Marine methanol engines: Technical overview and emissions

Contents

Introduction

The international shipping sector is undergoing a historic transformation to meet the IMO's target of achieving net-zero greenhouse gas emissions by or around 2050, compared to 2008 levels. In addition, the sector must comply with increasingly stringent regulations on sulfur, NO_x, and particulate emissions, while also ensuring fuel diversity and security of supply.

Methanol has emerged as one of the most prominent alternatives to conventional marine diesel and heavy fuel oil. Its growing relevance is due to several factors:

Flexible Production: Methanol can be produced from both fossil and sustainable sources. Conventional fossil-based methanol is typically synthesized from natural gas or coal via steam reforming, while green methanol can be produced from biogenic feedstocks or through Power-to-X processes - where renewable electricity is converted into hydrogen, which subsequently reacts with captured CO_2 to form methanol.

Favorable Emissions Profile: When combusted, methanol emits no sulfur oxides (SOx), extremely low levels of particulates (PM/soot), and - depending on the production pathway - can significantly reduce CO_2 emissions.

Established Logistics and Retrofit Potential: Methanol is already transported, stored, and handled globally. Additionally, engine manufacturers often offer retrofit solutions that allow existing engines to be upgraded for methanol operation, making its adoption more realistic in the short term.

While methanol as a commodity and fossil-based fuel is already available at scale, the production of green methanol - derived from biogenic biomass or Power-to-X technologies - is still under development. Capacity is expected to increase significantly. However, the global price and availability of green methanol remain challenges that will be crucial for the sector's ability to achieve real CO_2 reductions.

It is important to note that methanol has a high auto-ignition temperature and generally cannot ignite on its own in conventional reciprocating engines. For this reason, most modern marine methanol engines use a pilot fuel – a conventional marine diesel fuel - which is injected along with the methanol to initiate combustion. As a result, there will still be minor emissions typically associated with diesel operation.

A key advantage of methanol is that existing ships can, in many cases, be retrofitted for methanol operation. This usually involves replacement or adaptation of fuel systems, pumps, pipes, injectors, and control systems, as well as installation of additional safety equipment. However, it should also be noted that methanol has a lower energy density per unit volume than conventional marine fuels, meaning that larger storage tanks are required onboard to achieve the same operational range.

Methanol presents several challenges as a marine fuel: it is toxic, has a low flash point, and burns with an almost invisible flame. These properties demand special handling, robust detection systems, and enhanced fire safety measures. Materials must be compatible with methanol to prevent corrosion or leakage. Strict safety standards specifically addressing methanol are applied when it is used as a marine fuel.

The outlook for marine methanol engines

Since 2-stroke methanol engines became commercially available in 2021, the orders for ships with these engines have quickly reached a large market share within the segment of ships designed for alternative fuels[1]. According to DNV[2], 395 out of a total of 2000 ships to be powered by alternative fuels on order for delivery before 2030 will be delivered with engines capable of using methanol. The definition of alternative fuels used by DNV also include LNG (1271 ships), LPG (270 ships), hydrogen (40 ships) and ammonia (33 ships).

LNG and LPG powered ships are currently dominating in terms of orders placed for ships powered by alternative fuels. These ships do however not contribute significantly to the CO_2 reductions required to meet the ambitious targets set up by IMO. When it comes to CO_2 reductions, the planned methanol-powered ships offer a more effective solution. However, methanol still faces challenges in shipping due to the limited production of green methanol and a lack of infrastructure for distribution and bunkering in ports. Additionally, the price of green methanol remains higher than that of conventional fuels.

While the large ships are generally designed with 2-stroke propulsion solutions, there is a growing interest in using 4-stroke dual fuel methanol engines for smaller ships such as ferries, service vessels and tugs in short voyage operations.

Overview of 2-Stroke Methanol Engine Technology

The world's first 2-stroke dual fuel engine for methanol, the ME-LGIM (Liquid Gas Injection Methanol), was presented by MAN Energy Solutions (today now known as Everllence) in 2021[3], after 5 years of testing on two commercial ships.

In the ME-LGIM engine, the methanol is injected directly into the combustion chamber late in the compression stroke together with a small amount of pilot oil. This means that air and methanol are not premixed before intake or compression. Combustion therefore takes place as non-premixed (diffusion) combustion, similar to the principle of a conventional diesel engine.

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[1] Alternative fuels are fuels other than conventional marine fuel oils
[2] Numbers from DNV Veracity Alternative Fuel Info, January 2025
[3] Press release by MAN July 27, 2021: World-First Order for Methanol Engine within Container Segment

For LNG-fueled two-stroke engines, Everellence uses a similar injection principle, resulting in very low methane slip and improved emission performance compared to premixed gas admission concepts, where the gas is mixed with air inside the cylinder. Due to these advantages, Everellence has decided to remove the ME-GA (gas admission) engine from its two-stroke engine programme.

The first methanol engine was ordered by Mærsk, to be installed on a 2100 TEU containership which entered service in 2023. Later that year Mærsk ordered 8 additional 18000 TEU container ships also to be powered by methanol.

Since then, Mærsk and several other shipping companies have placed a total of new orders on ships with methanol dual fuel engines. At the beginning of 2025, more than 300 large ships (container ships, oil/chemical tankers, bulk and car carriers) are ordered for delivery before the year 2030[4].

Currently, 2-stroke methanol dual fuel propulsion engines are available from the market leaders, Everllence (ME-LGIM) and WinGD (X-DF-M).

2-stroke dual fuel engines operate with high pressure direct injection of methanol, ignited by pilot injection of fuel oil. Engines based on this principle are designed to substitute up to 95 % of the fuel oil heating value with methanol in dual fuel operating mode.

Overview of 4-stroke methanol engine technology

Wärtsilä was the first company to develop and demonstrate engine technology for methanol. The first major project was the retrofit of the four main engines on Stena Germanica during 2015-2017. I the beginning of 2022, Wärtsilä received its first order on five Wärtsilä 32 methanol engines for a wind installation vessel[5]. Since then, Wärtsilä has developed additional methanol dual fuel engine families, which are available in their engine program.

Since 2023, methanol 4-stroke dual fuel engines have been available from Anglo Belgian Corporation (ABC)[6], Hyundai Heavy Industries Engine Machinery Division (HHI-EMD)[7] and MAN Energy Solutions (Everllence)[8]. The Swedish company Scandinaos[9] offers methanol monofuel engines in the range 150 to 450 kW, based on Scania engines.

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[4] Numbers from DNV Veracity Alternative Fuel Info, January 2025

[5] Press release by Wärtsilä January 24, 2022: Wärtsilä hits methanol milestone with first newbuild engine order

[6] https://www.abc-engines.com/

[7] https://www.hyundai-engine.com/en/products/detail/117

[8] https://www.man-es.com/marine/products/four-stroke-engines/methanol-ready-engines

[9] https://www.scandinaos.com/index.html

Combustion principles

The 2-stroke dual fuel methanol engines currently available are based on direct injection of methanol, which is ignited by a diesel injection from separate injectors.

4-stroke dual-fuel methanol engines can operate either with premixed combustion—in which methanol is supplied through the cylinder inlet ports using low-pressure injectors - or with high-pressure direct injection systems similar to those used in 2-stroke engines.

In both cases, fuel oil or diesel is used for pilot injections to ignite the methanol. The pilot fuel ignition is required since methanol has a high auto ignition temperature and therefore does not ignite by itself. The pilot injection of diesel provides the energy necessary to ensure an effective ignition and fast combustion.

The premixed combustion concept offers a simple solution with low pressure port fuel injection, which can potentially be retrofitted to existing engines. The main benefits of this concept are the simplicity and lower cost of both the engine and fuel system, compared to a high-pressure direct injection solution. The main drawback is a limitation to the fuel oil replacement, mainly dictated by the requirement of the air-fuel mixture to be within certain limits.

The direct injection concept requires a more complex fuel system, including either dual fuel or dedicated injectors for methanol as well as high pressure pumps. The engine designs currently available are equipped with common rail injection systems for both the fuel oil and methanol. Due to the capability of controlling injection parameters, the energy share of methanol can be higher than in the premixed concept and operate with methanol in a wider load range.

Scandinaos[10] methanol engines are based on modified Scania ethanol engines. The engines use 97 % methanol mixed with 3 % of ignition improver (Beraid 3555M) to ensure ignition as well as lubrication and corrosion inhibitors. With the addition of an ignition improver, the fuel mixture attains diesel-like ignition properties.

Methanol engines can also utilize spark ignition, as in current passenger car methanol engines, or adopt advanced ignition principles such as pre-chamber combustion. However, this approach is currently uncommon in the maritime sector, as spark-ignition and pre-chamber technologies often face challenges in providing the high efficiency, power output, and reliability demanded by large marine engines.

[10] https://www.scandinaos.com/index.html

Emissions

Today's marine dual-fuel engines that use methanol rely on a small pilot injection of fuel oil or diesel to ignite the methanol. The system also allows the engine to run entirely on fuel oil or diesel when methanol is unavailable or too expensive to use. The emission products from the combustion of fuel oil are therefore unavoidable still a part of the emission from methanol dual fuel engines.

When a fuel oil containing hydrogen (H), carbon (C), and sulfur (S) reacts with air (O_2 and N_2), several combustion products are formed. The most common products are illustrated in the following unbalanced chemical reaction:

$$C_X H_Y S_Z + O_2 + N_2 \rightarrow CO_2 + H_2O + SO_2 + NO + NO_2 + CO + HC + PM$$

CO_2, H_2O and SO_2 are the ideal (complete) combustion products, while NO/NO_2, CO, hydrocarbons (HC) and particulate matter (PM) are undesired, but largely unavoidable.

SO_2 is a regulated emission and is the dominant sulfur compound formed during the combustion of fuel-bonded sulfur. The concentration of SO_2 is directly proportional to the sulfur content in the fuel. Some SO_3 may, however, also be produced during combustion. Both SO_2 and SO_3 can react with water vapor (e.g. in the atmosphere) to form acidic compounds such as sulfuric acid (H_2SO_4), which contribute to acid rain. Regulatory compliance can be achieved either by using low-sulfur fuels or by removing SO_2 through aftertreatment systems such as exhaust gas scrubbers.

NO_X, the sum of NO and NO_2, is a regulated emission for which conformity must be ensured by proper combustion control or aftertreatment. It is formed when atmospheric nitrogen and to a lesser extent when fuel bound nitrogen is oxidized at high temperatures. Compliance is ensured by the use of Exhaust Gas Recirculation (on 2-stroke engines) or Selective Catalytic Reduction (SCR, applicable to both 2 and 4-stroke engines).

CO, HC (or THC, for total hydrocarbons), and PM (particulate matter) are incomplete combustion products, which are not regulated for large marine engines. CO and HC are normally present in concentrations in the range of 50–500 ppm, with HC representing a broad spectrum of unburned or partially oxidized hydrocarbons from the fuel.

Particulate matter (PM), also known as soot, is a collective term for carbon particles produced during the combustion of fuel oil. Engine-generated PM also contains ash, lubricating oil, condensed hydrocarbons, and secondary particles. The term "black carbon" refers specifically to the soot fraction quantified by light absorption measurements, in contrast to the weight-based methods typically used for determining total PM.

The dual-fuel combustion process, where methanol is used as the main fuel, has a significant impact on the formation of SO_2, NO_x, and particulate matter (including black carbon). Furthermore, this process can lead to the creation of "new" emission species, which may require specific operating strategies for control and removal - potentially through dedicated exhaust gas aftertreatment systems.

Methanol is an alcohol that burns in a manner similar to hydrocarbon fuels, as illustrated by the following (unbalanced) chemical reaction:

$$CH_3O_H + O_2 + N_2 \rightarrow CO_2 + H_2O + NO + NO_2 + CO + HC + PM$$

Because methanol has a simple chemical structure and lacks internal carbon–carbon bonds, it is generally very effective at reducing particulate matter (PM) formation. When methanol is burned with excess air, it produces little to no visible smoke or flame. However, spray combustion of methanol in an engine under high load can still lead to some PM formation, though in lower amounts compared to fuel oil or diesel.

Methanol has a high heat of vaporization and a low boiling point, compared to heavier hydrocarbons. The evaporation of methanol effectively lowers the flame and overall combustion temperature, which significantly acts to reduce thermal NO_x-formation.

Combustion of methanol can, however, result in emissions of CO and hydrocarbons due to incomplete combustion. This may include unburned methanol (CH_3OH) and formaldehyde (CH_2O), which can be considered as new emission species compared to conventional fuels. Other HC emissions may also arise from interactions with the pilot fuel during the combustion process.

Methanol-, formaldehyde- and HC emissions

During combustion, methanol can locally undergo incomplete oxidation, leading to the formation of formaldehyde as an intermediate product. Under low-temperature or fuel-rich combustion conditions, the conversion of methanol to the ideal products - CO_2 and H_2O - may be incomplete, resulting in increased formation of formaldehyde:

$$CH3OH + 0.5\ O2 \rightarrow CH2O + H2O$$

Formaldehyde is typically formed at temperatures in the range of 500–900 °C[11]. Peak concentrations of formaldehyde occur around 650–800 °C, where oxidation of methanol to formaldehyde is significant, but further oxidation to CO and CO_2 is not yet complete. At higher temperatures (above ~900 °C), formaldehyde is rapidly oxidized, resulting in lower concentrations.

Even in engines operating with premixed combustion (such as Otto engines), where fuel and air are thoroughly mixed before ignition, localized regions can exist near cylinder

[11] Turns, S. R. (2012). *An Introduction to Combustion: Concepts and Applications* (3rd Edition). McGraw-Hill

chamber walls (cold zones) or within crevice volumes (such as piston ring grooves and cylinder head joints) where the temperature is too low for complete oxidation of methanol. In these areas, methanol may persist or be only partially oxidized to formaldehyde, which does not undergo further oxidation in the bulk gas and therefore leaves the cylinder as unburned fuel. Methanol and formaldehyde are not necessarily converted in the exhaust line, and can therefore be emitted directly if they are not fully oxidized during combustion.

Operating a spark-ignited engine allows for the investigation of HC emissions resulting solely from methanol combustion, without interference from another fuel. In a study by Güdden et al.[12], a large-bore, high-speed single-cylinder engine with port fuel injection and spark ignition (PFI SI) was used. Formaldehyde emissions were measured at approximately 1 g/kWh at an indicated mean effective pressure (IMEP) of 10 bar, with the highest values observed at a relative air-fuel ratio of around 1.55.

Methanol emissions are typically higher than formaldehyde emissions (often several times higher, depending on operating conditions and AFR) and increase under lean mixture conditions.

Although there do not appear to be any published measurements of formaldehyde emissions from large, methanol-fueled dual-fuel engines operating on the high pressure direct injection (HPDI) combustion principle (diesel-like combustion), it is known that the formation of unburned methanol and formaldehyde in such direct fuel injection engines differs from that in Otto engines. In smaller diesel engines fueled with methanol blended with an ignition improver, formaldehyde emissions have been measured in the range of 0.02–0.07 g per kg of fuel. These are low levels, significantly lower than typical values for Otto engines, and are also comparable to those observed in marine diesel engines operating on heavy fuel oil[13].

Dual-fuel methanol marine engines operating on the diesel-like principle - particularly large, low-speed types - are generally expected to emit very little formaldehyde. High combustion temperatures ensure almost complete oxidation of methanol and minimal fuel slip, so conditions favoring formaldehyde or unburned fuel formation are largely absent. As a result, hydrocarbon emissions are typically very low. However, engine design and load can still influence the balance between unburned methanol and formaldehyde emissions.

In-house testing of a high-speed, 9-liter dual-fuel HPDI engine operating at 1500 rpm has shown that injecting methanol a few crank angle degrees after the pilot diesel and

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[12] 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. Fuel, 303, 121292. https://doi.org/10.1016/j.fuel.2021.121292

[13] Aakko-Saksa, P., & Lehtoranta, K. (2019). *Ship emissions in the future: Review*. VTT Technical Research Centre of Finland. VTT Research Report No. VTT-R-00335-19.

before top dead center supports a combustion process similar to that in conventional diesel engines. Throughout these tests, the pilot fuel amount was kept constant, regardless of engine load. Emission measurements indicate that as the proportion of methanol increases, there is a marked reduction in hydrocarbon (HC) emissions and a moderate decrease in carbon monoxide (CO) emissions. These observations are in line with findings from the literature, where similar operating strategies have also resulted in lower HC and CO emissions with higher methanol content[14].

In HPDI engines the formation of unburned hydrocarbons (HC) can result from local interactions between diesel and low cetane number methanol in regions with high fuel concentration and insufficient oxygen or temperature, leading to incomplete combustion. At low engine load, HC emissions may be relatively high due to methanol's high latent heat of vaporization and lower reactivity, which can cool the charge and hinder complete oxidation. However, at medium to high engine loads, or when operating at higher methanol substitution ratios - while maintaining sufficient pilot diesel for ignition - the combustion conditions are improved. The hotter, more radical-rich environment under these conditions promotes more complete oxidation of both methanol and any remaining unburned diesel, resulting in a substantial reduction in HC emissions.

Carbon monoxide emissions (CO)

Like formaldehyde, carbon monoxide (CO) is formed as an intermediate during the incomplete combustion of carbon-containing fuels, particularly under fuel-rich conditions, at low temperatures, or in cold regions of the combustion chamber (quenching zones). CO is more stable than formaldehyde and is therefore more likely to persist.

According to Güdden et al.[15], CO emissions from a large-bore, high-speed PFI SI engine operating on methanol were measured at around 4 g/kWh over the entire range of lambda 1.4 to 1.8. CO emissions remained relatively high and varied only slightly with changes in the excess air ratio.

For pilot-ignited HPDI methanol combustion, a higher excess air ratio can help promote more complete combustion. Furthermore, wall quenching is less pronounced in engines operating under diesel-like conditions, since the fuel is injected directly into the

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[14] Dong, Yabin; Kaario, Ossi; Hassan, Ghulam; Ranta, Olli; Larmi, Martti; Johansson, Bengt. *High-pressure direct injection of methanol and pilot diesel: A non-premixed dual-fuel engine concept*. Fuel 277 (2020): 117932. **https://doi.org/10.1016/j.fuel.2020.117932**

[15] 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. Fuel, 303, 121292. https://doi.org/10.1016/j.fuel.2021.121292

combustion chamber and combustion primarily occurs away from the cooler cylinder walls and surfaces.

Based on tests with a high-speed engine[16], CO emissions from dual-fuel HPDI methanol/diesel combustion decrease markedly as both the methanol substitution ratio (MSR) and engine load (IMEP) increase. At low loads and low MSR, CO emissions range from 4 to 10 g/kWh, while at higher loads and higher MSR they drop below 1–2.5 g/kWh. Advancing the pilot diesel injection timing can further lower CO emissions. Overall, the study demonstrates that CO emissions remain generally low under favorable operating conditions, which aligns with the in-house test results. It is also expected that large, slow-speed marine engines will offer even more favorable conditions for complete combustion, potentially resulting in even lower CO emissions during typical operation.

At low engine load, CO emissions in HPDI may be relatively high due to the cooling effect and lower reactivity of methanol, which inhibit complete combustion and oxidation of intermediate species such as CO. However, at medium to high engine loads, or when operating at higher methanol substitution ratios - while maintaining sufficient pilot diesel for ignition - the combustion conditions are improved. The resulting higher in-cylinder temperatures and increased availability of reactive radicals promote more complete oxidation of CO to CO_2, leading to a substantial reduction in CO emissions.

Engines utilizing PPC (Partially Premixed Combustion) also differ by achieving lower CO and HC emissions, as the PPC concept enables advantageous mixing of fuel and air, which can suppress wall quenching effects, thereby limiting CO formation. Currently, PPC combustion is primarily at the research and development stage. While it has demonstrated promising results in terms of emissions reduction and efficiency in laboratory and prototype engines, widespread commercial adoption has yet to occur due to challenges such as controlling combustion phasing, fuel flexibility, and ensuring reliable operation under real-world conditions.

Nitrogen oxide emissions (NO_x)

Thermal NO_x, which includes both NO and NO_2, is formed in engines at high temperatures when nitrogen and oxygen in the combustion air react during combustion - a process that becomes significantly more pronounced above approximately 1800 °C.

In engines with premixed, lean combustion - such as methanol dual-fuel engines - the combustion temperature is relatively low due to the homogeneous fuel-air mixture and excess air. Additionally, methanol's high latent heat of vaporization provides a cooling effect in the combustion chamber, further lowering peak temperatures and suppressing

[16] Dong, Yabin; Kaario, Ossi; Hassan, Ghulam; Ranta, Olli; Larmi, Martti; Johansson, Bengt. *High-pressure direct injection of methanol and pilot diesel: A non-premixed dual-fuel engine concept*. Fuel 277 (2020): 117932. **https://doi.org/10.1016/j.fuel.2020.117932**

NO_x formation. This contrasts with diesel engines, where local hot spots promote increased NO_x production.

Experiments with a turbocharged, heavy-duty 6-cylinder diesel engine (9.7 L, 1500 rpm) operating in dual-fuel mode with premixed methanol (Pan et al.[17]) demonstrated that increasing the methanol substitution ratio to 40% by weight reduced NOx emissions by approximately 25–30% compared to pure diesel operation - from about 6.2 g/kWh (diesel) to 4.6 g/kWh (dual-fuel) at moderate intake air temperatures. Furthermore, Dong et al[18]. reported that, with dual-fuel HPDI methanol operation, NO_x emissions could generally be maintained below 4 g/kWh across the entire load range investigated.

NO_x emissions from the large, low-speed MAN B&W ME-LGIM engine (dual-fuel, high-pressure direct injection) are reported to be significantly lower when operating on methanol compared to conventional diesel operation[19]. NO_x formation is reduced by approximately 30%, primarily because methanol combustion results in lower temperatures than diesel. Under standard methanol operation, the engine can meet IMO Tier II NO_x emission requirements without aftertreatment.

The medium-speed large bore Wärtsilä 32 methanol dual-fuel engine achieves substantially lower NO_x emissions when running on methanol compared to conventional fuel oil. Operation on methanol leads to a 50% reduction in NO_x emissions[20] . The engine meets IMO Tier II NO_x requirements on methanol alone, without the need for additional aftertreatment.

Soot/PM emissions

Methanol has a very low tendency to form soot and particulate matter (PM) during combustion. This is mainly because the methanol molecule lacks carbon–carbon bonds, which greatly limits the formation of soot precursors - soot in engines typically arises from the breakdown and polymerization of hydrocarbon chains. Additionally, methanol's high oxygen content promotes more complete combustion and reduces the presence of oxygen-deficient zones where soot would otherwise form.

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[17] Pan, W., Yao, C., Han, G., Wei, H., & Wang, Q. (2015). The impact of intake air temperature on performance and exhaust emissions of a diesel methanol dual fuel engine. *Fuel*, 162, 101–110. https://doi.org/10.1016/j.fuel.2015.08.073

[18] Dong, Yabin; Kaario, Ossi; Hassan, Ghulam; Ranta, Olli; Larmi, Martti; Johansson, Bengt. *High-pressure direct injection of methanol and pilot diesel: A non-premixed dual-fuel engine concept*. Fuel 277 (2020): 117932. **https://doi.org/10.1016/j.fuel.2020.117932**

[19] MAN Energy Solutions (2021). *The methanol-fuelled MAN B&W LGIM engine – Application, service experience and latest development of the ME-LGIM engine*. Available online.

[20] Wärtsilä (2023). *The Wärtsilä 32 Methanol Engine*. Wärtsilä Corporation. https://wartsila.com/marine

According to DieselNet[21] - an authoritative online technical resource on engine emissions and fuels - alcohol-based fuels such as methanol and ethanol produce extremely low soot and particulate matter (PM) emissions. The absence of C-C bonds and the high oxygen content in these molecules nearly eliminates soot formation, even under fuel-rich conditions. DieselNet also notes that, even in compression ignition engines (dual fuel), PM emissions are typically much lower compared to conventional diesel engines. In fact, it is reported that PM emissions from methanol in a compression ignition engine can be less than 0.002 g/bhp-hr (0.003 g/kWh), and this low level is maintained over a wide equivalence ratio range.

Measurements from Everllence's (formerly MAN Energy Solutions) large two-stroke marine dual-fuel engines - operating on the diesel principle with methanol as the main fuel and pilot oil for ignition - demonstrate that particulate matter (PM) emissions during methanol operation are reduced by more than 95% compared to heavy fuel oil, often falling below 0.01 g/kWh[22].

The medium-speed Wärtsilä 32 dual fuel methanol marine engine achieves a 50% reduction in particulate matter (PM) emissions, measured as filter smoke number, compared to conventional fuel oil operation[23]. This significant reduction is due to the absence of sulfur and the clean combustion characteristics of methanol. This highlights methanol's potential for low particulate emissions across a range of operating conditions and engine types. Although methanol typically results in lower particulate emissions than diesel, some PM can still be generated - primarily from the pilot fuel and lubricating oil.

Role of catalysts or aftertreatment systems

As described in the previous sections, using methanol as a fuel in marine engines is expected to result in lower emissions of particulates and NO_x compared to conventional diesel engines. International experience shows that emissions of unburned hydrocarbons, carbon monoxide, and aldehydes from methanol-fueled engines are generally low. However, under certain operating conditions - such as cold start and low load - elevated concentrations of formaldehyde and other aldehydes may occur. Mitigation of formaldehyde exposure risk can include the use of catalysts or other technologies to reduce levels of formaldehyde to acceptable levels. To ensure that emissions of these organic compounds remain low in all operating conditions, the use of

[21] DieselNet Technology Guide: Alcohol Fuels. https://dieselnet.com/tech/engine_alcohol.php
[22] Aakko-Saksa, P., & Lehtoranta, K. (2019). *Ship emissions in the future: Review*. VTT Technical Research Centre of Finland.
[23] Wärtsilä, "The Wärtsilä 32 Methanol Engine," 2023)

diesel oxidation catalysts (DOC) as an aftertreatment system is considered a viable option[24].

DOC catalysts function by oxidizing CO, HC's, and aldehydes into CO_2 and water, provided that the exhaust temperature is sufficiently high. Experience from heavy-duty road vehicles and buses using alcohol-based engine technology demonstrates that DOC is effective in limiting aldehyde emissions in practice. This is evident, for example, in Swedish city buses equipped with ethanol engines, where DOC is integrated to comply with emission requirements and ensure low aldehyde output[25]. For methanol engines, it is likewise indicated that a standard oxidation catalyst is likely to help reduce both particulate mass and emissions of organic compounds.

However, it is important to note that the effectiveness of DOC depends on the exhaust temperature being sufficiently high (typically above 200°C), and that formaldehyde can be more difficult to oxidize than traditional hydrocarbons, which may present challenges during low load or cold start conditions. Furthermore, impurities in the fuel or lubricants can affect the lifespan and efficiency of the catalyst. Should stricter regulations on formaldehyde and other unregulated compounds be introduced in the future, it may be necessary to optimize the DOC system or supplement it with additional aftertreatment solutions.

Marine engines operating on methanol as the main fuel are expected to emit less NO_x than engines running on diesel fuels or HFO. Nevertheless, NO_x emissions can be further reduced through exhaust gas recirculation (EGR). Methanol combustion has a much lower tendency to produce soot, which allows high EGR rates to be used without the risk of soot formation. This, in turn, lowers the combustion temperature even further and contributes to additional NO_x reduction. High EGR rates are particularly well-suited to large, slow-speed two-stroke marine engines, where EGR can be implemented efficiently and is commonly used to meet stringent NO_x regulations.

Another option is to mix water with methanol fuel, which further reduces combustion temperature and NO_x generation. This approach has enabled certain engines to achieve IMO Tier III NO_x compliance without the need for traditional aftertreatment systems such as selective catalytic reduction (SCR) or EGR.

Human Exposure Risks from Unburned Methanol

Incomplete combustion of methanol in marine engines can lead to the release of unburned methanol as well as partially oxidized byproducts, most notably formaldehyde (CH_2O). While emissions of formaldehyde are not currently regulated in marine applications, certain operating conditions - such as cold start, low load, or faults in the

[24] IEA-AMF Annex 56 (2020), *Methanol as Motor Fuel. Summary Report*
[25] IEA-AMF Annex 46 (2016), Alcohol Applications in Compression Ignition Engines, Ed. Jesper Schramm

fuel injection system – may result in concentrations that exceed established safe exposure limits for humans. This raises important questions about the occupational and health risks facing crews and others who may be exposed to engine exhaust from methanol-fueled vessels. Understanding the formation, emission levels, and potential effects of methanol and formaldehyde is thus essential for ensuring safe working environments and for informing future regulatory developments.

Information on TWA limits (8-hour exposure limits) for chemical substances in Denmark is available in the guidelines of the Danish Working Environment Authority, which can be found on their website. For an overview of applicable limits at the EU level, the European Agency for Safety and Health at Work (EU-OSHA) publishes harmonized European exposure limits.

STEL (Short-Term Exposure Limit, 15 minutes) is the maximum allowed concentration of a chemical substance to which one may be exposed for up to 15 minutes without health risk. STEL protects against adverse effects from short-term, high exposures.

Information about STEL limits can be found in the Danish Working Environment Authority's guidelines (available on their website) and from the European Agency for Safety and Health at Work (EU-OSHA), which publishes European exposure limits.

Table 1 below shows the current Danish occupational exposure limits for methanol and formaldehyde as set by the Danish Working Environment Authority. For methanol, only an 8-hour time-weighted average (TWA) limit is specified, with no short-term exposure limit (STEL) established. In contrast, for formaldehyde, both an 8-hour TWA and a 15-minute STEL are provided. This means that formaldehyde is the primary concern for crews and passengers when considering exposure to exhaust gas. These limits represent the maximum permissible concentrations in workplace air and are intended to protect workers from adverse health effects caused by inhalation of these substances.

Table 1. TWA and STEL exposure limits for methanol and formaldehyde according to the Danish Working Environment Authority[26]

Species		**TWA (8-hour)**		**STEL (15-minute)**	
		mg/m³	ppm	mg/m³	ppm
Methanol	CH3OH	260	200	-	
Formaldehyde	CH2O	0.37	0.3	0.74	0.6

[26] https://at.dk/regler/bekendtgoerelser/graensevaerdier-stoffer-materialer-1619/bilag-2-graensevaerdier-luftforureninger/afsnit-a/

Determination of Methanol and Formaldehyde in Engine Exhaust

DNPH-HPLC (Formaldehyde)

To accurately quantify formaldehyde and other carbonyl compounds in exhaust gases from ship engines, a carefully controlled sampling and derivatization procedure is needed. The DNPH derivatization[27] method adheres to international standards such as ISO 8178 and SAE 930142HP, enabling precise determination of formaldehyde in ship engine exhaust.

Exhaust gas samples from the ship engine are first diluted using a partial flow dilution system, which ensures representative and manageable samples while preventing condensation. The diluted gas stream is then passed through a filter (e.g., a Teflon filter) to remove particulates, and subsequently through a DNPH cartridge (silica gel impregnated with 2,4-dinitrophenylhydrazine), where formaldehyde and other carbonyl compounds are collected by derivatization to stable hydrazones. The sampling flow through the DNPH cartridge is carefully controlled (typically at 1.0 L/min) to ensure that the total gas volume matches the cartridge's capacity and the manufacturer's recommendations.

After sampling, the hydrazones are extracted from the DNPH cartridge using acetonitrile, and the extract is analyzed by high performance liquid chromatography (HPLC) with a diode array detector. The analysis is performed on a Deltabond AK column and in accordance with the SAE 930142HP protocol. Quantification of formaldehyde and other carbonyl compounds is carried out by comparison with calibration curves for the relevant hydrazones.

GC-FID (Methanol)

Methanol in engine exhaust gas can be measured using gas chromatography with a flame ionization detector (GC-FID), as described by Gong et al.[28]. The method is in accordance with international standards[29], and is well suited for both research and regulatory documentation of methanol in engine exhaust emissions.

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[27] Agrawal, H., Welch, W. A., Henningsen, S., Miller, J. W., & Cocker, D. R. III (2010). Emissions from main propulsion engine on container ship at sea. Journal of Geophysical Research, 115, D23205. https://doi.org/10.1029/2009JD013346

[28] Gong, C. et al., Fuel 221 (2018), 188–195. https://doi.org/10.1016/j.fuel.2018.02.115

[29] **ISO 25140:2010** (*Stationary source emissions - Determination of the mass concentration of methanol - Method by gas chromatography*)

Sample collection is typically performed by capturing the exhaust gas in a Tedlar® bag or another gas-tight sampling bag, which makes it easy to transport and analyze the sample later. Alternatively, methanol can be collected by directing the exhaust gas through deionized water, in which methanol (and formaldehyde) dissolve very efficiently.

Depending on the situation, and to protect the equipment from clogging, it may be necessary to pass the exhaust gas through a pre-filter during sampling to remove particles and soot. It is also important to avoid condensation (water droplets) in the sampling system, because methanol is highly soluble in water and can be lost from the gas sample if condensation occurs. Therefore, sampling lines and collection systems should be kept warm (above 100 °C). Any samples with visible condensation should be discarded.

For analysis, an appropriate amount of gas is withdrawn from the bag with a gas-tight syringe and injected into the GC-FID instrument. If methanol has been collected in deionized water, a portion of this liquid can be directly injected into the GC-FID (if the instrument allows liquid injection). Inside the gas chromatograph, methanol is separated from other compounds as the sample moves through a specialized column. The FID detector then measures the amount of methanol passing through. To determine the precise amount of methanol in the sample, the FID is calibrated with standard solutions of known methanol concentrations; this allows the signal to be converted into an accurate concentration of methanol in the exhaust gas. If the sample contains a high concentration of methanol, it may be necessary to dilute the sample with clean air or nitrogen so that the measurement fits within the instrument's sensitivity range.

FTIR and FID

Fourier Transform Infrared Spectroscopy (FTIR) is also widely used for measuring methanol and formaldehyde in engine exhaust gases. With FTIR, the exhaust gas is directed into a heated measurement cell. The instrument analyzes the infrared absorption spectrum of the gas sample, where each compound, including methanol and formaldehyde, has its own characteristic absorption bands. By comparing these spectra to reference data, FTIR can simultaneously quantify the concentrations of many gases present in the exhaust.

The main advantage of FTIR is that it enables real-time, continuous measurement of multiple compounds at once, without the need for chemical derivatization or complex sample preparation. FTIR can provide immediate feedback on emissions and is well suited for monitoring dynamic changes during engine operation. The method is non-destructive, does not require consumables like chromatographic columns or reagents, and is capable of detecting a wide range of exhaust gases (such as methanol, formaldehyde, CO, CO_2, NO_x, and hydrocarbons) in a single analysis.

However, FTIR also has some limitations. Its sensitivity for certain compounds, especially at very low concentrations. Measurement accuracy can be affected by overlapping absorption bands (spectral interference) from water vapor, CO_2, or other gases in the exhaust, which can complicate the quantification of methanol and formaldehyde. FTIR instruments also require careful calibration with reference gases, regular maintenance, and advanced software for data analysis. The equipment is relatively costly, and accurate operation often requires experienced personnel.

As an alternative, methanol and formaldehyde emissions can be assessed using a stand-alone flame ionization detector (FID). The FID measures the total concentration of hydrocarbons present in the exhaust gas. In the case of a methanol engine - where the exhaust typically contains only small amounts of other hydrocarbons - the FID signal can serve as an indicator of the combined emissions of unburned methanol and formaldehyde. However, because FID does not distinguish between individual compounds, it cannot directly quantify methanol and formaldehyde separately without an additional separation step (like gas chromatography). In addition, the FID's response depends on the type of hydrocarbon it is calibrated with; if the instrument is calibrated with, for example, propane or methane, the measured concentration for methanol or formaldehyde must be corrected using an appropriate response factor to ensure accurate quantification, since FID is less sensitive to oxygenated compounds.

PTR-MS

Proton transfer reaction-mass spectrometry (PTR-MS) is a technique used for rapid and sensitive measurement of volatile organic compounds in gas samples.

PTR-MS operates by generating hydronium ions ($H3O^+$) in the ion source of the instrument, typically using a hollow cathode. These hydronium ions are then introduced into a reaction chamber (drift tube), where they are mixed with the sample gas containing the volatile organic compounds of interest—such as formaldehyde and methanol. The sample gas is often taken from a diluted gas stream to avoid excessively high concentrations and to minimize matrix effects. If an analyte in the sample, such as formaldehyde or methanol, has a higher proton affinity than water, it will accept a proton from a hydronium ion, forming a protonated molecule (MH^+) while water is simultaneously produced. The protonated molecules formed are subsequently separated and detected in a mass spectrometer (ToF-MS), enabling the identification and quantification of formaldehyde, methanol, and other volatile compounds in the gas sample.

PTR-MS can distinguish between different compounds because the protonated molecules each have their own characteristic mass-to-charge ratio. In this way, formaldehyde and methanol appear as separate and clearly distinct signals in the mass

spectrum, allowing them to be identified and quantified individually, even when both are present in the sample.

A significant advantage of PTR-MS is that the method can measure with high temporal resolution and provide real-time data—typically performing one complete mass spectral measurement every second (1 Hz).

According to Suarez-Bertoa et al. [30], a detection limit of 5 ppbv can be achieved for formaldehyde measurement in exhaust gas using PTR-MS. The authors also emphasize that the results obtained with PTR-MS were in very good agreement with those obtained using other established measurement methods.

Conclusion

The adoption of methanol as a marine fuel marks an important step in the shipping industry's transition toward lower emissions, driven by tightening regulatory requirements and the sector's commitment to decarbonization. Methanol offers several technical and environmental advantages: it eliminates sulfur oxide (SO_x) emissions, drastically reduces particulate matter (PM/soot), and produces significantly lower nitrogen oxide (NO_x) emissions compared to traditional marine fuels. Additionally, its flexibility in production from both renewable and fossil sources—together with established logistics, global availability, and retrofit potential—makes methanol a realistic and scalable alternative for a broad range of vessels.

Methanol-fueled marine engines, available in both two-stroke and four-stroke configurations, have proven capable of reliable and efficient operation. Modern engine concepts employing direct injection or premixed combustion ensure high substitution ratios of methanol for conventional fuels, while maintaining power output and operational flexibility. Emissions of unburned hydrocarbons, formaldehyde, and carbon monoxide are generally low under typical marine operating conditions, especially in large, slow-speed engines with direct injection. Advanced aftertreatment systems, such as diesel oxidation catalysts (DOCs), can be effective in reducing emissions of aldehydes and organic compounds during normal operation.

A key benefit of methanol combustion is the near-elimination of particulate and soot emissions—a direct result of its molecular structure and absence of carbon–carbon bonds—making it highly attractive from an air quality and regulatory standpoint. Formaldehyde and unburned methanol emissions may, however, require careful management, especially given their occupational exposure risks for crews. Well-

[30] Suarez-Bertoa, R., Clairotte, M., Arlitt, B., Nakatani, S., Hill, L., Winkler, K., Kaarsberg, C., Knauf, T., Zijlmans, R., Boertien, H. & Astorga, C. (2017). Intercomparison of ethanol, formaldehyde and acetaldehyde measurements from a flex-fuel vehicle exhaust during the WLTC. *Fuel*, 203, 330–340. https://doi.org/10.1016/j.fuel.2017.04.131

established measurement and monitoring techniques, such as GC-FID, FTIR, and PTR-MS, allow for robust detection and regulatory compliance.

Recent experience in both laboratory and full-scale marine engines confirms that NO_x emissions can be kept well below IMO Tier II requirements—and, with optimized combustion strategies or use of exhaust gas recirculation (EGR), may meet Tier III limits even without selective catalytic reduction (SCR) systems. Methanol's clean-burning characteristics also enable the use of high EGR rates for further NO_x suppression, while not posing risks for soot formation.

While the outlook for marine methanol is strong, several challenges remain—most notably, the large-scale availability and price of green methanol, and the need for continued development of bunkering infrastructure. The relatively low energy density of methanol compared to conventional fuels also requires larger storage volumes onboard, which must be factored into ship design and operations. Moreover, the toxicity, low flash point, and specific handling requirements of methanol demand rigorous safety standards and crew awareness.

In summary, the evidence indicates that today's marine methanol engine technologies, when combined with modern aftertreatment and robust monitoring, can deliver very low emissions for all regulated and most climate-relevant pollutants. Provided that challenges related to green methanol availability, fuel handling, and safety are addressed in parallel, methanol remains a strong and practical candidate to support the maritime sector's transition to net-zero and improved air quality worldwide.