (IMO 2020). Energy efficiency measures will not suffice for the necessary emission reductions in the sector. The biggest lever to reduce emissions is the shift from fossil fuels to alternative, climate-neutral marine fuels (DNV 2022c) - called renewable fuels of non-biological origin (RFNBOs). The limited energy density and weight constraints of batteries limit the direct use of electricity to certain niches of the market (such as ferries and other short sea shipping). While (advanced/sustainable) biofuels, made from residual or waste biomass, will likely be available sooner than RFNBOs, the production capacities and competition for biofuels will limit their use in the maritime sector and capability to decarbonise the sector. The use of RFNBOs (such as hydrogen, e-methanol, e-ammonia) will thus be the main emission mitigation measure for deep-sea shipping.

Upscaling the production and supply of RNFBOs to shipping will become crucial in the decades ahead to provide the large amounts needed in the sector. To date, little experience has been gathered with using hydrogen, e-methanol or e-ammonia as a marine fuel. Further, it is not yet clear which RFNBO is the most appropriate for use in shipping and which option will gain the highest share in the fuel mix by 2050. Each RFNBO has advantages and disadvantages regarding efficiency, costs, environmental impacts, risks, etc. The use of methanol has gained increasing attention in the discourse around RFNBOs in deep-sea shipping, alongside ammonia.¹ Studies have highlighted methanol and ammonia as the most promising options for deep-sea shipping, for example in terms of cost (Korberg et al. 2021; LR; UMAS 2020; Stolz et al. 2022). Specific studies have been published on the safety and regulatory aspects of methanol (DNV GL 2016; DNV 2022a). First methanol trials and ships are already underway. Large shipping companies recently announced the order of methanol-fuelled container ships.²

In this context, this study assesses whether the potential benefits and risks of methanol are sufficiently reflected in the current discussion about future marine fuels and whether methanol is preferable to current fossil marine fuels and other RFNBOs. Given the limited availability of bio-methanol, the study focuses on e-methanol as a marine fuel with a long-term potential for deep-sea shipping.

The second chapter provides the context of the discussion around e-methanol by describing the production process and volumes of methanol. The third chapter illustrates methanol's application in shipping, including fuel characteristics, propulsion options and bunkering infrastructure. Chapter four addresses environmental and safety risks associated with methanol usage as well as GHG emissions and air pollutants. Chapter five draws on the previous chapters to discuss advantages and disadvantages of methanol as a marine fuel. The last chapter provides a conclusion of the study.

¹ For a detailed perspective on ammonia as a marine fuel see Cames et al. (2021): <u>https://en.nabu.de/imperia/md/content/nabude/verkehr/210622-nabu-study-ammonia-marine-fuel.pdf</u>

² E.g. Maersk and COSCO: <u>https://www.maersk.com/news/articles/2022/12/12/maersk-accelerating-the-transition-from-fossil-fuel-follower-to-green-industry-leader, https://splash247.com/cosco-orders-twelve-methanol-fuelled-24000-teu-ships/</u>

2 Context

2.1 **Production process**

The production of e-methanol consists of several steps and is based on the availability of green hydrogen produced from renewable energy and water through water electrolysis. Given the need for more renewable energy capacities and their limitation today, green hydrogen production necessitates additional renewable electricity generation (Kasten et al. 2019). A synthesis gas is produced from hydrogen and CO_2 via the reverse water-gas shift reaction (WGSR) at 1000 °C. The technology readiness level of the WGSR is still rather low (Heinemann et al. 2019). The resulting synthesis gas is used for methanol synthesis which is an established process with a high efficiency of about 80 % (Brynolf et al. 2018; LR; UMAS 2019). The upscaling of green hydrogen production is critical for e-methanol's future in the shipping sector. There is also the opportunity of a direct methanol synthesis which is still being tested at laboratory scale (Goeppert et al. 2014; Olah et al. 2018). Today, methanol is mainly produced from fossil natural gas.

The climate impact of e-methanol is mainly determined by the use of renewable energy throughout the whole production process and by the source of CO_2 used as input to the production of the fuel. As the combustion (or its use in a fuel cell) of e-methanol releases CO_2 into the atmosphere at the end of the fuel's lifecycle, the CO_2 needs to be removed from the atmosphere beforehand in order to balance out the CO_2 emissions downstream. There are two options for a renewable CO_2 source: a biogenic source or obtaining CO_2 from the air. The availability of biogenic CO_2 sources as an input to the e-methanol production will likely be limited for a large-scale production (Heinemann et al. 2019). For the long term, the extraction of CO_2 from air via Direct Air Capture (DAC) is considered the more promising option. There is a vast potential for DAC given the abundant presence of CO_2 in the atmosphere. However, DAC is relatively energy-intensive compared to capturing CO_2 from (fossil) industrial point sources (Hank et al. 2020). The most advanced DAC technology is the Temperature Swing Adsorption (TSA) which is just starting to be scaled up. The technology readiness level for DAC is hence lower than, for example, the maturity of cryogenic air separation of nitrogen needed for the production of e-ammonia (Cames et al. 2021).

To reach the goals of the Paris Agreement, renewable energy capacities will need to increase significantly and fast. Especially in the short to medium term, these capacities will be limited given the increasing demand from many sectors. It is thus important to use the renewable energy as efficiently as possible. The overall energy efficiency of the e-methanol production process depends on future improvements in the efficiency of electrolysis, the WGSR process and the DAC technology. Current estimates of the efficiency of the e-methanol production process range between 41-45 % today and 56 % in the long term (Stolz et al. 2022; Heinemann et al. 2019). The energy efficiencies of carbon-based RFNBO production processes are typically approx. 40-50 %, with e-diesel having the lowest production efficiency (37-45 % today) and e-methane a slightly higher efficiency (46-48 % today). For comparison, the production process of e-ammonia has a higher energy efficiency than carbon-based RFNBOs of approx. 53 % today and potentially up to 60 % in the long term because fewer production steps and no DAC is needed (Heinemann et al. 2019; Stolz et al. 2022). The primary energy demand is thus higher for e-methanol than for e-ammonia. Energy efficiencies of all RFNBO production pathways will likely increase in the future. However, the general differences between the pathways will remain as pathways with more process/conversion steps (e.g. carbonbased RFNBOs) have more energy losses. Given the energy losses of the e-methanol production route, it is important that this route is not powered by fossil fuels but by additional renewable electricity (and consequently green hydrogen).

2.2 Production volumes, costs and use

According to DNV (2022a), there are currently over 90 methanol plants in operation worldwide (i.e. in Africa, Asia, Europe, the Middle East, and North and South America), which contribute to a global capacity of approx. 110 million tonnes (Mt). China is the largest producer with over half of global production (Kajaste et al. 2018; CAAEFA 2021). Given that China is the only country to still use coal in the production process of methanol, the emission intensity of its output is high (i.e. 300 gCO₂eq/MJ) relative to other countries (Methanol Institute 2022a). The majority of methanol is produced via the natural gas route, which is associated with a lower emission intensity (i.e. 110 gCO₂eq/MJ) but this will vary depending upon the efficiency of different methanol plants in different regions. The capacity of methanol production in Europe is estimated by Argus Methanol (2022) to be approx. 10 Mt in 2022 in total. Around 35 % of this capacity for methanol production is based within the EU-27 (i.e. at plants in Germany operated by BASF, Shell /DEA, Mider and BP RP and in the Netherlands operated by OCI) and Norway (i.e. at a plant operated by Equinor). The capacity of methanol production in 2022 is estimated to be approx. 23 Mt in North and South America and 33 Mt in the Middle East and Africa (Argus Methanol 2022).

Figure 1 shows the global demand of methanol by key derivation over the past several years. The use of methanol can be categorised into two main groups:

- Methanol used in chemical applications (i.e. as a feedstock to produce chemicals such as acetic acid and formaldehyde that are subsequently required as inputs to produce adhesives, foams, plywood subfloors, solvents and windshield washer fluid). More than half of all methanol is used in chemical applications.
- Methanol used in energy-related applications (i.e. as a liquid fuel to power cars, buses, trucks and ships). Less than half of all methanol is used in energy-related applications.

The largest growth in demand for methanol observed in Figure 1 is in the production of olefins or methanol-to-olefins (MTO), which is driven in particular by China who seek to replace the use of naphtha as a feedstock for the production of olefins that are used as raw materials in the manufacture of chemical and polymer products like plastic, rubber, and food packaging.



Figure 1: Global methanol demand between 2018 and 2022

In 2022, the production of methanol via alternative production pathways (i.e. bio-methanol from residual biomass or e-methanol, see above) was very limited. Its future availability will depend upon the level of investment in new capacity to ramp up production. DNV (2022a) expects that the first (noticeable) volumes of bio- and e-methanol will enter the market in 2024 or 2025. For example, shipping company Maersk formed and invested in partnerships to produce at least 600,000 tonnes per year of e-methanol and at least 130,000 tonnes per year of bio-methanol by the end of 2025.³

Figure 2 provides an overview of how methanol prices differ between 2019 and 2022 in key regional markets on both a spot and contract basis. Methanol prices on a contract basis were higher in all regions than methanol prices on the spot market. This is mainly due to the fact that spot prices are for immediate selling or buying whereas contracts delay payment and delivery on an agreed upon future date. It is often the case that contracts are more expensive than spot prices for commodities (referred to as Contango) such as methanol normally due to the cost of carry (i.e. the charges associated with storing either a physical product or retaining a financial instrument). With regards to the variation in spot prices, the average price in 2022 was higher in Europe at 385 USD per metric ton than both the US (i.e. 368 USD per metric ton) and China (i.e. 342 USD per metric ton) (Methanol Institute 2022b). These price differences reflect the supply and demand balance of methanol that

³ <u>https://www.maersk.com/news/articles/2022/03/10/maersk-engages-in-strategic-partnerships-to-scale-green-methanol-production</u>

are influenced by fossil fuel prices, capacity utilisation rates, transport costs, labour costs, exchange rates, inflation etc. For comparison, the MGO price was on average 577 USD/t in 2021.⁴



Figure 2: Comparison of methanol market prices in different regions over time

The actual cost of methanol production will vary depending on the feedstock used and the production pathway. Price estimates for RFNBOs like e-methanol vary significantly across studies depending on the assumptions made. For example, IRENA; Methanol Institute (2021) estimate the following production costs:

- Fossil fuel-based methanol is estimated to be in the range of as low as 100-250 USD per tonne;
- Bio-methanol is estimated to be in the range 320 USD/t and 770 USD/t;
- E-methanol is estimated to be in the range 800-1 600 USD/t assuming CO₂ is sourced from bioenergy with carbon capture and storage (BECCS) at a cost of 10-50 USD/t. It is important to acknowledge that these production costs are expected to decline significantly as the volume of production of e-methanol increases over time.

The larger range of uncertainty in the cost of methanol from alternative production pathways (i.e. bio-methanol and e-methanol) is due to the fact that production is currently low and therefore data on actual costs limited. On average, studies show that e-diesel is the most expensive alternative to fossil marine gas oil (MGO), and that other RFNBOs are three to four times the cost of fossil MGO – with ammonia being less expensive than methanol (Brynolf et al. 2018; Korberg et al. 2021; Stolz et al. 2022; LR; UMAS 2020).

Source: Methanol Institute (2022b)

⁴ MGO price ranging between 450 and 650 USD/t for sales at the port of Rotterdam: <u>https://shipandbunker.com/prices/emea/nwe/nl-rtm-rotterdam#MGO</u>

The production costs of RFNBOs like e-methanol are determined by the capital expenditure of production facilities, the capacity of the production facilities and the cost of renewable energy (Heinemann et al. 2019). A particular bottleneck for RNFBOs is the cost of electrolysers and cost for renewable electricity needed to power them. It is anticipated that the upscaling of production processes and decreasing electricity costs will result in fuel cost reductions over time.

3 Methanol in the shipping sector

3.1 Characteristics and propulsion options

A comparison of the characteristics of existing and potential marine fuels is provided in Table 2. Methanol (CH₃OH) is liquid at ambient temperatures, less energy dense than conventional fossil fuels (like MGO), but more energy dense than ammonia or hydrogen. Based on the energy density, tanks onboard a vessel would hence be larger for methanol than MGO tanks but similar in size to liquefied natural gas (LNG) tanks. Methanol tanks can be installed in areas of the ship (e.g. at the bottom) where other fuel tanks, such as ammonia and LNG, could not be installed due to their more complicated fuel characteristics (like pressure and toxicity) (Kirstein et al. 2018). As a result, the overall space consumption for methanol on board is a little less compared to LNG and ammonia. According to engine manufacturers (Wärtsilä 2022), tanks for methanol will (depending on the ship design) only be 1.6 times larger than for MGO (not up to 2.5 based on energy density, Table 2). Due to the larger tank size, there can be a trade-off between the cargo carrying capacity and the refuelling pattern when using methanol as a marine fuel. Stolz et al. (2022) examine a switch of the European bulk carrier fleet to different alternative fuels. They find that - if the cargo-carrying capacity is maintained, a methanol-fuelled fleet could maintain 93 % of the current cargo (bulk) operations. MMKMC (2022b) look at the conversion of 15 000 TEU container vessels, and conclude that the vessels can maintain their full operating range with a container space loss of less than 1 %. The latter studies, DNV (2022b) and experts from the industry thus confirm that a loss in cargo-carrying capacity of ships running on methanol is expected, but that there is enough bunkering space onboard to maintain today's trade route or operating range.

Fuel	Gravimetric energy density [MJ/kg]	Volumetric energy density [MJ/I]	Storage pressure [bar]	Storage temperature [°C]	Tank size* based on energy density			
Liquefied hydrogen	120	8.5	1	-253	7.6			
Ammonia	19	12.7	1 or 10	-34 or +20	4.1			
Liquefied methane	50	23.4	1	-162	2.3			
Methanol	20	15.8	1	Ambient	2.3 - 2.5*			
MGO	43	36.6	1	Ambient	1			
HFO	40	35	1	Ambient	1			

Table 2: Overview of fuel characteristics

Notes: *tank volume relative to conventional MGO tank.*tanks can be placed more flexible and space saving depending on the ship design.

Sources: KR (2020), MAN (2019), Vries (2019), DNV (2022a)

Methanol is an alcohol, flammable and toxic (further details in section 4.1). Safety measures have been developed for handling the fuel as a cargo (DNV GL 2016). International safety standards by the IMO currently do not cover the use of methanol, ammonia, and hydrogen as marine fuels whereas LNG (and thus bio- or e-methane) is covered. However, interim guidelines exist that can be used under specific circumstances for the design process of methanol-fuelled ships (DNV 2022c). For maritime applications, methanol can be used in internal combustion engines (ICE) as well as in fuel cells.

Methanol use in ICE and retrofitting

Methanol cannot be used neat in conventional (mono-fuel) diesel ICE designed for heavy fuel oil (HFO) or marine diesel variants (like marine gas oil (MGO) without modifications. It can be blended with diesel-like fuels, but only at very low levels, thus inhibiting the complete switch to methanol (Cames et al. 2023). Dedicated (2-stroke and 4-stroke) methanol engines developed by the major marine engine manufacturers exist today and are often dual fuel (DF) engines. Methanol engines have a similar energy efficiency (approx. 45 %) as other existing engines.

Compared to conventional (HFO optimised) engines, methanol engines require modifications to a diesel engine such as specific fuel injection design, cylinder heads and piping (Ming and Chen 2021; Wärtsilä 2022). DF engines allow for the operation with two different fuels – typically an alternative fuel like methanol, and a conventional fossil fuel like HFO or MGO. Methanol has poor autoignition properties (DNV 2022a). As is also the case with other fuels like LNG, large marine (DF) engines use pilot fuel (approx. 5 %) to facilitate the combustion of methanol (EC 2021d; DNV 2022a). This pilot fuel can either be a third fuel for ignition (e.g. biodiesel) or HFO or marine diesel which is already available on the ship as a second (or back-up) fuel for the alternate DF mode. For a climate-neutral operation of a ship, this pilot fuel has to a be climate-neutral fuel, too. For example, Maersk plans to use biodiesel as a pilot fuel for their future methanol-fuelled ships in order to have carbon-neutral vessels (see below). Smaller 4-stroke ICE running on methanol are still being developed and expected in the years ahead (DNV 2022c). If methanol is not used in DF engines, it might be blended with small amounts of substances to facilitate the combustion (section 0). Compared to hydrogen or ammonia, the combustion technology is much more mature for methanol overall (ibid, Cames et al. (2021)).

According to Smith et al. (2021), almost half of the global fleet in 2050 will consist of ships that have been retrofitted to run on alternative, climate-neutral fuels like e-methanol. In addition to newbuilds, the ability to retrofit an existing vessel with a methanol engine will therefore be critical to the fuel's contribution to emissions reductions by 2050. Methanol engines can be retrofitted to an existing vessel with minor modifications to the vessel (EC 2021d). Retrofit kits (or full conversion solutions) are also offered by engine manufacturers which do not only contain the retrofit of the engine (or rather adjustments of the existing engine) but also other necessary changes like a new fuel supply system (such as a methanol fuel pump unit and methanol fuel valve train) (Wärtsilä 2022). In theory, every vessel can be retrofitted to run on methanol and there are, in principle, retrofit kits available for all alternative fuels. However, it is rather a cost-benefit consideration if and when a certain vessel is converted/retrofitted to run on methanol. For example, MAN states that basically any of their electronically-controlled engines, such as mono-fuel fuel oil and LNG engine, can be converted to their DF methanol engine (ME-LGIM) (MAN 2022). The specific changes to an engine to run on methanol would be similar for a mono-fuel or DF LNG engine. It is likely not worthwhile retrofitting or converting a mechanically-controlled engine, which is usually 15 to 20 years old, due to the residual value of ship versus the cost of the extensive retrofit (MAN 2022). In terms of the extent of a full conversion, some retrofit aspects (e.g. changes to the fuel supply system) might be different for a

DF LNG-to-methanol versus a monofuel-to-methanol conversion because a DF LNG vessel already has two tank systems (and the respective space) onboard, which are needed for a DF methanol operation.

Overall, retrofitting will play a crucial role in the transition of the shipping sector up to 2050. The percentage of newbuilds capable running on alternative fuels (incl. LNG) is increasing (DNV 2022c) and simultaneously retrofitting programs have also already started. The extent of retrofits, however, remains difficult to predict as the decision about a retrofit or a newbuild will be individual for each ship. The cost-benefit of a retrofit versus a newbuild also depends on the risk of stranded assets. Based on calculations on stranded assets of LNG ships, Fricaudet et al. (2022, p. 5) argue that *"[e]arly clarification of policy is key for avoiding a build-up of stranded value in the shipping industry*". The (un)certainty about future regulation and choice of fuel will thus influence the share of retrofits up to 2050.

Methanol and fuel cells

Methanol can also be used in a fuel cell, either directly or as a hydrogen carrier. For the latter, methanol needs to be reformed or cracked to receive the hydrogen which can then be fed into a variety of fuel cells, such as Proton Exchange Membrane fuel cells (PEMFC) or Solid Oxide fuel cells (SOFC). PEMFC and SOFC have both higher efficiencies compared to ICE with 50-60 % and 60 % respectively (Tronstad et al. 2017). Further efficiency gains can be expected in future and the recovery of waste heat can also increase efficiency of the fuel cell system. For example, the SOFC efficiency can thereby increase up to 85 % (Tronstad et al. 2017). A direct methanol fuel cell does not require the reforming step but is still under development and has a lower efficiency of 20 % according to Tronstad et al. (2017). Powering vessels with fuel cells instead of ICE requires a different design of the ship, including an electric engine. Many ships have though already a diesel electric system today. The power output of a fuel cell is limited today. A fuel cell system might thus require considerable space onboard a ship despite the higher efficiency of fuel cells. Furthermore, reforming methanol onboard to hydrogen would require energy which adds to the overall energy input for this fuel pathway, unless sufficient waste heat is recovered.⁵ Fuel cells might also be more suitable for 4-stroke application, such as smaller ships or cruise ships, than for replacing large 2stroke engines on long voyages due to the limited power output. However, a study of Mao et al. (2020) indicates a future potential of fuel cells powering 2-stroke deep-sea ships today: the authors examined and showed that operating large container vessels between the USA and China solely on hydrogen fuel cells is possible, but minimal cargo loss and operational changes would have to be accepted. Retrofitting ships with fuel cells is possible but, in addition to high capital costs, it is not easy since the fuel system (e.g. crackers) is different and a conversion from a diesel-mechanical engine would be a very high effort (DNV GL 2019; Cames et al. 2023). Fuel cells currently have a shorter lifetime than ship engines, with approx. 15 years compared to 30 years of an ICE (Horton et al. 2022; Korberg et al. 2021). Considering these technical constraints, fuel cells are rather a solution for the longer term with much higher benefits for those ship types that use electric drives already. Hybrid systems are a likely entry point of fuel cells to the market and first trials have already started (section 3.2).

⁵ For example, concept by Freudenberg uses waste heat from the fuel cell for the reformation step: <u>https://www.freudenberg.com/de/presse-medien/pressemitteilungen/detail/um-schiffslaengen-voraus</u>

3.2 Use and projects in the shipping sector

Globally, methanol use as a fuel in shipping is still insignificant: over 98 % of fuel used is conventional fossil fuel (HFO or MGO) (DNV 2022c). With the implementation of a global sulphur cap and increasing environmental regulations, a switch away from HFO to slightly less polluting fossil fuels, such as MGO and LNG, can be observed. There are already over 900 ships capable of running on LNG (DNV 2022c). In the EU, only 0.01 % of the 46 Mt of fuel used in 2019 was methanol (EC 2021a).

In February 2023, 22 ships were running on methanol with the majority being tankers.⁶ The *Stena Germanica* is an example of a RoPax ferry which was retrofitted with a DF methanol engine already in 2015.⁷ Among the ships running with an alternative fuel or propulsion, methanol-fuelled ships are a minority. For comparison, there are approx. 400 ships using batteries or a hybrid system (DNV 2022c). According to DNV (2022c), 35 methanol-fuelled ships were on order at the beginning of 2022, representing 1.45 % of the world's fleet on order in gross tonnage. However, major shipping companies have recently announced a large number of methanol new orders:

- Maersk 19 DF methanol container ships,⁸
- COSCO 12 DF methanol container ships,⁹
- CMA CGM 6 DF methanol container ships.¹⁰

Fahnestock and Bingham (2021) list a further 10 projects of methanol-fuelled newbuilds, retrofits and ship technology research (with an ICE as propulsion). This trend is also reflected in the increasing share of methanol newbuilds since the beginning of 2022: methanol newbuilds have represented a similar share in terms of the number of vessels and the gross tonnage compared to LNG-fuelled newbuilds (excluding LNG carriers).¹¹ In early 2023, over 80 methanol-fuelled ships were in operation and on order in total.¹² Especially in the container sector, methanol-fuelled newbuilds have represented approx. 50 to 60 % of new orders since the second half of 2022.¹³ While this indicates a trend towards fuelling newbuilds with methanol, the majority of new orders globally are still LNG and battery/hybrid vessels (DNV 2022c).

Fuel cells using methanol in the maritime sector are still in the development and testing stage with only few projects today (EC 2021d). A demonstration project is the MS Innogy which is powered by a PEMFC with previous methanol reformation onboard.¹⁴ The use of a high-temperature PEMFC, with hydrogen reformed from methanol, is already being tested on the AIDAnova as part of a hybrid onboard energy system.¹⁵ The future cruise ship Silver Nova will also employ a hybrid system of fuel cells and batteries next to the main (fossil) fuel LNG.¹⁶

⁶ DNV – Alternative Fuels Insight Platform: <u>https://afi.dnv.com/</u>

^{7 &}lt;u>https://www.stenaline.com/media/stories/stena-germanica-refuels-with-recycled-methanol-from-residual-steel-gases/</u>

^{8 &}lt;u>https://www.maersk.com/news/articles/2022/12/12/maersk-accelerating-the-transition-from-fossil-fuel-follower-to-green-industry-leader</u>

⁹ <u>https://splash247.com/cosco-orders-twelve-methanol-fuelled-24000-teu-ships/</u>

¹⁰ <u>https://lngprime.com/asia/cma-cgm-orders-six-methanol-fueled-containerships-in-china/58880/</u>

¹¹ DNV – Alternative Fuels Insight Platform: <u>https://afi.dnv.com/</u>

¹² DNV – Alternative Fuels Insight Platform: <u>https://afi.dnv.com/</u>

¹³ <u>https://splash247.com/methanol-boxship-orders-growing-more-rapidly-than-all-other-fuel-types/</u>

^{14 &}lt;u>https://mfame.guru/first-methanol-fuel-cell-powered-vessel/</u>

¹⁵ https://www.now-gmbh.de/en/projectfinder/pa-x-ell2/

¹⁶ https://www.meyerwerft.de/en/ships/silver_nova.jsp

3.3 Infrastructure and projections

The International Maritime Organization (IMO) (2021) reported that 203 million tonnes of fuel oil were consumed in 2020 for a smaller sub-set of all ships of 5 000 GT and above that fall within the scope of regulation 22A of MARPOL Annex VI. HFO and light fuel oil (LFO) account for 50 % and 32 % of total consumption respectively. Diesel (MDO) and marine gas oil (MGO) together contributed to a further 13 % of total fuel oil consumption in 2020. In contrast, the role of methanol as a marine fuel was considerably smaller accounting for 77,631 tonnes equivalent to 0.04 % of total fuel oil consumed in 2020 (IMO 2021). Given this small demand for methanol as a marine fuel, Fastwater (2021) argues that the existing storage capacity and infrastructure is built to supply the demand for chemical and energy applications. He also argues that it is likely more or larger terminals would be needed to meet the additional demand for methanol as a marine fuel. Although experience with supplying methanol to ships as a marine fuel is currently still limited, it is not envisaged that bunkering practices for methanol would differ from established marine fuels (Fastwater 2021).

The term bunkering refers to the supply of bunker fuels to ships and according to Fastwater (2021) the main methods include:

- *Truck-to-ship bunkering* is the most common method of bunkering methanol as there is already considerable experience with transporting the fuel to a variety of different consumers by road. This bunkering method is today often used for LNG.
- Ship-to-ship bunkering may be undertaken while a ship is alongside at port or while at anchor with fuel supplied via a bunker supply ship, tanker, or barge to the receiving vessel. This method of bunkering is more common for larger vessels as larger quantities can be bunkered compared to truck-to-ship.
- Land storage tank or terminal-to-ship bunkering via pipe or hose is a common solution for vessels operating out of a home port or for those operating on fixed routes that bunker from the same port.

The available bunkering option for methanol will vary depending on the port and the amount of fuel demanded. Initially, new fuels will likely be delivered truck-to-ship or ship-to-ship. Although the properties of methanol (i.e. such as its flammability, toxicity and corrosivity) present risks for the bunkering of the fuel, ports already have a lot of experience in safely handling methanol (Horton et al. 2022) and the fuel is available in over 100 ports globally (EC 2021d). Figure 3 provides an overview of the available methanol storage capacity available at ports across different countries. In total, the research identified a total methanol storage capacity at ports of approx. 25 Mt. Iran, the Netherlands, China, Saudi Arabia and Belgium collectively account for 60 % of the global methanol in Figure 3 represents a potential and this will only be made available in practice if there is sufficient demand in the future for methanol as a marine fuel. It is expected that existing infrastructure for petroleum products (like HFO) could be converted to methanol storage and distribution with only minor modifications that would further increase capacity (Fastwater 2021).



Figure 3: Ports with available methanol storage capacity in 2020

Note: Bulk liquid storage refers to ports with the potential to store chemicals, such as methanol and ethanol, whereas confirmed methanol supply / storage refers only to the capacity of ports to supply methanol. Source: https://www.methanol.org/marine/

As future fuel prices and availabilities are uncertain, projections of the future fuel mix in shipping vary a lot. DNV (2022c) models 24 scenarios of the fuel mix of the global fleet in 2050. Five of these scenarios show significant shares of e-methanol with up to more than 60 %, assuming low electricity prices, decarbonisation by 2050 and a substantially increasing uptake of methanol in the late 2030s. MMKMC (2021) find that significant shares of e-methanol would mainly emerge in 2050 if ammonia were deemed unfavourable or too risky for its use in shipping. Together with bio-methanol, e-methanol could contribute almost 50 % to the fuel mix in 2050. Although methanol's share in the future fuel mix is uncertain, studies with a techno-economic perspective highlight methanol together with ammonia as the most promising candidates for a large share in the future fuel mix (Korberg et al. 2021; Horvath et al. 2018; LR; UMAS 2020).

25 Mt of storage have been already identified with further potential to convert fossil fuel oil infrastructure if there is sufficient demand. This implies that additional investment in infrastructure will be required if the demand for methanol as a marine fuel increases considerably in the future. However, methanol can also use existing infrastructure for conventional fuels (with minor modifications) compared to other alternative fuel options, like ammonia (EC 2021d; Horton et al. 2022).

4 **Risks and environmental impacts**

4.1 Environmental and safety risks

Methanol is a clear, colourless, volatile, highly flammable liquid with a sweet odour. It is the first and simplest aliphatic alcohol.

Toxicity for humans and marine environment

The following description of the eco-toxicological data for methanol is based on the registration dossier for *methanol* (EC Number: 200-659-6, CAS Number: 67-56-1) from the European Chemicals Agency (ECHA).¹⁷

Methanol is classified as acutely toxic under category 3 (H301, H311, H331) according to EU Regulation 1272/2008¹⁸. Methanol is easily absorbed by inhalation, ingestion or skin contact. The toxicity to humans is mainly caused by the degradation products of methanol, e.g. formaldehyde and formic acid. Especially, formic acid can lead to a metabolic acidosis after a latency period of 6 to 30 hours. The leading effect of methanol in humans is a central nervous system toxicity and neurotoxicity including optical nerve toxicity (Frederick et al. 1984; Greim 2001; Kawai et al. 1991). Degeneration of the optic nerve can lead to blindness, and this damage is irreversible. Death may occur as a consequence of respiratory paralysis. In a summary of several studies on methanol poisoning accidents, WHO, UNEP et al. (1997) concluded that the minimum oral lethal dose is about 1 g/kg body weight. Buller and Wood (1904) stated that an oral (swallowing) methanol dose of 1.4 g/kg body weight would be lethal to 40 % of the humans.

In terms of the effects of methanol on animals, the studies on mammals still cited today are quite old. As methanol is already classified as an acute toxic category 3 according to EU Regulation 1272/2008, animal testing regarding acute dermal toxicity is not necessary. Early studies from Gilger and Potts (1955) and Cooper and Felig (1961) investigated Rhesus monkeys. In Gilger and Potts (1955), the monkeys received an oral dose of 6000 mg/kg body weight and showed extensive oedema of the retina and optic nerve papilla, and pupils were unresponsive. Some of the monkeys showed cystic degeneration of the outer granular layer of the retina, demyelinisation of the optic nerve and histological lesions in the putamen and nucleus caudatus. In the study of Cooper and Felig (1961) the LC50¹⁹ for the monkeys ranged from 7000 to 9000 mg/kg body weight. In rats, LC50 values of 87.5 mg/l (6 hours) and 128.2 mg/l (4 hours) were determined (BASF AG 1980a; 1980b). In mice, LC50 values of 79 mg/l are reported (Burg 1994). In cats, Burg (1994) determined a LC50 value of 43.7 mg/l. No studies on the toxic effects on birds were available.

Data on the toxicity of methanol on aquatic organisms are provided in Table 3. The results show that methanol is hardly toxic for fish, invertebrates, algae and microorganisms in the short term.

¹⁷ <u>https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1</u>.

¹⁸ https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=celex:32008R1272.

¹⁹ The median lethal concentration, LC₅₀, is the concentration required to kill 50 % of a tested population after a specified test duration. LC₅₀ values are frequently used as a general indicator of a substance's acute toxicity.

Organisms	Parameter	Value [mg/l]	Species
Fish	LC ₅₀ (96h)	28100	Pimephales promelas
	LC ₅₀ (96h)	20100	Oncorhynchus mykiss
	LC ₅₀ (96h)	15400	Lepomis macrochirus
Daphnids	EC ₅₀ ²⁰ (48h)	18000	Daphnia magna
	EC ₅₀ (48h)	> 10000	Daphnia magna
Green algae	EC ₅₀ (96h)	ca. 22000	Selenastrum capricornutum
Microorganisms	EC ₅₀	19800	activated sludge
	IC ₅₀ ²¹	>1000	activated sludge
	IC ₅₀	880	Nitrosamonas
	toxic limit concentration	530 - 6600	Pseudomonas, Microcystis aeruginosa

	O I I I I I I I		
l able 3:	Short term toxicity	y of methanol	on aquatic organisms

Notes: LC_{50} = median lethal concentration; EC_{50} = median effective concentration; IC_{50} half maximal inhibitory concentration. Source: $ECHA^{22}$

According to ECHA, there are no guideline studies on long-term toxicity of methanol to aquatic species available. Methanol belongs to a category of chemicals acting with a non-specific mode of action (simple narcosis). Therefore, the chronic toxicity to aquatic organisms can be reasonably predicted from data on acute toxicity by using an appropriate acute-to-chronic ratio (ACR). An ACR of 10 has been proposed in the literature for this kind of chemical. With Structure-Activity Relationship models (QSARs), data for long-term toxicity of methanol have been predicted (Table 4).

²⁰ The half maximal effective concentration (EC₅₀) is defined as the concentration substance required to obtain a 50% effect.

²¹ The half maximal inhibitory concentration (IC₅₀) is defined as the concentration of a substance required to obtain a 50% effect in inhibiting a specific biological or biochemical function.

²² https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1.

Table 4.

Table 4: Long-term toxicity of methanol							
Organisms	Parameter	Value [mg/l]	Species				
Fish	NOEC ²³ (predicted chronic value)	447	Pimephales promelas				
	NOEC (200-h)	7900 - 15800	Oryzias latipes				
Daphnids	NOEC (21-d)	208 (predicted)	Daphnia magna				
	NOEC (21-d)	122	Daphnia magna				
Note: NOEC = no Source: ECHA ²⁴	effect concentration.						

According to the Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection hazard procedure system, methanol is fully biodegradable with no potential to bioaccumulate. Although methanol is toxic to humans, it is not rated as toxic to aquatic organisms using the GESAMP rating system (GESAMP 2019)²⁵. Therefore, acute danger for maritime life due to methanol spills is highly unlikely.

Hazard statements of methanol compared with other fuels

Table 5 shows the hazard statements of methanol compared with other fuels according to the Globally Harmonized System of Classification and Labelling of Chemicals (GHS).

Table 5. Thazard Statements of methanol compared with other rules										
Hazard statements	Hazard category	Methanol ²⁶	Ammonia 27	CNG ²⁸	LNG ²⁹	LSHFO ³⁰	VLSFO ³¹	HSHFO ³²	MGO ³³	H2 ³⁴
H220 Extremely flammable gas	1A			Х	Х					Х
H221 Flammable gas	2		Х							

Table 5 Hazard statements of methanol compared with other fuels

²³ No effect concentration (NOEC) is a risk assessment parameter that represents the concentration of a pollutant that will not harm the species involved.

²⁴ https://echa.europa.eu/de/registration-dossier/-/registered-dossier/15569/6/2/1.

²⁵ The GESAMP Hazard Evaluation Procedure provides criteria for evaluating the hazards to human health and the marine environment of chemicals that may enter the marine environment through operational discharge, accidental spillage, or loss overboard from ships.

²⁶ https://ch-msds.shell.com/MSDS/00000000808 DE EN.pdf.

²⁷ Sigma-Aldrich, Safety Data Sheet Ammonia. See also Cames et al. (2021).

²⁸ https://www.boconline.co.uk/en/images/10021935 tcm410-55840.pdf.

²⁹ https://www.pgworks.com/uploads/pdfs/INGSafetyData.pdf.

https://sasoldcproducts.blob.core.windows.net/documents/Safety%20Datasheets/2b5bc04e-30 d0a6 ZA Low%20Sulphur%20Heavy%20Fuel%20Oil EN-ZA.pdf.

³¹ https://monjasa.com/wp-content/uploads/VLSFO-SDS-Final.pdf.

³² https://deutschemaxcom.com/sites/default/files/files/MSDS_deutsch.pdf

³³ https://www.bomin.com/fileadmin/content/global content/downloads/bomin-matrix/SDS Bomin DMA.pdf.

³⁴ https://produkte.linde-gas.at/sdb konform/H2 10021694EN.pdf.

Hazard statements	Hazard category	Methanol ²⁶	Ammonia 27	CNG ²⁸	LNG ²⁹	LSHFO ³⁰	VLSFO ³¹	HSHFO ³²	MGO ³³	H2 ³⁴
H225 Highly Flammable liquid		х								
H226 Flammable liquid and vapour	3								Х	
H227 Combustible liquid	4					Х				
H280 Contains gas under	Compressed gas			х						х
heated	Liquefied gas (b)		х							
H281 Contains refrigerated gas; may cause cryogenic burn or injury	Refrigerated liquefied gas		Х							
H304 Toxic if swallowed		Х				Х	Х	Х		
H304 May be fatal if swallowed and enters airways	1								Х	
H311 Toxic in contact with skin		Х								
H314 Causes severe skin burns and eye damage	1B		х							
H315 Causes skin irritation	2					Х				
H331 Toxic if inhaled	3	Х	Х							
H332 Harmful if inhaled	4					Х	Х	Х		
H350 May cause cancer	1B					Х	Х	Х		
H351 Suspected of causing cancer	2								Х	
H361 Suspected of damaging fertility or the unborn child	2					х	Х	Х		
H370 Causes damage to organs, optic nerve, central nervous system										
H373 May cause damage to organs through prolonged or repeated exposure	2					х	Х	Х		
H410 Very toxic to aquatic life with long lasting effects	1		X			Х	Х	X		
H411 Toxic to aquatic life with long lasting effects	2								Х	

Notes: CNG= Compressed Natural Gas, LNG= Liquefied Natural Gas, VLSFO= Very low sulphur fuel oil, LSHFO= Low sulphur Heavy Fuel Oil, MGO= Marine Gas Oil; H: Hazard statement, 2: Physical hazard, 3: Health hazard, 4: Environmental hazard. Source: Authors' own compilation

This categorisation clearly shows that methanol, similar to the established fuel oils, is toxic to humans (by oral ingestion and skin contact). In contrast to fuel oils and ammonia, it is not toxic to aquatic organisms and has no long-lasting effects on them. Gases like hydrogen or natural gas don't show toxic effects according to the GHS statements.

Risks from leakages

According to the Standard European Behaviour Classification (HNS-MS, 2021³⁵) methanol is classified as a "dissolver evaporator". When methanol is spilled to the marine environment, it forms two phases: a non-aqueous liquid phase on the water surface and a vapor phase in the air above.

Methanol has a low viscosity. After spilling a non-aqueous liquid layer of methanol is immediately formed. Since it is highly soluble and completely miscible with water, it disperses rapidly in the water (Kass et al. 2021). Most of the spilled methanol dissolves in the surrounding water.

As methanol is very volatile, a highly flammable vapor phase forms relatively quickly above the nonaqueous liquid surface phase. Methanol has a high diffusivity in air and therefore spreads quickly. In air, methanol is photo-oxidized with a half-life-rate of 3 to 30 days.

Due to its high diffusivity and rapid dispersion in water, methanol is considered unlikely to accumulate on the water surface. Machiele (1989) showed in computer simulations that a release of 10,000 tons of methanol at sea would reach a concentration of 0.36 % within 1 hour of release.

Conclusions on toxicity and risks

Methanol is easily absorbed by inhalation, ingestion or skin contact and it is rapidly distributed in the body. It is highly flammable und acutely toxic to humans and mammals. Methanol poisoning can cause irreversible damage to nerves, especially the typical damage to the optic nerve caused by methanol can lead to blindness. However, methanol is unlikely to be ingested in the normal handling of a fuel, so this risk of poisoning is considered to be very low. In contrast to the toxicity to humans, methanol is less toxic to aquatic organisms (fish, invertebrates, algae and microorganisms).

If methanol is spilled into sea water most of it will disperse rapidly in the water because of the high solubility. Depending on the temperature some of the methanol will form a vapor phase above the water, which is also dispersed quickly. It is fully biodegradable with no potential to bioaccumulate. This makes methanol the fuel with the lowest toxicity and the lowest hazard compared to diesel, heavy fuel oil or ammonia.

4.2 GHG emissions and air pollutants

The well-to-wake (WtW) climate impact of e-methanol mainly depends on the well-to-tank (WtT) **GHG emissions** during the production and transport of the fuel. Tank-to-wake (TtW) GHG emissions of e-methanol are the same as from fossil methanol because they are chemically the same. The combustion of e-methanol (or its use in a fuel cell) still leads to CO_2 emissions but these are compensated by negative emissions WtT, provided that e-methanol is produced only using renewable electricity. If transport and distribution are carried out with zero-emission vehicles, for example with an e-methanol tanker using its own cargo as fuel, the WtW GHG emissions are virtually zero. As long as the electricity used and the CO_2 source are not renewable and the transport of fuel

³⁵ See <u>https://www.hns-ms.eu/result/72</u>, last accessed 10.02.2023.

is not decarbonised, GHG emissions can occur in the WtW emissions profile. For example, methanol is today mainly produced with natural (fossil) gas (section 2.1 and 2.2). This so-called grey methanol has similar or even higher WtT GHG emissions than MGO depending on the assumptions and source considered (IRENA; Methanol Institute 2021; MMKMC 2022a; Harris et al. 2022). For example, the proposal on the FuelEU Maritime provides an emission factor (WtT) of 14.4 gCO₂eq/MJ for MGO and of 31.3 gCO2eq/MJ for methanol from natural gas (EC 2021c). TtW GHG emissions do not differ for fossil and e-methanol. However, synthetic fuels like e-methanol burn much cleaner than fossil fuels resulting in lower air pollutant emissions (see below). Fossil methanol is therefore not a climate change mitigation option for the shipping sector. As most methanol-fuelled ships will be equipped with DF engines, ship operators could also revert to bunkering MGO if e-methanol is not available.

Further, methanol combustion produces NO_x , but emissions are 25 % lower than from HFO or MGO. If an exhaust gas recirculation (EGR) system or exhaust gas aftertreatment system (selective catalytic reduction (SCR)) is used, NO_x emissions can be lowered by 80 % (DNV 2022a; LR; UMAS 2019). The use of the latter systems or the injection of water (which lowers the combustion temperature) reduces NO_x emissions to levels compliant with IMO regulation Tier III limits (DNV 2022a; MAN 2021).

Generally, **SO**_x **emissions** are generated through the combustion of sulphur-containing fuels or lubricant oils. **Particulate matter** (PM) emissions (which typically encompass black carbon) are a result of incomplete combustion of fuels and lubricant oils and to a large degree determined by the sulphur and ash content of the fuel. E-Methanol is sulphur-free, but SO_x and PM emissions might occur through the use of a pilot fuel like MGO or HFO and/or the lubricating oil (Aakko-Saksa et al. 2023). However, the amounts are negligible with a reduction of 95 % to 98 % and over 90 % of SO_x and PM respectively compared to HFO (DNV 2022a; MAN 2021). PM emissions can be further reduced by modifying the engine and exhaust aftertreatment technologies.

Formaldehyde (CH₂O) emissions can also occur in the exhaust gas from marine engines and represent a significant risk to human health given its carcinogenic properties. According to Aakko-Saksa et al. (2023), CH₂O emissions result from the incomplete combustion of a carbon-containing fuel. These emissions generally vary depending upon different variables, such as the engine and the fuel used. The following values from literature have been compiled by Aakko-Saksa et al. (2023):³⁶

- Medium speed diesel marine engines using HFO or distillate fuels (MGO) reported average emission factors for CH₂O ranging from 0.017–0.048 g/kWh.
- For a DF natural gas (LNG) engine, an average emission factor for HCHO of 0.189 g/kWh was reported.
- For a DF methanol engine, the CH₂O emissions reported have been negligible (0.00049 g/kWh) and also low for small alcohol diesel HSD engines using methanol additised with an ignition improver (0.004–0.014 g/kWh).

In contrast, Güdden et al. (2021) came to a very different conclusion regarding the significance of CH_2O emissions associated with the performance of a high speed marine engine converted from a diesel to a methanol combustion system. The experiment revealed comparably high formaldehyde emissions (~1 g/kWh). Hence, Güdden et al. (2021) suggest that the use of an oxidation catalyst should be obligatory in the future and that the additional effort required should be "manageable" as the catalyst technology required for the reduction of formaldehyde is not as sophisticated as that for

³⁶ The dataset on average emission factors cited in the bullet points below are for a marine engine size of over 1 MW and an engine load of over 40 %.

natural gas engines due to the stability of the methane molecule. CIMAC (2014) and Verhelst et al. (2019) also suggest already available oxidation catalysts to reduce CH_2O emissions from marine engines. The number of studies on formaldehyde emissions from marine methanol engines is limited. Therefore, further research will be required to comprehensively determine CH_2O emission levels from different engines, the associated level of health risks posed by the use of methanol as a marine fuel and the need for mitigating actions. The conclusions from the two studies cited above may reflect the fact that they focus on different engine types and sizes, but further comparison is beyond the scope of this study.

Table 6 provides an overview of the changes to GHG emissions and air pollutants of e-methanol compared to HFO. Except for the uncertainties around CH_2O , methanol has a lower emissions impact.

Table 6:	Qualitative impact of e-methanol compared to HFO							
Emissions	Without exhaust gas aftertreatment	With exhaust gas aftertreatment						
GHG	++	++						
NOx	+	++						
SOx	++	++						
PM	+	+ to ++						
CH ₂ O	?	+						

Note: A "+" or "++" indicates the improvement of this negative environmental impact by using e-methanol compared to HFO. Source: Own compilation based on Aakko-Saksa et al. (2023), MAN (2021), DNV (2022a), LR; UMAS (2019)

Additionally, to the fuel itself, lubricant oils (or lube oils) and fuel additives could also have an impact on the emissions from ICE. Fuel additives are not commonly used in shipping today according to industry experts. However, it could be that fuel additives might be used to improve the combustion of future alternative fuels. This depends though on the engine type. Dual fuel methanol engines, like current marine engines, do not require fuel additives. Lubricant oils are used in marine engines for different purposes, such as lubricating and cleaning the engine, and protecting the engine from corrosion. In the past, lubricant oils were also important for protecting the engine from sulphuric acid due to the high sulphur content in marine fuels. As the characteristics of marine fuels are changing with the new sulphur content regulation of the IMO, the composition and purpose of lubricant oils also changes. With engines running on alternative fuels like e-methanol, lubricant oils will also be important in future to keep the machinery intact. Besides this purpose, the focus will shift from protection against sulphuric acid (e.g. methanol is sulphur-free) to improving the combustion characteristics and keeping the cylinders clean (Chevron 2022). Lubricant oils are comprised of a base oil for lubrication and additives. Base oils can be made out of fossil/mineral oil, synthetic oils or vegetable oils (the latter having only a small share in the market)³⁷. Additives are inorganic or organic compounds dissolved in the oil which are used to enhance existing or suppress undesirable base oil properties (e.g. thermally stabilising the lubricant, corrosion protection), and/or add new properties like detergents (primarily based on calcium and magnesium chemistry³⁸). Different lubricant oils are

³⁷ Machinery Lubrication - Understanding the differences between base oil formulations: <u>https://www.machinerylubrication.com/Read/30730/base-oil-formulations</u>.

³⁸ Machinery Lubrication - Lubricant Additives - A Practical Guide: <u>https://www.machinerylubrication.com/Read/31107/oil-lubricant-</u>

used depending on the engine type and fuel (Chevron 2022). Lubricant oils can lead to emissions, for example in the case of cylinder lube oils which are directly injected in the combustion chamber in large 2-stroke engines. These emissions are PM and GHG, like CO₂, if the lubricant contains fossil fuels/components. PM emissions could be decreased by using exhaust gas aftertreatment systems like particulate filters (Chevron 2022). The level of emissions is very small though because the amount of lubricant oil used is small compared to the fuel consumed. The amount of lubricant oil used varies depending on the engine but is in the order of 1 g per kWh of lubricant oil in an engine with 160 g per kWh fuel oil consumption. However, as fuels become cleaner and eventually carbon-neutral, the relative contribution of lubricant oils to exhaust gas emissions will increase. Already today, lubricant oils exist which are based on a renewable or synthetic substance.³⁹ Thus, similar to pilot fuels (section 3.1), lubricant oils can also be renewable in the long term. It is hence important that, alongside with marine fuels, lubricant oils are decarbonised and produced in a more sustainable manner in the long run.

Fuel cells can generally provide lower GHG emission and air pollutant levels compared to ICE on a TtW basis. As described in section 3, methanol can either be used directly in a methanol fuel cell without the reforming step or as a hydrogen carrier as input to a PEMFC or SOFC. In both cases, CO_2 emissions are released which are ideally compensated by the extraction of CO_2 WtT as described above (Tronstad et al. 2017). Air pollutants, such as SO_x, particulate matter and NO_x, are not expected for hydrogen fuel cells and direct methanol fuel cells (Vries 2019; DNV GL 2018). NO_x can occur in high-temperature PEMFC or SOFC (Tronstad et al. 2017).

5 Advantages of and limitations to methanol use in shipping

While it is clear that alternative, carbon-neutral fuels will be the main lever to decarbonise shipping, it is still uncertain which fuel will be most suitable for a broad application in the sector (DNV GL 2021). This section summarises the information from the previous chapters to discusses the advantages of methanol as a marine fuel but also its limitations. Comparisons with other fuels are also drawn.

If e-methanol is produced with renewable energy and a sustainable source of CO_2 , it can contribute to reducing GHG emissions from shipping up to almost zero. From a well-to-wake perspective, any combustion emissions onboard would be compensated by the CO_2 extracted from air or sustainable biomass in the production process. Compared to other fuels like ammonia, the production process of methanol has a lower energy efficiency (section 2.1). Hence, methanol has a higher primary energy consumption compared to other RFNBOs such as hydrogen or ammonia. The production of e-methanol requires the upscaling of green hydrogen production and the nascent DAC technology as biogenic CO_2 will remain limited in the face of a potentially large demand for methanol (section 2.2). Given that the additional demand for methanol by the shipping sector would need to be met by new production facilities, it would be a prerequisite for the decarbonisation of shipping that these additional amounts of methanol are e- or bio-methanol. Shipping companies like Maersk have already taken steps in this direction by securing e- or bio-methanol from dedicated production plants (section 2.2). However, it is likely that methanol production based on fossil fuels (grey methanol) would be expanded if demand increases from shipping (and potentially from other sectors).

additives#:~:text=Detergents%20are%20primarily%20used%20in,of%20calcium%20and%20magnesium %20chemistry.

³⁹ For example, SinNova: <u>https://novvi.com/products/synnova/</u>.

Incentives like the Alternative Fuels Infrastructure Regulation (AFIR) to steer investments in new methanol production plants towards green methanol production are therefore needed. Additionally, as most methanol-fuelled vessels will be equipped with DF engines (and thus two tank systems), vessels could always revert to marine diesel (instead of grey methanol) in case e- or bio-methanol is not available in a bunkering port. At least for the short and medium term, e-methanol will be much more expensive than fossil fuels and also more costly than e-ammonia (section 2.2). From the fuel production point of view, e-methanol is thus less advantageous than, for example, e-ammonia or e-hydrogen.

Considering the fuel characteristics (section 3.1), methanol has some advantages over other RFNBOs. Methanol is easier to store and handle than hydrogen, ammonia and liquefied methane because it is liquid at ambient temperatures and less toxic than ammonia. Storage facilities for fossil marine fuels can be more easily converted to methanol storage with just minor modifications than to other alternative fuels (section 3.3).

However, methanol is toxic to humans (by oral ingestion and skin contact), similar to the established marine fuels. In contrast to fuel oils and ammonia, it is not toxic to aquatic organisms and has no long-lasting effects on them. Gases like hydrogen or natural gas do not show toxic effects, too. In the case of spillages, methanol dissolves very quickly in the sea water and as a vapour into the air (section 4.1).

Methanol has a head start, compared to ammonia and hydrogen, as (interim) safety rules for using methanol as a fuel (and not only as a cargo) are already in place and as a small fleet of ships is already operating on methanol safely (section 3.1).

Further, methanol engines for deep-sea shipping are commercialized whereas ammonia and hydrogen engines are still being developed. Retrofits are and will be available for a variety of alternative fuels. The effort or complexity of a retrofit is rather determined by the onboard fuel supply system than by the changes to the engine (section 3.1). The retrofitting of the fuel supply system is in turn dependent on the fuel characteristics which influence storage conditions, energy content etc. Therefore, methanol has with its slightly higher energy density and easier storage conditions has an advantage over ammonia and other liquified gas. Besides other environmental risks like toxicity, the reduction of GHG emissions and air pollutants is important for a real climate and environmental benefit of alternative marine fuels. As for all RFNBOs, the supply of green hydrogen will be essential. A renewable CO₂ source (and a thorough certification system) will be needed in order for e-methanol to fulfil its full potential as a carbon-neutral fuel. Similar to other RFNBOs, the use of e-methanol will also substantially reduce emissions of air pollutants.

Table 7 provides an overview of a qualitative comparison between e-methanol and other fuels. The comparison assumes the use in ICE from a well-to-wake perspective. The comparison is done horizontally across fuels. The higher the given number, the better the performance of the fuel. The table encompasses criteria elaborated in this and previous sections. The infrastructure criterium considers not only the existence of current infrastructure (production plants, marine bunkering infrastructure) but also the ability to convert existing HFO/MGO infrastructure. The technology readiness level (TRL) and retrofit criterium considers the maturity of the fuel production pathways (including, for example, DAC), the availability of marine engines and retrofits.

Table 7:Comparison of RFNBOs with the status quo of fossil HFO/MGO based on
key criteria

Criterium	E-Methanol	Hydrogen	E-Ammonia	HFO
GHG reduction potential (lifecycle)	5	5	4*	1
Air pollutants (incl. exhaust gas aftertreatment)	4	5	5	1
Aquatic ecotoxicity	5	5	2	1
Human toxicity	3	5	2	3
Flammability	2	1	2	5
Explosion risks	5	2	4	5
Infrastructure (plants, bunkering)	4	1	3	5
TRL production/engine, retrofits	3	1	2	5

Notes: Ranking: 1= high risk/ low performance to 5=low risk/ high performance, assuming fuel use in ICE with exhaust gas aftertreatment system; *uncertainty about N_2O emissions, TRL=technology readiness level. Source: Authors' own compilation

Compared to its use in ICE, the use of methanol in fuel cells will be less relevant, at least in the short to medium term. Pure hydrogen fuel cells could play a role in certain shipping sectors, like short-sea shipping or cruise ships, with hybrid systems as a likely entry point of fuel cells to the market. Further, a decrease in cost and an increase in lifetime would be needed for a wider application of methanol fuel cell in deep-sea shipping (section 3.1).

The electrification of ships with batteries as the main source of energy has clear environmental advantages: zero GHG emissions and air pollutants as well as most efficient use of primary energy. However, the applicability of batteries for deep-sea shipping is even more limited than for fuel cells. Weight constraints and energy density limits of battery-electric systems reduce space for cargo and voyage lengths, making such systems unfavourable for deep-sea shipping. For short-sea shipping, ferries and other RoRo ships and cruise vessels, the use of batteries is already used or in test and presents a valid alternative to fossil fuels.

Overall, there are many aspects to consider with regard to the suitability of a future marine fuel. It is clear that the future fuel mix will be more diverse than the current 97 % dominance of petrol-based fuels across all segments of the shipping industry. While e-methanol and e-ammonia are discussed as promising candidates for the decarbonisation of the shipping sector (e.g. DNV GL 2020), both fuels have advantages and disadvantages. Considering the urgency of the climate crisis and thus the need to reduce GHG emissions, the years up to 2030 will likely be decisive. From a pure cost perspective, ammonia-fuelled vessels may be cheaper in the long run (although bunkering infrastructure costs are uncertain). However, methanol is a technically mature option today with less uncertainty about the tank-to-wake GHG emissions.

To be a lever to decarbonise shipping, the production as well as the use of e-methanol needs to be incentivised. High production costs, lacking bunkering volumes around the world, and the necessity of retrofits present barriers to the uptake of methanol in shipping. Recent legislative proposals at the EU level could be means to overcome these barriers. While short-term allowance prices in the upcoming maritime EU Emission Trading System (ETS) will not be high enough to fully bridge the price gap between fossil marine fuels and e-methanol from the start, the maritime ETS is still an incentive to reduce emissions (EC 2021b). E-methanol is an option to accommodate the

requirements of the ETS and will become more attractive with increasing ETS prices in the medium to long term.

The FuelEU Maritime Initiative will have a more profound effect on the fuel mix as it imposes a GHG emission standard on the energy used onboard ships, with an increasing stringency up to 2050 (EC 2021c). The reduction targets in the original proposal by the European Commission would allow fossil fuels, like LNG, to be compliant for a long time despite the need to trigger the transition to non-fossil fuels as soon as possible (EC 2021c). More ambitious GHG reduction targets and the introduction of an RFNBO quota would provide higher incentives for shipowners to switch to RFNBOs, like e-methanol, and make the necessary investments. An ambitious outcome of the negotiations will determine the development in EU-related shipping, especially due to a potential RFNBO quota.

One option to improve the availability of RFNBOs is to revise the requirements of the AFIR in order to ensure RFNBO bunkering infrastructure in European ports. Further, the revision of the EU ETS foresees the use of ETS revenues in the Innovation Fund for Carbon Contracts for Difference (CCfDs). To close the price gap between fossil fuels and RFNBOs, like e-methanol, CCfDs could be used to ensure the production of e-methanol in the EU and its supply to the maritime sector via offtake agreements (Clark et al. 2021). Discussions at IMO are progressing on implementing a market-based policy in combination with a fuel standard on the global level. All these policy instruments can incentivise RFNBOs as long as they consider GHG emissions from a well-to-wake perspective.

6 Conclusions

This study assesses whether the potential benefits and risks of e-methanol are sufficiently reflected in the current discussion about future marine fuels and whether methanol is preferable to current fossil marine fuels and other RFNBOs.

There are many aspects to consider with regard to the suitability of a future marine fuel. E-methanol and e-ammonia are discussed as promising candidates for the decarbonisation of deep-sea shipping, and both fuels have advantages and disadvantages.

The characteristics of methanol make it easier to handle and combust than, for example, ammonia and hydrogen. E-methanol can offer reductions in GHG and air pollutant emissions. While further research on the level of formaldehyde emissions from marine engines is necessary, those emissions can likely be reduced with exhaust gas aftertreatment systems. To be carbon-neutral, it is of upmost importance that the fuel is produced from renewable energy and a sustainable CO_2 source, ideally DAC. Carbon-free RFNBOs (like e-ammonia) have the advantage of not needing CO_2 as an input and of therefore higher conversion efficiency in the production process. Green hydrogen production and the DAC technology need to be scaled up significantly in order to provide substantial amounts of e-methanol for shipping.

Globally, there is currently sufficient supply to meet the demand for methanol. However, this methanol production is primarily based upon the use of natural gas. China, which is the biggest producer of methanol, still even uses coal. To meet the future demand for methanol and to pursue an ambitious pathway of decarbonisation, it will be necessary to considerably scale up the production of e-methanol. This is unlikely to happen in sufficient volumes before 2030. Therefore a higher uptake rate in the 20-year period up to 2050 will be required to ensure maritime transport can be decarbonised.

In comparison with other fuels, methanol's future will not only be decided by the upscaling of the production but also by its availability in different ports and by future fuel cost.

The storage of methanol at ports for use as a marine fuel is already taking place, albeit at low volumes, to supply the current global demand mainly from initial pilot projects. However, the potential for storage has already been quantified globally at approx. 25 Mt with further considerable potential to scale up this capacity by converting the existing storage infrastructure for petroleum-based products if there is sufficient demand. Projections for demand could exceed 200 Mt annually based on ambitious pathways to decarbonising maritime transport by 2050. This would require additional investment in new storage capacity for methanol if such a demand by the shipping sector were to be realised as envisaged by ambitious decarbonisation pathways. Given the flexibility of methanol as a product, it is widely regarded as a storage medium that has a potential to help in facilitating the wider energy transition. For example, methanol can be converted back to electricity via the use of a direct methanol fuel cell, used as a gasoline substitute and, if upgraded to dimethyl ether (DME), also as a diesel replacement and used as feedstock in the chemical industry (Bos 2019). Each end use of e-methanol though has to be carefully compared with other energy storage options (e.g. direct use of green hydrogen) given the energy losses and costs for the respective production pathways.

Some long-term cost scenarios indicate that ammonia-fuelled vessels will be less expensive than methanol-fuelled vessels. Fuel cost decreases will be subject to upscaling of DAC and green hydrogen as well as decreases in renewable electricity prices. However, the acceptance of ammonia's toxicity and the implementation of international safety guidelines could influence the preference of shipowners for one fuel or the other.

Methanol is toxic to humans, especially when ingested orally, which however hardly happens during normal handling of the fuel. For aquatic organisms, however, it is hardly toxic. In case of spillages, methanol dissolves very quickly in the sea water. Vapours that get into the air are also dispersed very quickly. Safety guidelines for methanol in the shipping sector are already in place and ships exist that are running on methanol. From an eco-toxicological health and overall risk assessment it seems to be the least dangerous fuel, even compared to today's conventional fuels.

In conclusion, e-methanol has low environmental risks compared to other future fuels (except hydrogen), can offer sufficient energy density for most voyages, is easy to handle, and enables a well-to-wake climate-neutral operation of a ship.

It is clear that the future fuel mix will be more diverse than the current 97 % dominance of petroleumbased fuels across all segments of the shipping market. E-methanol could play an important role in this. Its exact share in the fuel mix will be determined by several factors: upscaling of green methanol production, decrease in renewable electricity and thus fuel cost, and acceptance of ammonia in the maritime sector. The years up to around 2030 will likely be key as this decade will be decisive for where investments will be made. Policy makers should therefore implement the right incentives as soon as possible. On the one hand, it will be important to ensure the supply of e-methanol to the sector. This could include support for investments in green methanol production plants or the use of CCfDs. On the demand side, on the other hand, European policy makers should ensure an ambitious outcome of the Fit-for-55 package, namely the FuelEU Maritime initiative, with strong incentives for RFNBOs including a RFNBO sub-quota.

List of References

- Aakko-Saksa, P. T.; Lehtoranta, K.; Kuittinen, N.; Järvinen, A.; Jalkanen, J.-P.; Johnson, K.; Jung, H.; Ntziachristos, L.; Gagné, S.; Takahashi, C.; Karjalainen, P.; Rönkkö, T.; Timonen, H. (2023): Reduction in greenhouse gas and other emissions from ship engines: Current trends and future options. In: *Progress in Energy and Combustion Science* 94. Online available at https://doi.org/10.1016/j.pecs.2022.101055.
- Argus Methanol (2022): Market Snapshot. Argus Methanol. Online available at https://www.argusmedia.com/-/media/Files/samplereports/20220729methanol.ashx?la=en&hash=FDAA09E0CEEF4BC55B2AE401739F258E4C5 6AB97.
- BASF AG (1980a): Bestimmung der akuten Inhalationstoxizität LC50 von Methanol (Merck min. 99,8%) als Dampf bei 4stündiger Exposition an Sprague-Dawley-Ratten.
- BASF AG (1980b): Bestimmung der akuten Inhalationstoxizität LC50 von Methanol (Merck min. 99,8%) als Dampf bei 6stündiger Exposition an Sprague-Dawley-Ratten.
- Bos, M. (2019): Storage of renewable electricity in methanol, Technology development for CO2 air capture and conversion to methanol. Online available at https://ris.utwente.nl/ws/portalfiles/portal/118422552/Martin_Bos_Storage_of_renewable_electricity_in_methanol.pdf, last accessed on 10 Feb 2023.
- Brynolf, S.; Taljegard, M.; Grahn, M.; Hansson, J. (2018): Electrofuels for the transport sector: A review of production costs. In: *Renewable and Sustainable Energy Reviews*, pp. 1887–1905.
- Buller, F. and Wood, C. A. (1904): Poisoning by wood alcohol. Cases of death and blindness from columbian spirits and other methylated preparations. In: *JAMA*. Online available at https://www.semanticscholar.org/paper/POISONING-BY-WOOD-ALCOHOL.CASES-OF-DEATH-AND-FROM-Buller-Wood/5fd6ff46e93c2da2fdf1475468fc296021180425.
- Burg, R. von (1994): Methanol. In: *Journal of Applied Toxicology* 14 (4), pp. 309–313. DOI: 10.1002/jat.2550140412.
- CAAEFA (2021): Methanol Fuel in China 2020. China Association of Alcohol and Ether Fuel and Automobiles. Online available at https://www.methanol.org/wp-content/uploads/2020/04/China-Methanol-Fuel-Report-2020_final-1.pdf.
- Cames, M.; Graichen, J.; Kasten, P.; Kühnel, S.; Faber, J.; Nelissen, D.; Scheelhaase, J.; Grimme, W.; Maertens, S. (2023): Climate protection in aviation and maritime transport: Roadmaps for achieving the climate goals (Texte, ###/2023). Umweltbundesamt.
- Cames, M.; Wissner, N.; Sutter, J. (2021): Ammonia as a marine fuel. Oeko-Institut. Berlin. Online available at https://en.nabu.de/imperia/md/content/nabude/verkehr/210622-nabu-study-ammonia-marine-fuel.pdf, last accessed on 14 Sep 2021.

- Chevron (2022): The future of marine two-stroke engine lubrication. Online available at https://www.chevronmarineproducts.com/en_mp/home/resources/Chevron-Marine-Lubricants-white-paper-assesses-future-cylinder-oil-needs.html, last accessed on 10 Feb 2023.
- CIMAC International Council on Combustion Engines (2014): Methane and Formaldehyde Emissions of Gas Engines, CIMAC Position Paper. Online available at https://www.cimac.com/publications/publications350/cimac-wg17-methane-and-formaldehydeemissions-of-gas-engines.html, last accessed on 3 Feb 2023.
- Clark, A.; Ives, M.; Fay, B.; Lambe, R.; Schiele, J.; Larrson, L.; Krejcie, J.; Tillmann-Morris, Leah, Barbrook-Johnson, Peter; Hepburn, C. (2021): Zero-Emissions Shipping: Contracts-fordifference as incentives for the decarbonisation of international shipping. SSEE; Smith School; Unvisersity of Oxford and Pinsent Masons (ed.). Online available at https://www.smithschool.ox.ac.uk/sites/default/files/2022-02/zero-emissions-shipping.pdf, last accessed on 26 Jul 2022.
- Cooper, J. R. and Felig, P. (1961): The biochemistry of methanol poisoning: II. Metabolic acidosis in the monkey. In: *Toxicology and Applied Pharmacology* 3 (2), pp. 202–209. DOI: 10.1016/S0041-008X(61)80006-9.
- DNV (2022a): Alternative Fuels for Containerships. Online available at https://www.dnv.com/maritime/publications/alternative-fuels-for-containerships-download.html, last accessed on 13 Dec 2022.
- DNV (2022b): Alternative ship fuels status and outlook, DNV Webinar 28.04.2022.
- DNV (2022c): Maritime Forecast to 2050, Energy Transition Outlook 2022. Online available at https://www.dnv.com/maritime/publications/maritime-forecast-2022/index.html, last accessed on 13 Sep 2022.
- DNV GL (2016): Methanol as marine fuel, Environmental benefits, technology readiness, and economic feasibility. Online available at http://www.imo.org/fr/OurWork/Environment/PollutionPrevention/AirPollution/Documents/Report Methanol 21.01.2016.pdf, last accessed on 12 Sep 2020.
- DNV GL (2018): Assessment of selected alternative fuels and technologies.
- DNV GL (2019): Maritime Forecast to 2050, Energy Transition Outlook 2019. Online available at https://eto.dnv.com/2019/Maritime/forecast, last accessed on 17 Mar 2021.
- DNV GL (2020): Maritime Forecast to 2050, Energy Transition Outlook 2020. Online available at https://brandcentral.dnvgl.com/dloriginal/gallery/10651/files/original/b3002f4841aa463abdd4a9b 469b1ed08.pdf?f=DNVGL_2020_Maritime_Forecast_to_2050_WEB.pdf, last accessed on 24 Oct 2020.
- DNV GL (2021): Maritime Forecast to 2050, Energy Transition Outlook 2021. Online available at https://eto.dnv.com/2021/maritime-forecast-2050/about, last accessed on 9 Aug 2022.
- EC European Commission (2021a): 2020 Annual Report on CO2 Emissions from Maritime Transport (SWD(2021) 228 final). Brussels. Online available at

https://ec.europa.eu/clima/system/files/2021-08/swd_2021_228_en.pdf, last accessed on 7 Mar 2021.

- EC European Commission (2021b): Proposal for a Directive of the European Parliament and the Council amending Directive 2003/87/EC establishing a system for greenhouse gas emission allowance trading within the Union, Decision (EU) 2015/1814 concerning the establishment and operation of a market stability reserve for the Union greenhouse gas emission trading scheme and Regulation (EU) 2015/757 (COM(2021) 551 final). Online available at https://ec.europa.eu/info/sites/default/files/revision-eu-ets_with-annex_en_0.pdf, last accessed on 3 Mar 2022.
- EC European Commission (2021c): Proposal for a Regulation of the European Parliament and of the Council on the use of renewable and low-carbon fuels in maritime transport and amending Directive 2009/16/EC, COM(2021) 562 final. Online available at https://eur-lex.europa.eu/legalcontent/EN/TXT/?uri=CELEX:52021PC0562, last accessed on 13 Dec 2022.
- EC European Commission (ed.) (2021d): Assessment of impacts from accelerating the uptake of sustainable alternative fuels in maritime transport, Final Report. CE Delft; Ecorys. Online available at https://cedelft.eu/wpcontent/uploads/sites/2/2021/11/CE_Delft_Ecorys_200249_Final_Report.pdf, last accessed on 11 Apr 2022.

Fahnestock, J. and Bingham, C. (2021): Mapping of zero emission pilot and demonstration projects, Insight brief prepared for the Getting to Zero Coalition (Second edition). Global Maritime Forum. Online available at https://www.globalmaritimeforum.org/content/2021/03/Mapping-of-Zero-Emission-Pilots-and-Demonstration-Projects-Second-edition.pdf, last accessed on 19 Mar 2021.

- Fastwater (2021): Report on methanol supply, bunkering guidelines, and infrastructure. Online available at https://www.fastwater.eu/images/fastwater/news/FASTWATER_D71.pdf.
- Frederick, L. J.; Schulte, P. A.; Apol, A. (1984): Investigation and control of occupational hazards associated with the use of spirit duplicators. In: *American Industrial Hygiene Association journal* 45 (1), pp. 51–55. DOI: 10.1080/15298668491399361.
- Fricaudet, M.; Taylor, J.; Smith, T.; Rehmatulla, N. (2022): Exploring methods for understanding stranded value: case study on LNG-capable ships. UCL. Online available at https://safety4sea.com/wp-content/uploads/2022/09/UCL-Stranded-value-case-study-on-LNGcapable-ships-2022_09.pdf, last accessed on 20 Oct 2022.
- GESAMP (2019): GESAMP Hazard Evaluation Procedure for Chemicals Carried by Ships, 2019, Joint Group of Experts on the Scientific Aspects of Marine Environmental Protection, Rep. Stud. GESAMP No. 102. Online available at http://www.gesamp.org/site/assets/files/2133/rs102e.pdf, last accessed on 10 Feb 2023.
- Gilger, A. P. and Potts, A. M. (1955): Studies on the visual toxicity of methanol. V. The role of acidosis in experimental methanol poisoning. In: *American journal of ophthalmology* 39 (2 Pt 2). DOI: 10.1016/0002-9394(55)90010-6.

- Goeppert, A.; Czaun, M.; Jones, J.-P.; Surya Prakash, G. K.; Olah, G. A. (2014): Recycling of carbon dioxide to methanol and derived products - closing the loop. In: *Chemical Society reviews* 43 (23), pp. 7995–8048. DOI: 10.1039/c4cs00122b.
- Greim, H. (2001): Methanol. MAK Value Documentation, 1999, In: Occupational Toxicants, vol 16. Wiley-VCH, Weinheim. DOI: 10.1002/3527600418.mb6756e0016.
- Güdden, A.; Pischinger, S.; Geiger, J.; Heuser, B.; Müther, M. (2021): An experimental study on methanol as a fuel in large bore high speed engine applications Port fuel injected spark ignited combustion. In: *Fuel* 303. Online available at https://doi.org/10.1016/j.fuel.2021.121292.
- Hank, C.; Sternberg, A.; Köppel, N.; Holst, M.; Smolinka, T.; Schaadt, A.; Hebling, C.; Henning, H.-M. (2020): Energy efficiency and economic assessment of imported energy carriers based on renewable electricity. In: *Sustainable Energy Fuels* 4 (5), pp. 2256–2273. DOI: 10.1039/D0SE00067A.
- Harris, R.; Conclan, M.; Simon, J. (2022): Summary of LNG and Methanol Marine Fuel Options. IGP Energy. Online available at https://igpmethanol.com/igpmwp/wpcontent/uploads/2022/03/Summary-of-LNG-and-Methanol-Marine-Fuel-Options-03-11-2022.pdf, last accessed on 3 Mar 2023.
- Heinemann, C.; Kasten, P.; Bauknecht, D.; Bracker, J.; Bürger, V.; Emele, L.; Hesse, T.; Kühnel, S.; Seebach, D.; Timpe, C. (2019): Die Bedeutung strombasierter Stoffe für den Klimaschutz in Deutschland, Zusammenfassung und Einordnung des Wissenstands zur Herstellung und Nutzung strombasierter Energieträger und Grundstoffe. Oeko-Institut. Online available at https://www.oeko.de/fileadmin/oekodoc/PtX-Hintergrundpapier.pdf, last accessed on 15 Mar 2020.
- Horton, G.; Finney, H.; Fischer, S.; Sikora, I.; McQuillen, J.; Ash, N.; Shakeel, H. (2022): Technological, operational and energy pathways for maritime transport to reduce emissions towards 2050, Final report for OGCI/Concawe. Ricardo Energy & Environment. Online available at https://www.concawe.eu/wp-content/uploads/Technological-Operational-and-Energy-Pathways-for-Maritime-Transport-to-Reduce-Emissions-Towards-2050.pdf, last accessed on 20 May 2022.
- Horvath, S.; Fasihi, M.; Breyer, C. (2018): Techno-economic analysis of a decarbonized shipping sector_Technology suggestions for a fleet in 2030 and 2040, (2018). In: *Energy Conversion and Management* 164, pp. 230–241. DOI: 10.1016/j.enconman.2018.02.098.
- IMO International Maritime Organization (2020): Fourth IMO Greenhouse Gas Study 2020, Reduction of GHG Emissions from Ships (MEPC 75/7/15). London. Online available at https://docs.imo.org/Shared/Download.aspx?did=125134, last accessed on 24 Oct 2020.
- IMO International Maritime Organization (2021): Energy efficiency of ships, Report of fuel oil consumption data submitted to the IMO Ship Fuel Oil Consumption Database in GISIS (Reporting year: 2020). Online available at https://wwwcdn.imo.org/localresources/en/OurWork/Environment/Documents/Air%20pollution/M EPC%2077-6-1%20-

%202020%20report%20of%20fuel%20oil%20consumption%20data%20submitted%20to%20the %20IMO%20Ship%20Fuel%20Oil%20Consumption%20Database%20in%20GISIS.pdf.

- IRENA International Renewable Energy Agency; Methanol Institute (2021): Innovation outlook, Renewable Methanol. Online available at https://www.irena.org/publications/2021/Jan/Innovation-Outlook-Renewable-Methanol, last accessed on 3 Mar 2023.
- Kajaste, R.; Hurme, M.; Oinas, P. (2018): Methanol-Managing greenhouse gas emissions in the production chain by optimizing the resource base. In: *AIMS Energy* 6 (6), pp. 1074–1102. Online available at :10.3934/energy.2018.6.1074.
- Kass, M. D.; Sluder, C. S.; Kaul, B. C. (2021): ORNL/SPR-2021/1837 Spill Behavior, Detection, and Mitigation for Emerging Nontraditional Marine Fuels, Oak Ridge: Oak Ridge National Laboratory. Online available at https://www.maritime.dot.gov/sites/marad.dot.gov/files/2021-05/ORNLAIt_Fuels_Spill_Study_Report_19Mar2021.pdf, last accessed on 10 Feb 2023.
- Kasten; Peter; Heinemann; Christoph (2019): Not to be taken for granted: climate protection and sustainability through PtX, Discussion of requirements for and first approaches to developing verification criteria for a climate-friendly and sustainable production of PtX. Impulse paper on behalf of BUND as part of the Copernicus project "P2X". Oeko-Institut. Online available at https://www.oeko.de/fileadmin/oekodoc/Impulse_paper_criteria_for_e-fuel_production.pdf, last accessed on 15 Feb 2023.
- Kawai, T.; Yasugi, T.; Mizunuma, K.; Horiguchi, S.; Hirase, Y.; Uchida, Y.; Ikeda, M. (1991): Methanol in urine as a biological indicator of occupational exposure to methanol vapor. In: *Int. Arch Occup Environ Heath* 63 (5), pp. 311–318. DOI: 10.1007/BF00381580.
- Kirstein, L.; Halim, R.; Merk, O. (2018): Decarbonising Maritime Transport: Pathways to zerocarbon shipping by 2035. International Transport Forum. Online available at https://www.oecdilibrary.org/transport/decarbonising-maritime-transport_b1a7632c-en, last accessed on 3 Feb 2023.
- Korberg, A. D.; Brynolf, S.; Grahn, M.; Skov, I. R. (2021): Techno-economic assessment of advanced fuels and propulsion systems in future fossil-free ships. In: *Renewable and Sustainable Energy Reviews* 142, p. 110861. DOI: 10.1016/j.rser.2021.110861.
- KR Korean Register (2020): Forecasting the Alternative Marine Fuel Ammonia. Online available at https://www.krs.co.kr/TECHNICAL_FILE/KR_Forecasting%20the%20Alternative%20Marine%20 Fuel_Ammonia.pdf, last accessed on 20 Feb 2023.
- LR Lloyd's Register; UMAS (2019): Fuel production cost estimates and assumptions, last accessed on 15 Feb 2021.
- LR Lloyd's Register; UMAS (2020): Techno-economic assessment of zero-carbon fuels. Online available at https://www.lr.org/en/insights/global-marine-trends-2030/techno-economic-assessment-of-zero-carbon-fuels/, last accessed on 7 Sep 2022.

Machiele, P. A. (1989): A Perspective on the Flammability, Toxicity, and Environmental Safety Distinctions Between Methanol and Conventional Fuels. US Environmental Protection Agency (ed.). Online available at

https://nepis.epa.gov/Exe/ZyNET.exe/94005L0X.TXT?ZyActionD=ZyDocument&Client=EPA&In dex=1986+Thru+1990&Docs=&Query=&Time=&EndTime=&SearchMethod=1&TocRestrict=n& Toc=&TocEntry=&QField=&QFieldYear=&QFieldMonth=&QFieldDay=&IntQFieldOp=0&ExtQFie IdOp=0&XmlQuery=&File=D%3A%5Czyfiles%5CIndex%20Data%5C86thru90%5CTxt%5C0000 0037%5C94005L0X.txt&User=ANONYMOUS&Password=anonymous&SortMethod=h%7C-&MaximumDocuments=1&FuzzyDegree=0&ImageQuality=r75g8/r75g8/x150y150g16/i425&Dis play=hpfr&DefSeekPage=x&SearchBack=ZyActionL&Back=ZyActionS&BackDesc=Results%20 page&MaximumPages=1&ZyEntry=1&SeekPage=x&ZyPURL, last accessed on 15 Feb 2023.

- MAN MAN Energy Solutions (2019): Engineering the future two-stroke green-ammonia engine. Copenhagen. Online available at https://fathom.world/wpcontent/uploads/2020/05/engineeringthefuturetwostrokegreenammoniaengine1589339239488.p df, last accessed on 3 Mar 2021.
- MAN MAN Energy Solutions (2021): The Methanol-fuelled MAN B&W LGIM Engine, Application, service experience and latest development of the ME-LGIM engine. Online available at https://man-es.com/docs/default-source/document-sync/the-methanol-fuelled-man-b-w-lgim-engine-eng.pdf?sfvrsn=36b925d2_2, last accessed on 15 Dec 2022.
- MAN MAN Energy Solutions (2022): Scalable energy transition Methanol as fuel for large merchant marine vessels, MAN ExpertTalk, Webinar Recording. Online available at https://man-es.com/marine/products/man-b-w-me-lgim?9b498b80-aa1b-4114-ba91-d5880081d645%5B%5D=0, last accessed on 31.02.2023.
- Mao, X.; Rutherford, D.; Osipova, L.; Comer, B. (2020): Refueling assessment of a zero-emission container corridor between China and the United States: Could hydrogen replace fossil fuels?, Working Paper 2020-05. International Council on Clean Transportation. Online available at https://theicct.org/sites/default/files/publications/Zero-emission-container-corridor-hydrogen-3.5.2020.pdf, last accessed on 6 Apr 2021.
- Methanol Institute (2022a): Carbon Footprint of Methanol. Methanol Institute. Online available at https://www.methanol.org/wp-content/uploads/2022/01/CARBON-FOOTPRINT-OF-METHANOL-PAPER_1-31-22.pdf.
- Methanol Institute (2022b): Methanol price and supply/demand. Online available at https://www.methanol.org/methanol-price-supply-demand/, last accessed on 25 Jan 2023.
- Ming, L. and Chen, L. (2021): Methanol as a marine fuel, Availability and Sea Trial Considerations. Maritime Energy & Sustainable Development. Online available at https://www.methanol.org/wpcontent/uploads/2020/04/SG-NTU-methanol-marine-report-Jan-2021-1.pdf, last accessed on 13 Dec 2022.
- MMKMC Maersk Mc-Kinney Møller Center (2021): Position Paper Fuel Options Scenarios. Online available at https://cms.zerocarbonshipping.com/media/uploads/documents/Fuel-Options-Position-Paper_Oct-2021_final.pdf, last accessed on 20 Oct 2022.

- MMKMC Maersk Mc-Kinney Møller Center (2022a): Methanol as a marine fuel Prospects for the shipping industry, Documentation of assumptions for NavigaTE 1.0. Online available at https://cms.zerocarbonshipping.com/media/uploads/documents/Methanol-Documentation-for-Navigate-1.0_2022-06-07-104417_jrhh.pdf, last accessed on 3 Mar 2023.
- MMKMC Maersk Mc-Kinney Møller Center (2022b): Preparing Container Vessels for Conversion to Green Fuels, A technical, environmental, and techno-economic analysis of the impacts of preparation and conversion. Online available at https://safety4sea.com/wpcontent/uploads/2022/09/Center-for-Zero-Shipping-Preparing-Container-Vessels-for-Conversion-to-Green-Fuels-2022 09.pdf, last accessed on 21 Oct 2022.
- Olah, G. A.; Goeppert, A.; Prakash, G. K. S. (2018): Beyond Oil and Gas: The Methanol Economy 3. aktualis. u. erw. Auflage. Weinheim: Wiley-VCH Verlag GmbH & Co. KGaA. Online available at http://nbn-resolving.org/urn:nbn:de:bsz:31-epflicht-1098817.
- Smith, T.; Baresic; Domagoj; Fahnenstock, J.; Galbraith, C.; Perico, C. V.; Rojon, I.; Shaw, A. (2021): A strategy for the transition to zero-emission shipping, An analysis of transition pathways, scenarios, and levers for change. UMAS; Getting to Zero Coalition. Online available at https://www.globalmaritimeforum.org/content/2021/10/A-Strategy-for-the-Transition-to-Zero-Emission-Shipping.pdf, last accessed on 19 Aug 2022.
- Stolz, B.; Held, M.; Georges, G.; Boulouchos, K. (2022): Techno-economic analysis of renewable fuels for ships carrying bulk cargo in Europe. In: *Nat Energy. DOI:* 10.1038/s41560-021-00957-9.
- Tronstad, T.; Åstrand, H. H.; Haugom, G. P.; Langfeldt, L. (2017): Study on the use of fuel cells in shipping. DNV GL. EMSA European Maritime Safety Agency (ed.). Online available at http://safety4sea.com/wp-content/uploads/2017/01/DNV-GL-EMSA-Study-on-the-use-of-Fuel-Cells-in-Shipping-2017_01.pdf, last accessed on 26 Oct 2018.
- UNEP United Nations Environment Programme; WHO World Health Organization; ILO -International Labour Organisation (1997): Methanol - Environmental Health Criteria 196, IPCS, International 2539 Programme on Chemical Safety. In collaboration with Division, E. (92 4 157196 9). Online available at https://wedocs.unep.org/handle/20.500.11822/29474.
- Verhelst, S.; Turner, J. W. G.; Sileghem, L.; Vancoillie, J. (2019): Methanol as a fuel for internal combustion engines. In: *Progress in Energy and Combustion Science* (70). DOI: 10.1016/j.pecs.2018.10.001.
- Vries, N. de (2019): Safe and effective application of ammonia as a marine fuel. Report (thesis), TU Delft, 2019. Online available at https://repository.tudelft.nl/islandora/object/uuid%3Abe8cbe0a-28ec-4bd9-8ad0-648de04649b8, last accessed on 5 Dec 2022.
- Wärtsilä (2022): Wärtsilä 32 methanol the power to reach carbon-neutral, Webinar 23.11.2022. Online available at https://www.wartsila.com/insights/webinar/wartsila-32-methanol-the-powerto-reach-carbon-neutral, last accessed on 31.02.2023.