

LIGHTHOUSE REPORTS

Aftertreatment of methane slip from marine gas engines

An overview of the issue in a context of emission levels, engine trends and sustainability matters, including a case study involving installation of a catalyst on a tanker



En förstudie utförd inom Trafikverkets branschprogram Hållbar sjöfart som drivs av Lighthouse

Aftertreatment of methane slip from marine gas engines

An overview of the issue in a context of emission levels, engine trends and sustainability matters, including a case study involving installation of a catalyst on a tanker

Författare

Hulda Winnes and Erik Fridell (IVL)

Joanne Ellis and Björn Forsman (SSPA)

William Ramsay and Henrik Westermark (Daphne technology)

In cooperation with

Clas Gustafsson at Furetank Rederi

Detta projekt har genomförts inom Trafikverkets branschprogram Hållbar sjöfart, som drivs av Lighthouse.

This project has been a part of the Swedish Transport Administration programme "Sustainable Shipping", managed by Lighthouse Swedish Maritime Competence Centre.

Summary

The emissions from marine gas engines are determined partly by the fuel and partly by the combustion technology used. Natural gas, bunkered on ships in liquefied form as Liquefied Natural Gas (LNG), is a clean fuel compared to fuel oils, causing low levels of emissions of sulphur dioxide, particles and soot. Also, CO₂ emissions per energy unit is relatively low from LNG combustion due to more chemically bound energy per carbon content in natural gas than in fuel oil. Further, the engines operating on natural gas are often of a “low-pressure” type. These engines have low NO_x emissions compared to “high-pressure” diesel engines. The LNG engines are either spark ignited using the gas as the only fuel, or they use a dual fuel technology where a pilot fuel injection is used for ignition. The pilot fuel is responsible for a large part of emissions of SO₂ and particles, although it only contributes 5% or less of the energy. Another type of dual fuel engine is the high-pressure engine using LNG as fuel in a diesel combustion cycle. Like in other diesel cycle engines, the NO_x emissions from those engines are high, comparable to emissions from fuel oil combustion. The low-pressure dual fuel engines are by far the most used engine type on ships that are not LNG carriers.

A side effect from the combustion in the low-pressure engines is a slip of unburnt methane through the combustion process. For some engines using LNG as main fuel, the methane slip causes total emissions of CO₂-equivalents to be higher than from comparable engines using only marine gasoil. The issue of methane slip is addressed by engine manufacturers aiming for improved designs and combustion technology.

Another way to approach the matter is to treat the exhaust gases. In this study we have analysed different ways to oxidise methane in the exhaust pipe of marine engines. Methane engines used on land are often equipped with oxidation catalysts. There are however still no systems commercially available for marine applications. Factors that present a challenge to the use of catalysts on ships include a high sulphur content of the pilot fuel, low temperatures of the exhausts, and high contents of water vapor. Our analyses also include studies of a more innovative solution for methane oxidation based on a non-thermal plasma technology. Laboratory tests are positive and indicate a good potential, although tests at a larger scale are needed before installation on a ship is possible.

Costs of methane catalysts on ships are expected to mainly depend on technical challenges at installation, and the needed catalytic metals. Since no regulations cover methane emissions from ships, installations are completely voluntary and require ship owners to accept the extra costs. In a case study, we study the costs associated with installation and operation of an oxidation catalyst on one of Furetank’s vessels. Yearly operating costs are estimated to be approximately 110 000 euro, and installation cost to be 450 000 euro. The uncertainties are however high since no real examples could be used for benchmark values.

A full-scale demonstration of methane oxidation catalysts on ships is needed and should be technically possible. Before any demonstration, further guidance on

operational practices should be developed and be accurately addressed for the specific case.

High costs may slow down the introduction of methane aftertreatment technology on ships on a commercially viable scale. It is therefore urgent to investigate potential incentives and regulatory means to facilitate development and introduction of methane oxidation technology for the marine sector. Methane emissions can be expected to increase in the future, with an increasing number of ships driven by LNG, which makes these studies even more relevant.

Sammanfattning

Utsläppen från marina LNG-motorer¹ bestäms delvis av bränslet och delvis av vilken motorteknik som används. LNG är ett rent bränsle jämfört med eldningsolja, och har låga utsläpp av svaveldioxid, partiklar och sot. Dessutom är koldioxidutsläppen per energienhet relativt låga vid LNG-förbränning på grund av mer kemiskt bunden energi per kolinnehåll i naturgas än i eldningsolja. Naturgasmotorerna arbetar också ofta med lågt tryck enligt Otto-cykeln. Dessa motorer har låga NO_x-utsläpp jämfört med utsläppen från dieselmotorer, vilka arbetar med högt tryck. Otto-motorerna kan vara antingen tändstiftsmotorer då gasen är det enda bränslet, eller av ”dual fuel”-typ då man använder en liten mängd eldningsolja för att starta förbränningen i motorn. Utsläpp av SO₂ och partiklar från motorerna kan till stor del tillskrivas pilotbränslet, även om det bara bidrar med 5% eller mindre av energin. En annan typ av ”dual fuel”-motor använder LNG som bränsle i en dieselförbränningscykel under högt tryck. Som i andra dieselmotorer är NO_x-utsläppen från dessa motorer höga, jämförbara med utsläppen från förbränning av eldningsolja. Motorerna som använder ”dual-fuel”-teknik och arbetar efter Otto-cykeln är den överlägset mest använda motortypen på fartyg med undantag för LNG-tankers.

En bieffekt av förbränningen i Otto-motorerna är att en viss mängd metan går oförbränt genom förbränningsprocessen. Detta kallas ofta metan-slip. För vissa LNG-motorer gör metan-slipet att de totala utsläppen av koldioxidekvivalenter är högre än från jämförbara motorer som endast använder marin gasolja. Metan-slip är en aktuell fråga för motortillverkare som jobbar med att minska detta genom förbättrad design och förbränningsteknik.

Ett annat sätt att närma sig frågan är att installera efterreningsteknik för avgaserna. I denna studie har vi analyserat olika sätt för att oxidera metan i avgaserna från marina motorer. Metanmotorer som används på land är ofta utrustade med oxidationskatalysatorer. Det finns dock ännu inga kommersiellt tillgängliga system för fartyg. Anledningar som försvårar användningen av katalysatorer på fartyg är hög svavelhalt i pilotbränslet, låga temperaturer i avgaserna och höga halter av vattenånga. I projektet analyserar vi också en mer innovativ lösning för metanoxidation baserad på en plasmateknik, ”non-thermal plasma”. Laboratorietesterna visar positiva resultat och pekar på en god potential, även om test i större skala krävs innan tekniken kan användas på ett fartyg.

Kostnadsfrågan är också viktig. Eftersom det saknas regler för metanutsläpp från fartyg är installationer helt frivilliga och beroende av att fartygsägare är villiga att betala en extra kostnad. I en fallstudie beräknar vi förväntade kostnader för installation och drift av en oxidationskatalysator på ett av Furetanks fartyg. Installationskostnaderna uppskattas till 450 000 euro och de årliga kostnaderna för driften till cirka 110 000 euro. Osäkerheten är dock stor eftersom inga riktiga exempel kan användas som riktvärden.

¹ LNG är en förkortning av ”Liquefied Natural Gas” vilket på svenska översätts till förvätskad naturgas

En fullskalig demonstration av katalysatorrening för metan på fartyg behövs och bör vara tekniskt möjlig. Inför demonstrationer krävs tydliga riktlinjer för hur katalysatorn ska skötas och att de förhållanden som krävs för att den ska ha lång livslängd utarbetas för varje specifikt fall.

De höga kostnaderna kommer påverka viljan att installera efterbehandling av metan på fartyg i stor skala. Det är därför viktigt att undersöka möjliga ekonomiska incitament och styrmedel som kan underlätta utveckling och införande av tekniker för metanoxidation för den marina sektorn. Att detta är angeläget understryks av att metanutsläppen kan förväntas öka framöver i och med att allt fler fartyg som beställs är LNG-drivna.

Contents

1	Introduction	7
2	Background	9
2.1	Engine types for LNG/LBG fuel on ships.....	9
2.2	Engines in use and on order	10
2.3	LNG as a fuel.....	11
2.3.1	Composition	12
2.3.2	Fuel use in marine engines.....	13
2.3.3	Methane slip in marine engines.....	13
2.4	Emission factors for marine LNG engines	15
2.4.1	Engine development.....	17
2.4.2	Other pollutants	18
3	Available after-treatment technologies	21
3.1	Non thermal plasma technology	21
3.2	Catalysts	22
3.2.1	Diesel oxidation catalyst.....	22
3.2.2	Three way catalyst.....	23
3.2.3	Heating of the exhaust gas stream.....	23
3.3	Discussions with catalyst manufacturers	23
4	Total emissions of methane from the fleet	24
5	Sustainability of the different options	29
6	Tests of methane oxidation in Daphne Technology’s R&D Facility.....	30
7	Case study on a low-pressure dual fuel engine	33
7.1	Exhaust Gas Characteristics for the case study engine	34
7.2	Catalyst System Description	34
7.3	Cost Assessment Components.....	35
7.3.1	CAPEX Cost Estimates	35
7.3.2	OPEX	36
7.3.3	Cost Data Summary.....	37
8	Conclusions and recommendations	38
9	Referenser.....	39

1 Introduction

The use of liquefied natural gas (LNG) as a marine fuel has increased significantly the last two decades. In 2010, 1.4% of the delivered ships were built for LNG propulsion. This share increased to 5.7% in 2017 and further to 13.5% by 2018 (Le Fevre, 2018). A number of driving forces have led to LNG being introduced as a marine fuel in other ship types than LNG tankers, for which cargo boil-off² has been used as fuel for several decades. Factors that have influenced this development were, and are, regionally stricter rules for ships' emissions of sulphur and nitrogen oxides, and a relatively low price for LNG compared to marine gasoil (MGO).

From an air quality perspective, LNG fuel has many advantages compared to the traditional marine fuels. The emissions of sulphur dioxide (SO₂) are low due to low or non-existing sulphur content of the gas. The low sulphur content also contributes to low particle levels, the absence of fuel aromatics is also keeping the particle formation low. Further, the most widely used marine LNG engines have significantly lower emissions of nitrogen oxides (NO_x) than the traditional marine diesel engines. Most LNG engines comply with the strictest emission limits for NO_x (IMO Tier III)³.

The natural gas produces approximately 25% less emissions of carbon dioxide per energy unit than fossil oil; it has a higher energy content per carbon content. However, many of the LNG engines that are delivered today have problems with unburned methane passing through the engine and being emitted with the exhaust gases. Methane is a potent climate gas with a shorter atmospheric lifetime than CO₂ and has a high global warming potential. The established time frames presented by the intergovernmental panel on climate change (IPCC) are 20 years, 100 years and 500 years and the importance of methane is relatively high in a shorter time frame (IPCC, 2013). IPCC estimates that the heating from 1 emitted gram methane corresponds to 30 grams CO₂ from a 100-year perspective, and to 82 grams of CO₂ from a 20-year perspective.

The issue of methane emissions from LNG-driven ships have been described from different angles in several studies. Bengtsson et al., 2012; Thomson et al., 2015; Pavlenko et al., 2015; Schuller O. et al., 2019; and Brynolf et al., 2014 focus on methane as a greenhouse gas (GHG) and compare it to the use of other marine fuels, Stenersen and Thonstad, 2017; Ushakov et al., 2019; and Anderson et al., 2015, quantify the emissions in measurement studies, and de Wit et al., 2003; Roosjen and Meyer, 2020; and Mörkkåsa Sandvik, 2016 investigate technical possibilities to reduce the emissions by an oxidation of methane in the exhaust gas. Some studies indicate that GHG emissions from LNG can be lower than from fuel oil (Baresic et al., 2018; Bengtsson et al., 2012; Schuller et al., 2019; Thomson et al., 2015) and some studies that they can be higher (Thomson et al., 2015; Pavlenko et al., 2020). There are

² As the cargo (LNG) rises in temperature during storing on board, a small share of the cargo evaporates. This gas is used as fuel in the engines on board.

³ The IMO NO_x regulations have three tiers. The "Tier III regulations" are the strictest requiring approximately 90% reduction of NO_x emissions compared to unregulated emissions. They apply only in designated nitrogen emissions control areas.

different input and assumptions used for the studies, but the crucial parameter is whether studies use a 100-year perspective or a 20-year perspective to weigh the relative importance of CO₂ and CH₄. It has long been customary to use the longer time perspective although there is not a standard procedure to follow (Shine, 2009).

Recent measurement studies indicate a methane slip of 2.3-4.1% for the most common engines that are in operation today (Stenersen and Thonstad, 2017). The slip, measured as CO₂-equivalents from a 100-year perspective, is large enough to cause greenhouse gas emissions from LNG to be comparable to those from MGO (Pavlenko et al., 2020). From a 20-year perspective, a slip in the reported range causes emissions of CO₂-e from LNG engines to exceed those from MGO engines.

Methane emissions from ships are not yet incorporated in any regulations on GHG emissions from ships. In the Initial IMO Strategy on reduction of GHG emissions from ships, the reduction of methane is mentioned as a candidate short term measure to reduce emissions (IMO, 2018). Measures were categorised as “short term” if they could be finalised before 2023. At the MEPC 74 (13-17 May 2019), the intersessional Working Group on Reduction of GHG Emissions from Ships were given a task to “further consider concrete proposals to reduce methane slip and emissions of Volatile Organic Compounds (VOCs)”. MEPC 75 is scheduled for 16-20 Nov 2020 and the intersessional Working Group have meetings numbers 6 and 7 during this period. At meeting number 6 it was concluded that “the issue of methane slip would need further consideration including an enhanced understanding of the problem, how methane could be measured, monitored and controlled and which measures could be considered by the Organization to address”. This, and the available submissions to the following intersessional meetings suggest that the question will become of more interest from a policy perspective in possibly a near future. The Society for Gas as a Marine Fuel suggests adding methane slip on a CO₂-e basis to existing and coming regulations and guidelines for CO₂ reduction (ISWG-GHG 7/3/1), a submission by a number of NGO’s including World Wildlife Fund (WWF) and Greenpeace International suggests including all relevant GHGs including methane in future phases of the Energy Efficiency Design Index (EEDI) and that emissions be considered from a 20-year perspective (ISWG-GHG 7/3). Noted though, that these two suggestions are not giving a complete picture of interests and potential ways forward.

The EU MRV (Monitoring, Reporting, and Verification) shipping regulation, EU 2015/757, aims at GHG emissions but only involves CO₂ emissions for the actual reporting. CO₂ emission factors are “average emission rate of a greenhouse gas relative to the activity data of a source stream, assuming complete oxidation for combustion and complete conversion for all other chemical reactions”. Thus, the CO₂ reporting to MRV does not consider methane slip.

There is on-going development at engine manufacturers to reduce the slip and the work has been successful, resulting in significant reductions of slip since the problem was observed. There seems, however, to be a limit for slip reduction by design measures (Pavlenko et al., 2020). A methane slip through the engines corresponding to approximately 1.5% would cause LNG to emit similar amounts of GHG emissions

as fuel oil, measured in CO₂-equivalents from a 20-year perspective. The climate impact could also be reduced by replacing LNG with a non-fossil liquefied biogas (LBG). The LBG still has the methane slip, but the emitted CO₂ is biogenic. A life-cycle study indicated that the environmental and climate impact from a regionally produced LBG is lower than the impact from LNG and MGO from a 100-year perspective and similar to that of MGO from a 20-year perspective (Winnes et al., 2020). However, the availability of LBG is uncertain and there is a growing demand for LBG from other sectors.

Aftertreatment of methane in the exhaust stream has not yet been tested in a marine application. There are challenges related to too high levels of water vapor and sulphur dioxide in the exhaust and too low temperatures for an efficient catalytic reaction (Raj, 2016). The technology is however used on trucks. Other aftertreatment methods include plasma-based treatment - a method still in a test bed stage. Aftertreatment of methane is necessary on trucks to fulfil the Euro VI standard on emissions at transient operations (ETC). The limit value for methane emissions from gas engines in heavy vehicles is 0.5 g/kWh (EG/595/2009) for the Euro VI-category while the limits for Euro IV and Euro V are 1.1 g/kWh, and for Euro III 1.6 g/kWh.

2 Background

2.1 Engine types for LNG/LBG fuel on ships

There are four main engine technologies that are available for using LNG/LBG as fuel in internal combustion engines on ships, as follows (IMO, 2020; Sharafian et al., 2019):

- **2-stroke slow speed high-pressure dual fuel (HPDF or LNG Diesel):**
These engines operate on the diesel cycle, with the gas injected into the cylinder at pressure at the top of the compression cycle (top dead centre). A liquid pilot fuel is used for ignition and injected at the same time as the gas. Methane emissions from the exhaust are much lower for this engine concept as compared to the low-pressure concepts (Sharafian et al., 2019; Pavlenko et al., 2020). This is because there is almost complete combustion of the gas, which is ignited when it is injected. The pressure of the gas has to be boosted to about 300 bar for injection, thus the up-front cost for using this system on LNG carriers is higher than for the low-pressure system, due to the more expensive fuel gas supply system (Lipsith, 2019). MAN is the only manufacturer of a 2-stroke HPDF marine engine (IMO 4th GHG Study, 2020).
- **2-stroke slow speed low-pressure dual fuel (LPDF SS or LNG Otto SS):**
This concept is referred to as lean burn or Otto-cycle (Lipsith, 2019). The gas is admitted to the cylinder during the compression stroke when the pressure is low (Huan et al., 2018) and is ignited by a small volume of liquid fuel. Currently the only supplier of this concept is Wärtsilä, who produces engines under license from Winterthur Gas and Diesel (WIN GD). MAN has announced the development of a 2-stroke LPDF engine, the “ME-GA”, with commercial deliveries beginning in 2021 (MAN, 2020).

- **4-stroke low-pressure dual fuel engines (LPDF MS):** These engines operate on the Otto-cycle and low-pressure gas is admitted to the air intake of the engine cylinder (Wärtsilä, 2019), where it is ignited by a pilot injection of liquid fuel. Wärtsilä engines are the most common LPDF engine used by ships in service as of early 2020, accounting for 70% of the engines in this category. Other manufacturers of LPDF 4-stroke engines include MAN, MaK, and ABC.
- **4-stroke lean burn spark ignition engines (LBSI):** These engines also operate on the Otto-cycle but is single fuel, burning only natural gas, with ignition achieved using a spark plug. Most of the engines within this category are medium-speed Rolls-Royce Bergen engines (now distributed by Kongsberg Marine) – other manufacturers include Mitsubishi, which also includes high-speed engines in its portfolio.

Steam turbines fuelled by LNG are also used by some vessels for propulsion power, but these are considered to be of limited future significance due to lower efficiency as compared to the other technologies (Pavlenko et al., 2020). The steam turbines are presently common on LNG carriers. IMO assumes that 45% of the ships using LNG as main fuel are LNG carriers (IMO, 2020). However, their significance for fleet methane emissions is limited; the methane emission factor for steam turbines is more than a factor 100 less than the average emission factor for the internal combustion engines of the LNG-driven fleet (IMO, 2020).

2.2 Engines in use and on order

At the start of 2020, there were 175 LNG-fuelled ships in operation, not including the 600 LNG carriers that are predominantly fuelled by LNG (sea-lng.org, 2020). Over 200 LNG vessels were on order (sea-lng.org, 2020).

The first ships to use LNG were LNG carriers using boil-off gas, and LNG-fuelled ships are still dominated by the LNG carrier ship type. LNG carriers account for the majority of the ships using 2-stroke engines, and of those using the LPDF 4-stroke engines. There are also a significant number of older LNG carriers using gas turbines. The pure gas LBSI engines are used predominantly by small car and passenger ferries in short distance service, and offshore supply and service vessels. New orders are stated to be increasingly focused towards deep-sea vessels including cruise ships, container vessels, tankers, and bulk carriers (sea-lng.org, 2020).

A summary of the number of LNG-fuelled ships using internal combustion engines in service and on order in 2018 and early 2020, along with the main engine manufacturers and vessel types, is shown in Table 1.

Table 1. Approximate number of ships with LNG-fuelled internal combustion engine by engine type (adapted from Pavlenko et al., 2018).

Engine Type	Ships in operation or on order as of mid-2018 (min. #) ¹	Ships in operation or on order as of early 2020 (min. #) ²	Engine manufacturers (larger suppliers) ³	Vessel Types ⁴
2-stroke high-pressure dual fuel slow speed (HPDF SS)	90	120	MAN is the only supplier	LNG carriers predominantly, a few container ships, general cargo carriers, and general cargo ships
2-stroke low-pressure dual fuel slow speed (LPDF SS)	50	150	Wärtsilä/WinGD sole current supplier; MAN starting from 2020	LNG carriers, oil and product tankers, container ships
4-stroke low-pressure dual fuel medium speed (LPDF MS)	300	410	Wärtsilä; MAN; MaK; ABC; Hyundai Himsen; Caterpillar	Includes LNG carriers, passenger and RoRo ships, cruise ships, product tankers, offshore supply and gas processing vessels, and others
Lean Burn Spark Ignited (LBSI)	45	75	Rolls-Royce Bergen; Mitsubishi	Passenger and car ferries (predominantly), other types include ropax and roro, patrol vessels, offshore supply, and general cargo

1. From Pavlenko et al., 2018, (cited as IHS Ship Registry bespoke dataset)

2. IHS Markit, 2020 (authors' compilation from Ship Registry)

3. Public sources, including engine manufacturer websites and catalogues

4. Public sources including Pavlenko et al., 2020; Stenersen and Thonstad, 2017; news sites such as www.ship-technology.com

The number of vessels using LPDF engines, both 2-stroke and 4-stroke, have increased considerably from mid-2018 to 2020. The 2-stroke LPDF segment has shown a dramatic increase. Lipsith (2019) noted that although high-pressure engines still dominated the 2-stroke sector for dual-fuel LNG engines in 2019, sales of low-pressure 2-stroke engines were significantly higher than 4-stroke. In response to the increased interest in low-pressure 2-stroke engines, MAN, which had supplied only high-pressure engines in the 2-stroke range, announced that they were designing a new low-pressure 2-stroke engine series, the ME-GA (Lipsith, 2019). The reasoning for the popularity in the LPDF 2-stroke engine is that the costs associated with investments are lower than that of the HPDF engine type, which has a relatively high cost for the high-pressure fuel gas supply system when installed on a gas carrier, the vessel type that is the largest segment for 2-stroke dual fuel LNG engines.

2.3 LNG as a fuel

Natural gas contains a mix of volatile hydrocarbons. At minus 162°C the gas becomes liquid at atmospheric pressure. The liquefaction of natural gas reduces the volume by a factor of more than 600 and the gas can be stored in so called cryogenic

tanks, that are insulated and pressurised to keep the LNG in a liquid state. The density of LNG varies between 0.41 and 0.51 kg/dm³, depending on the storing conditions temperature and pressure, and the composition of the gas (American Petroleum Institute, 2015).

2.3.1 Composition

The distributed natural gas often contains >90% mole methane. Minor amounts of heavier hydrocarbons and non-hydrocarbon species such as CO₂, nitrogen, water and dihydrogen sulphide (H₂S) can also occur in the gas. Typical ranges of different compounds in natural gas are presented in Table 2. Heating values depend on the composition of the gas. The lower heating value expressed per mass unit varies accordingly and a typical range is between 48.5 MJ/kg to 52.5 MJ/kg, and a high content of ethane, propane, and butane gives a higher heating value (American Petroleum Institute, 2015). Heating values depend on the composition of the gas. An ISO standard, “ISO/FDIS 23306 Specification of liquefied natural gas as a fuel for marine applications” is under development. Table 3 presents heating values of the LNG components at atmospheric conditions.

Non-hydrocarbon content and hydrocarbon compounds that could freeze during the liquefaction is removed prior to liquefaction. The remainder, in general between 4 and 10%, are primarily other hydrocarbon gases, of which ethane and propane are most abundant (see e.g. Uniongas, 2020; Kimpton and Brown, 2010).

Table 2. Typical composition of natural gas (Uniongas, 2020; Kimpton & Brown, 2010; IEA-AMF, 2020; Tractebel Engineering S.A., 2015).

Component	Unit	Range
Methane	% mole	82-99
Ethane	% mole	0.1-13
Propane	% mole	0.2-5.0
Iso-butane	% mole	Trace-1.5
Normal-Butane	% mole	Trace-1.5
Iso Pentane	% mole	Trace-0.3
Normal pentane	% mole	Trace-0.5
Hexane +	% mole	Trace-0.2
Nitrogen	% mole	0.2-5.5
Carbon dioxide	% mole	0.05-1
Oxygen	% mole	Trace-0.1
Hydrogen	% mole	Trace-0.05
Gross Heating Value dry	MJ/m ³	36-40.2
Sulphur	mg/m ³	3-10
Molecular weight	g/mole	17.7-20.6

Table 3. Carbon content and Higher heating value of methane, ethane, propane and butane.

	Carbon content (wt%)	Higher heating value (MJ/Nm ³)*
Methane	74.8%	37.62
Ethane	79.8%	65.90
Propane	81.6%	93.80
Iso-Butane	82.6%	121.2
n-butane	82.6%	121.5

*101.325 kPa, 15.6° C

The sulphur content of natural gas is naturally low and sulphur containing compounds are removed prior to the liquefaction process. Typically, less than 4 ppmv H₂S are allowed by LNG product specifications (American Petroleum Institute, 2015). It is however common to add odorants to the gas in order to make leakages detectable by the human nose. Many of these compounds contain sulphur. One example is mercaptan, with an odor threshold limit of 1 ppb (<https://naturalgasodorization.com/odorant-added-natural-gas-make-smell/>). According to safety data sheets typically 2 ppm of mercaptan odorant is added to the natural gas (<https://www.pgworks.com/uploads/pdfs/NaturalGasSafetyData.pdf>).

2.3.2 Fuel use in marine engines

The conversion efficiency of a modern marine LNG engine is comparable to a modern marine diesel engine. A typical specific fuel consumption in a dual fuel engine operated with LNG as main fuel is approximately 150 g LNG/kWh although a span from 135 g/kWh for the high pressure dual fuel 2-strokes, to 156 g/kWh for the lean burn spark ignited engines are acknowledged in the 4th IMO GHG report (IMO, 2020). The specific fuel consumption for fuel oil engines are higher than in LNG engines, but since the LNG heating value is higher than that of MGO, the amount of energy input per unit work out is comparable.

2.3.3 Methane slip in marine engines

Combustion characteristics determine the slip through the engine and thereby also the specific emission. Differences can be large between old and new engines and the working principle of the engine is crucial. As explained in the following also the operational profile of the engine is very important. This study focuses on the methane slip in the exhausts. There is however slips both to the crank case and from the fuel supply system. We give a brief overview of the different sources:

- Methane in the exhaust gases
 - **Overlap of open valves.** For certain engines it can be beneficial to have a short period of overlap in the opening of the exhaust valve and the intake valve. This ensures that all the gas in the combustion chamber is exchanged as the next one starts. This is a rather common characteristic of diesel engines. In engines where air and methane are mixed prior to the intake, this overlap causes a slip of methane through the exhaust valve. This is primarily a concern for older diesel engines that have been rebuilt to LNG dual fuel engines (Pavlenko et al., 2020).

- **Gas in enclosed spaces.** Minor parts of the combustion chamber are not reached by the combustion. In a low-pressure engine, there is a mix of methane and air present in the cylinder through parts or the full compression stroke and in some engines also during the intake stroke. Small volumes of the gas mix enter crevices and other available spaces that are sheltered from the combustion in one way or another. During the expansion stroke the gas escapes the hidden spaces and becomes part of the exhausts. Locations of importance for these mechanisms are mainly at the piston head gaskets and the rings between the piston head and the cylinder lining. This slip is minimised through design changes and it is potentially a larger problem in rebuilt diesel engines than in new gas and dual fuel-engines. Another way to avoid this slip is to use direct injection ignition as is done in the high-pressure gas engines (Pavlenko et al., 2020).
- **Incomplete and inefficient combustion.** The flame propagates from the ignition source through the cylinder in the presence of a combustible gas in sufficient concentrations. In certain conditions, the mixture is too lean for a complete combustion close to the walls of the combustion chamber. A too lean mixture can also result from a too strong mixing of the gases in the cylinder. A related phenomenon that occurs close to the cylinder linings is a drop in temperature close to the cylinder linings. Heat is conducted away from the chamber by the walls. This results in so called “quench zones”, which are spaces close to the cylinder walls where the temperature is too low for an efficient combustion (Pavlenko et al., 2020).
- Methane evasion through the crank case and the fuel supply system
 - A comprehensive overview of the methane emissions from LNG engines should also consider slips to the crank case during combustion and leakages and controlled emissions from the fuel supply system. It is believed that emissions that passes through the crank case is accountable for the highest slip of these (Pavlenko, 2020). This issue only exists in four-stroke engines and the leakage occurs between the piston rings and the cylinder walls during the compression stroke. There are technical solutions that involve an enclosed crank case and where the slip is redirected to the engine intake air. In order to apply such a solution to a marine engine, it needs to be certified that the turbo charger can work despite the oil residues that is part of the crank case gases (Pavlenko et al., 2020). It is difficult to quantify this emission; it has been estimated to be approximately 1 g/kWh (Pavlenko et al., 2020).

Unintentional leakages from the fuel supply system are unwanted. In enclosed spaces on a ship an accumulation of methane is a safety risk and there are regulations and instruction specifying how to avoid this. These slips have not been quantified. Occasionally, there are

ventilations of the systems at preparations for repair and maintenance work. For LNG driven trucks intentional ventilations have been measured to correspond to 1% of the fuel, at transient operations. No such measurements have been made for marine engines and to which extent similar ventilations are needed is not known (Pavlenko et al., 2020).

Under certain situations during normal operation of a dual fuel engine there may be a need to safely ventilate the fuel gas piping in a controlled way – for example during a stop sequence during gas operation or when switching over to fuel oil. Small amounts of gas may be ventilated to the atmosphere, at safe locations where there is no ignition source present (Wärtsilä, 2019).

These parts of the methane slip cannot be solved by aftertreatment of exhaust gases and are not treated further in this report.

2.4 Emission factors for marine LNG engines

Emissions of air pollutants SO₂, PM and NO_x are significantly lower from LNG engines compared to the traditional marine diesel engines operating on gas oil or fuel oil. The low sulphur content of the gas results in low SO₂ emissions. PM emissions are kept low partly due to the low sulphur content, but also due to the absence of polyaromatics and combustion specifics. NO_x emissions are low when low-pressure technology is used. Temperatures during combustion in those engines are lower than in the high-pressure engines resulting in a less efficient NO_x formation. Complexity increases when dual-fuel engines are used. During a combustion cycle in dual fuel mode, these engines get between 1-5% of the provided energy from the oil, which is used for ignition as a pilot fuel. Consequently, SO₂ and PM emissions are higher in the dual fuel engines compared to the spark ignition engines that operate on LNG solely.

As mentioned previously, the relatively high emission levels of methane from the most widely used low-pressure LNG engines often cause the total emissions of greenhouse gases measured as CO₂-equivalents to be higher than if fossil fuels are used (Winnes et al., 2020; Pavlenko et al., 2020). In a comparison between the engine types, the HPDF engine performs better from a GHG perspective since the slip is low from these engines. The reason for this is that there is only air present in the cylinder during the compression stroke and the fuel is burnt directly upon injection, whereas the low-pressure engines compress an air/fuel mixture (Ushakov, 2019). Average emission factors for methane from marine LNG engines have been reported to be 6.9 g/kWh (appr. 4.1% of the fuel) for "Low-Pressure Dual Fuel" engines (LPDF), and 4.1 g/kWh (appr. 2.3% of the fuel) for "Lean Burn Spark Ignition"-engines (LBSI). "High-pressure dual fuel" engines (HPDF) have a significantly lower slip. MAN reports a slip from their engines in this category to be 0.2-0.4 g/kWh. Mainly measurements on 4-stroke engines have been published (Ushakov et al., 2019; Lehtoranta et al., 2019; Anderson et al., 2015). One study including total hydrocarbon measurements on a low-pressure 2-stroke engine have been published by the engine

manufacturer (Nylund et al., 2016). We assume that the hydrocarbons are only methane and weight emissions according to ISO 8178 test cycle E2/E3⁴. An overview of results from emission measurement studies are presented in Table 4 (measurement results) and Table 5 (suggested average values per engine type).

Table 4. Specific emissions from marine LNG engines, results from measurement studies.

Study engine	Engine type	Engine load (%)	CH ₄ (g/kWh)	Study
Average 7 engines: on board and test bed	LPDF 4-stroke	Weighted	6.9	Ushakov et al., 2019
Average 9 engines: on board and test bed	LBSI	Weighted	4.05	Ushakov et al., 2019
Test bed engine	LPDF 4-stroke (CNG)	0.4	13.8	Lehtoranta et al., 2019
		0.85	5.6	Lehtoranta et al., 2019
Cruise/Ferry	LPDF 4-stroke	0.4	3.4	Anderson et al., 2015
		0.9	2.975	Anderson et al., 2015
		0.32	4.25	Anderson et al., 2015
		0.72	0.935	Anderson et al., 2015
		0.29	5.695	Anderson et al., 2015
Test bed engine	LPDF 2-stroke	Weighted	3.2	Nylund et al., 2016

⁴ The ISO 8178 describes steady-state engine dynamometer test cycles for exhaust emission measurement from a number of non-road engine applications. More information available on e.g. (<https://dieselnet.com/standards/cycles/iso8178.php>).

Table 5. Suggested average emission factors for methane for different types of marine LNG engines.

	4-stroke lean burn spark ignition engines (LBSI)	2-stroke slow speed low pressure dual fuel (LPDF SS or LNG Otto SS)	4-stroke low pressure dual fuel engines (LPDF MS or LNG Otto MS)	2-stroke slow speed high pressure dual fuel (HPDF or LNG Diesel):
CH ₄ (g/kWh)	4.1	3.2	6.5	0.35
Source	Ushakov et al., 2019	Nylund et al., 2016	Ushakov et al., 2019; Lehtoranta et al., 2019; Anderson et al., 2015	MAN Diesel & turbo, 2015

2.4.1 Engine development

Engine manufacturers have put effort in technology development that addresses and reduces the methane emissions in the last decade. Marintek conducted a survey of methane slip from the few LNG engines on ships in Norway in 2010 (Marintek, 2010). The measurement data, see Table 6, represent early methane engine technology. These engines were mainly installed on smaller ships like coastal ferries and offshore supply ships. The reported methane slip is significantly higher than on more modern ships and the reduction is due to design efforts by engine manufacturers.

Table 6. Methane emissions from early installations of marine methane engines (Marintek, 2010).

Engine type	CH ₄ emission factor (weighted according to ISO cycle)	
	kg CH ₄ /ton LNG	g CH ₄ /kWh
Lean burn spark ignition	44	8.5
Low pressure dual fuel	80	15.6

In discussions with an engine manufacturer on the development of reduction measures for the methane slip, it seems evident that the slip of the coming engine generations will be significantly lower than that reported in measurement studies available in literature, e.g. Ushakov et al., 2019. As an example, in-house measurements indicate a specific methane emission for a modern low-pressure dual fuel engine of approximately 2.8 g/kWh, which could be compared to the corresponding emission factor for low-pressure dual fuel engines of 6.9 g/kWh presented by Ushakov et al. (2019). Land based gas engines from the same engine manufacturer have even lower methane slip (1 g/kWh) which is also believed to be possible to reach for marine engines within the coming decade. The most modern engines have not yet been included in measurement studies on operational ships, but the historical trend with reduced methane emissions for each engine generation is

confirmed to continue. Another example of engine manufacturers' ambitions are from Win GD who is an important supplier of 2-stroke low-pressure engines. Their newly presented next engine generation uses exhaust gas recirculation in a design which is said to cut methane emissions in half (WinGD, 2020).

Engine load

Emissions from different engine loads are customary to weight according to those described in test cycles E2 and E3 in the NO_x technical code. Discussions with a Swedish ship owner company with several LNG-driven ships in its fleet reveal that the operation of ships is automatically switched to “gasoil mode” at engine loads below approximately 25%. This means no LNG is used at the low engine loads, which would be beneficial for lowering the methane emissions, since these increase significantly at engine loads below 25% (Ushakov et al., 2019).

2.4.2 Other pollutants

A selection of emissions of other combustion gases are available in some of the measurement studies presented above. Approximate emission factors presented in these studies are presented in Table 7 (g/kWh) and Table 8 (g/MJ).

NO_x emissions are low for all low-pressure LNG dual fuel engines compared to similar engines operated on marine fuel oil. Estimates by engine manufacturer MAN are that NO_x emissions from an LNG engine are approximately 13-24% lower per kWh than those from its fuel oil driven counterpart, but can be expected to be equally high as for MGO combustion for HPDF engines (MAN Diesel & Turbo, 2015, and MAN Diesel & Turbo 2015a).

Particle emissions are only available from one source (Anderson et al., 2015). Stenersen and Thonstad (2017) estimate emissions of particles to be reduced by >99%, 95-98%, 95-98%, and 30-40% for LBSI engines, LPDF 4-stroke engines, LPDF 2-stroke engines and HPDF 4-stroke engines, respectively. MAN estimate PM reduction of approximately 40% in a HPDF 2-stroke engine (MAN Diesel & Turbo, 2015). No emission measurement studies covering black carbon (BC) from marine LNG engines are found. Lehtoranta et al. (2019a) states that measurements of elemental carbon from LNG combustion show low emissions but the study does not provide any data.

Table 7. Emission factors as g/kWh from marine LNG engines.

Study engine	Engine type	Engine load (%)	NO _x (g/kWh)	CO ₂ (g/kWh)	PM _{tot} (g/kWh)	NMVOC (g/kWh)	CO (g/kWh)	Study
Average 7 engines	LPDF 4-stroke	Weighted	1.9	444.2		0.38	1.86	Ushakov et al., 2019
Average 9 engines	LBSI	Weighted	1.3	472.4		0.38	1.74	Ushakov et al., 2019
Test bed engine (CNG)	LPDF 4-stroke	0.4	3.6	490			3.7	Lehtoranta et al., 2019 and 2019a
		0.85	2.7	410			1.6	Lehtoranta et al., 2019 and 2019a
Cruise/Ferry	LPDF 4-stroke	0.4	0.7	451			3.8	Anderson et al., 2015
		0.9	0.95	398	0.002		2.7	Anderson et al., 2015
		0.32	0.7	454			4.3	Anderson et al., 2015
		0.72	0.5	414			1.4	Anderson et al., 2015
		0.29	0.9	485			4.8	Anderson et al., 2015

Table 8. Emission factors as g/MJ from marine LNG engines.

Study engine	Engine type	Engine load (%)	NO _x (g/MJ)	CO ₂ (g/MJ)	PM _{tot} (g/MJ)	NMVOC (g/MJ)	CO (g/MJ)	Study
Average 7 engines	LPDF 4-stroke	Weighted	1.9	444.2		0.38	1.86	Ushakov et al., 2019
Average 9 engines	LBSI	Weighted	1.3	472.4		0.38	1.74	Ushakov et al., 2019
Test bed engine (CNG)	LPDF 4-stroke	0.4	3.6	490			3.7	Lehtoranta et al., 2019 and 2019a
		0.85	2.7	410			1.6	Lehtoranta et al., 2019 and 2019a
Cruise/Ferry	LPDF 4-stroke	0.4	0.7	451			3.8	Anderson et al., 2015
		0.9	0.95	398	0.002		2.7	Anderson et al., 2015
		0.32	0.7	454			4.3	Anderson et al., 2015
		0.72	0.5	414			1.4	Anderson et al., 2015
		0.29	0.9	485			4.8	Anderson et al., 2015

3 Available after-treatment technologies

The technologies studied for this report include non-thermal plasma (NTP) and methane oxidation catalysts. Methane oxidation catalysts are used on methane engines in land-based applications, but not yet on marine engines. Technical issues in ship applications relate to a low catalytic activity caused by high content of water and sulphur in the exhaust, often combined with relatively low temperatures. Low temperatures emphasise the negative effects from the sulphur and water. The NTP technology is insensitive to exhaust gas temperature, SO₂ and water content. This technology is however less proven for large scale methane oxidation and development work remain.

3.1 Non thermal plasma technology

Non-thermal plasma (NTP), also called cold plasma, is a partially ionized gas, like any other plasma, but with energy (temperature) stored mostly in electrons and not in the gas (Scholtz et al., 2015; Moreau et al., 2008). Although the energy of the electrons in NTP can be tens of electronvolts (eV) (1eV ~ 10⁴ K), the background gas temperature is low enough to be touched by a finger, Figure 1 (Takamura et al., 2012). These energetic electrons in NTPs produce active species in the form of free radicals and ions (as well as additional electrons through electron impact dissociation, excitation and ionization of background gas molecules) (Chu et al., 2013). These active species – free radicals and ions – oxidise, reduce or decompose pollutant molecules. As such, NTP is a powerful decontamination approach with proven success in removing pollutant molecules in various sectors including food, medical, healthcare and (exhaust or flue) gas cleaning.



Figure 1. Typical demonstration of non-thermal plasma.

NTP-induced gas cleaning research and industrial practices include simultaneous NO_x and SO₂ removal, dust removal, mercury (Hg) oxidation, flue gas preprocessing, plasma-induced soot combustion, decomposition of dilute volatile organic compounds (VOCs), diesel exhaust treatment and tar cracking (Chu et al., 2013). Pollution control techniques using NTP have been widely studied because it is one of the most promising technologies for pollution control with higher energy efficiency (Matsumoto et al., 2012).

Although NTP technology has been applied to dry reforming methane (CH₄) into syngas and other valuable chemicals (Tu and Whitehead, 2012), eliminating methane slip from LNG engines with NTP is a rare application of this technology. The oxidation of methane with NTP technology is expected to follow a similar mechanism derived for methane oxidation in the troposphere (Monks and Paul, 2005), whereby the main products are carbon monoxide (CO) and carbon dioxide (CO₂), see Figure 2.

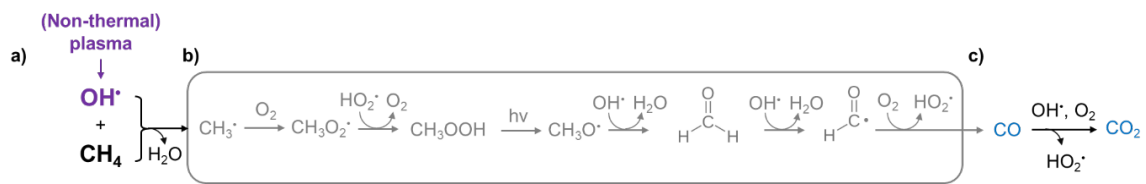


Figure 2. Simplified mechanism for the oxidation of methane (CH₄) with NTP: a) Methane breakdown is initiated via a NTP-derived hydroxyl radical (OH•), and a series of transient species (b) leads to the main products of methane oxidation, carbon monoxide (CO) and carbon dioxide (CO₂) (c).

3.2 Catalysts

3.2.1 Diesel oxidation catalyst

Diesel oxidation catalysts are commonly used under lean combustion conditions. A lean combustion involves a surplus of oxygen and air that assure a complete combustion. This is often referred to in terms of the λ -value representing the ratio between air and fuel. A λ -value of 1 corresponds to stoichiometric conditions during combustion, and lean combustion has values >1 . The internal combustion engines can operate either lean or stoichiometric. Diesel engines always operate under lean conditions while Otto-cycle engines are closer to stoichiometric. Both the dual fuel engines and the spark ignition engines of the LNG-driven ships in use are of the lean burn type, despite the Otto-cycle primarily being used.

Marine methane oxidation catalysts

A catalytic oxidation of methane requires high temperatures and only catalysts that are based on precious metals are active enough in the exhaust gas temperatures of marine methane engines (380-450°C) (e.g. de Wit et al., 2003). Options include palladium (Pd), rhodium (Rh), and platinum (Pt). Tests have however indicated that these catalysts have a rapidly decreasing activity for methane oxidation in the interval 400 - 500°C; catalysts have been shown to deactivate in less than 50 hours (de Wit et al., 2003). Lehtoranta et al., 2016 studied a platinum-palladium (1:4) methane oxidation catalyst (MOC) in a test bed situation using natural gas as fuel in a rebuilt gasoline engine. A 50% oxidation of methane was observed at 500 °C, but only a negligible oxidation at 400°C. The study also indicated a significantly increased efficiency at lower mass flow rates through the catalyst. Approximately 65% of the methane oxidised at a flow rate of 40 kg/hour and 38% oxidised at 80 kg/hour. The temperature was 450 °C during the tests (Lehtoranta et al., 2016).

In a comparison between Pd, Rh, and Pt, the palladium-based catalysts are more efficient at oxidising methane than rhodium and platinum. Palladium based catalysts are however sensitive to sulphur dioxide and deactivate at very low concentrations of SO₂ in the exhaust stream (de Wit et al., 2003). Natural gas can contain sulphur from odorizing additives in the gas. Another source of SO₂ in the exhaust can be sulphur from the lubricant oil. In dual fuel engines the ignition fuel contains sulphur and this is a major source of SO₂ in the exhausts from this type of engines.

A test with a Rh-based catalyst is described by de Wit et al., 2003. A catalyst was placed in the exhaust gases of a ship with a 1 MW gas-fuelled Caterpillar lean burn gas engine and monitored occasionally under a period of 5000 hours. The activity decreased rapidly during the first 1000 hours, which is explained as a consequence of the sulphur content of the exhausts. The remaining 4000 hours the activity remained at a stable level. The tests were conducted at 430°C and an oxidation of approximately 50% was achieved in the long run tests. The test also included measurements at higher exhaust temperatures and concluded that efficiencies were significantly higher at higher temperatures.

3.2.2 Three way catalyst

Three Way Catalyst (TWC) are, contrary to DOCs, used in exhausts after stoichiometric combustion. In order to ensure high conversions, the engine must be operated within a narrow air-to-fuel ratio window. There is first a reduction reaction over a catalyst where NO forms N₂, and secondly an oxidation reaction where hydrocarbons and carbon monoxide are oxidised to carbon dioxide and water. The three-way catalyst does not work under the lean burn conditions of the studied gas engines (CIMAC, 2014).

3.2.3 Heating of the exhaust gas stream

In order to assure the required exhaust gas temperatures of over 400°C, a burner can be installed between the engine and the catalyst. The burner will involve a fuel penalty, and the amount of fuel burned will also determine the temperature elevation. The burner will be placed upstream of the catalyst and may reduce costs for the catalysts as the operational conditions. The burner will also oxidise unburnt hydrocarbons in the exhausts, including methane to a minor extent (de Wit et al., 2003). Another option to heat the exhaust gases upstream a catalyst is to employ a burner at engine start up and use heat absorbing materials that elevate the temperature over the catalyst as the burner is stopped. It is also possible to make use of the heat that is generated at the oxidation reaction in the catalyst. De Wit et al. (2003) state temperature elevations in a range between 30°C and 50°C from catalysts at oxidation of carbon monoxide and uncombusted hydrocarbons from gas engines (de Wit, 2003). If heat exchange technology is used to capture the energy from the reaction, it would need an external energy supply at start up.

3.3 Discussions with catalyst manufacturers

Within this project two leading companies for catalyst aftertreatment were interviewed regarding their views on the status of systems for aftertreatment of methane slip from LNG-engines. Both confirm that this is a highly interesting topic and that they are working with research and development to be able to offer systems but that they are, at present, not ready. Both point at palladium (Pd) as the most active catalyst but also mentioned that other materials may be possible. The costs of Pd is one main issue. Further, the issues discussed here were confirmed: high temperature is needed and there are problems with deactivation in mixtures containing SO₂ and H₂O. One possibility may be to use low sulphur ignition fuel and to inject fuel in order to increase the catalyst temperature. The catalyst may also need to be regenerated at high temperature and rich (or stoichiometric) conditions.

4 Total emissions of methane from the fleet

A bottom up method based on information of existing LNG engines was used to estimate total emissions of methane from the global LNG-driven fleet. For each engine type and ship type, the LNG used to fuel the main engine is then calculated as energy according to the following:

$$E = P \times t \times EL$$

Where E is energy, P is installed power in the engine, t is time at sea, and EL is engine load at sea.

The calculations consider the following parameters:

- **Engine type:** The analysis is done separately for four gas engine types in order to account for the different emission factors and engine efficiencies. Further, for dual fuel engines the amount of energy in each stroke that can be attributed to the pilot fuel is slightly different, which is considered in the calculations.
- **Ship type:** specific information on engine types on different ship types has been used for this study. Further, the operating profiles differ for different ship types and can be due to different time requirements for loading and offloading/discharging, timetables and service demand. Literature values of typical operating profiles were found for bulk carriers, container ships, and tankers. We have used these values according to what is specified in Table 9. The time (t) spent at sea per year is calculated by multiplying the share of time at sea with the number of hours per year.
- Installed ME power (P) from tabulated values. We assume LNG is used only for main engine drive, and thus only time at sea is used in our calculations. This is not correct in all cases but information on auxiliary power is scarce and previous studies from the Swedish fleet indicate that MGO is used for auxiliary engines in many cases when LNG is used for the main engine (Yaramenka et al., 2019).
- Main engine load (EL) at sea is assumed to be on average 70%

Table 9. Estimated time at sea for different ship types. “Used values” are those values used in our calculations and are based and derived from the “Literature values”.

Ship type	No of ships / No of years	Total time at sea	Total time in port	Share of time at sea	Source
LITERATURE VALUES:					
Bulk carrier A ~5000 GT	1 / 1	-	-	57%	Johnson and Styhre, 2015
Bulk carrier B ~5000 GT	1 / 1	-	-	48%	Johnson and Styhre, 2015
Container ships, 8000 TEU	9 / 1	40.62	22.67	64%	Moon and Woo, 2014
Bulk carrier vessels	4 / 3	-	-	75%	Banks C, et al., 2013
Tanker, Handysize	1 / 2	-	-	43%	Banks C, et al., 2013
Tanker, Aframax	4 / 7	-	-	57%	Banks C, et al., 2013
Tanker, Suezmax	5 / 7	-	-	67%	Banks C, et al., 2013
Container ships, post panamax	2 / 9	-	-	67%	Banks C, et al., 2013
Container ships, post panamax plus	4 / 6	-	-	71%	Banks C, et al., 2013
Average (weighted by number of ships in the studies)				65%	-
USED VALUES:					
Bulk Carriers	-	-	-	67%	-
Container Ships	-	-	-	66%	-
Tankers (all types) 10 000 – 30 000 DWT (Handysize)	-	-	-	43%	-
Tankers (all types) 80 000 – 120 000 DWT (Aframax)	-	-	-	57%	-
Tankers (all types) 120 000 – 200 000 DWT (Suezmax)	-	-	-	67%	-
Tankers, other sizes	-	-	-	61%	-
All other	-	-	-	65%	-

There are many uncertainties and we have calculated a “central estimate” of LNG fuel combusted that we believe is most representative for the current LNG driven fleet. An important assumption for the central estimate is that LNG carriers are

assumed to only use LNG when laden. This is approximated as 50% of the time. However, market analysts have judged LNG carriers with dual fuel engines to increasingly use only LNG as fuel following the sulphur regulations of 2020 (McKinsey & company, 2019). Since 74% of all engine power in marine gas engines are found on LNG carriers, this assumption has a large effect on the results. Another assumption is that LNG is always used in the main engines on all other ship types, when the ships are at sea. For ships with dual fuel engines, this is of course optional, and this assumption may thus lead to an overestimation of the amount of used LNG. Another issue relates to data quality and data availability. We only included ships that were “in service/commission” which is vessels that are in the trading fleet.

In our minimum estimate we assume only 40% of time is spent at sea for all ship types. The lowest literature value for time at sea is 43%, representing Handysize tankers and this guides the minimum estimate. This is also a value indicating that 40% of the time spent at sea in LNG mode and thus accounts for some of the uncertainty relating to use of fuel oil in dual fuel engines. For the “minimum estimate” the engine load is set to 60%, and engine efficiency to 45%.

The maximum estimate is more than twice the central estimate. This is mainly due to the assumption that LNG tankers use LNG as main fuel 100% of their time. Another assumption that increases this value compared to the central estimate is that engine loads are 80% at sea. Like in the central estimate the time at sea is set to 70% and engine efficiencies are according to information from engine manufacturers.

Overviews of the calculated methane emissions are given in

Table 10 and Figure 3.

Table 10. Calculated amount of energy from LNG used in shipping 2019, the resulting methane emissions, and the corresponding CO₂-equivalents.

	Energy (TJ)			Methane emissions (tonnes)		
	Min. estimate	Central estimate	Max. estimate	Min. estimate	Central estimate	Max. estimate
2-Stroke Engines - HPDF	15 000	21 000	52 000	450	940	3500
2-Stroke Engines - LPDF	12 000	17 000	28 000	3200	6800	17 000
4-Stroke Engines - LBSI	6 600	12 000	13 000	2200	5800	10 000
4-Stroke Engines - LPDF	87 000	150 000	280 000	46 000	120 000	340 000
SUM	120 000	200 000	380 000	50 000	130 000	370 000
CO₂-e (100 år)	-	-	-	1 500 000	3 900 000	11 000 000
CO₂-e (20 år)	-	-	-	3 700 000	9 300 000	26 000 000

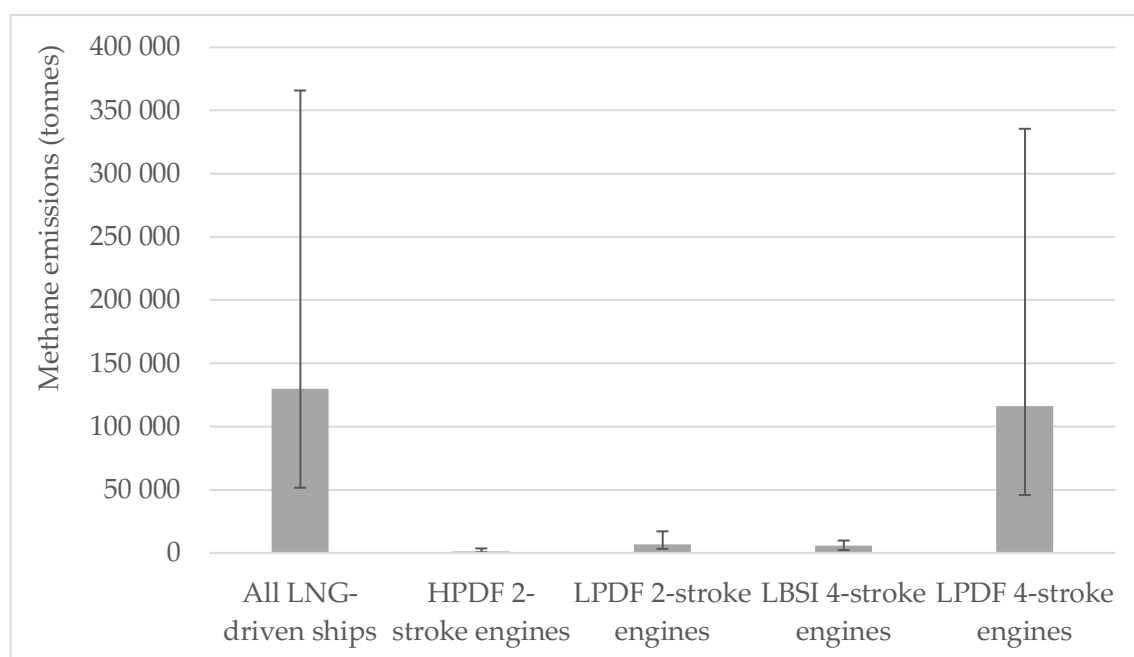


Figure 3. Calculated methane emissions from marine LNG engines 2019.

The values on CO₂-e emissions in

Table 10 can be compared to estimates of total emissions of CO₂-e from global shipping. IMO's latest estimate from the 4th GHG report was approximately 1080 million tonnes CO₂-e from global shipping in 2018 (IMO, 2020). ICCT used a similar methodology and estimated 932 million tonnes of CO₂-e emitted in 2015 (ICCT, 2017).

Two previous estimates of total methane emissions from global shipping have been found. In a study by ICCT, it was estimated that 363 000 tonnes methane were emitted from global shipping in 2015 (ICCT, 2017). Their model for calculation is based on AIS data signals, and they use an assumption that all LNG compatible ships use LNG as main fuel. The 4th IMO GHG report arrives at a figure very close to our central estimate. However, the IMO report uses an average CH₄ emission factor for LNG-engines of 12 kg/ton which is much lower than the emission factor we have used, approximately 34 kg/ton. On the other hand, the IMO report considers LNG consumption to be much higher than we do in our study, 11 million tonnes compared to 4 million tonnes, approximately. The main reason is that they include consumption in, and emissions from, steam turbines on LNG carriers in their estimate. This gives the relatively low average emission factor, and, due to an assumption that all LNG compatible engines use only LNG, the total volume of LNG is higher than ours. The resulting estimate of total emissions of methane from LNG as marine fuel is approximately the same, 140 000 tonnes. Some details are given in Table 11.

A top-down approach could be possible if data on the supplied LNG bunker for shipping were available. Since the number of LNG driven ships increase steadily these data are only relevant if they are very recent. No such statistics were available to this study.

Table 11. Input values and results on methane emissions from global shipping in the 4th IMO GHG report (IMO 2020), ICCT (2017), and this study (EF = emission factor).

	4th IMO GHG study (IMO 2020)	ICCT, 2017	This study (central estimate)
LNG consumption (million tonnes)	11	2% of 298 Mtonnes (Mt) (appr. 6 Mt)	4
CH₄ EF (ton/1000 tonne)	12	-	34
Total emissions (tonne)	140 000	360 000	130 000
EF CH₄ MGO and HFO (kg/tonne)	0.05	-	-
Total consumption HFO + MGO	326	-	-
Total emissions CH₄ (tonnes)	16 300	-	-
Year	2018	2015	2019

IEA summarizes annual global methane emissions to around 570 million tonnes (Mt), although subject to a high degree of uncertainty. Natural sources contribute approximately 40% of emissions, while the rest are from human activities. Of the human, or anthropogenic sources, agriculture and the energy sector are the two largest (<https://www.iea.org/reports/methane-tracker-2020>).

5 Sustainability of the different options

The use of the different options to oxidise methane in the exhaust gases are associated with resource use that could be considered in an environmental trade-off with the benefits of the reduced emissions of GHGs.

Exhaust gas catalysts contain one of the three metals platinum, palladium, or rhodium, from the platinum group metals (PGM). All PGMs are rare metals in the earth's crust. A review for the European Commission further classifies the PGMs as critical raw materials in an evaluation matrix with the parameters supply risk and economic importance (European Commission, 2017). Supply risks relate to the most critical points of the raw material production stages in the supply chain. Of the PGMs, the main global supplier of rhodium and platinum is South Africa, while Russia is the largest supplier of palladium. The total reserves of PGM is 69 000 tonnes, of which South Africa has 91%. Resources in total are estimated to be more than 100 000 tonnes. (European Commission, 2017)

The amount of PGM used in a catalyst for methane oxidation after a marine LNG engine needs to be estimated on a case by case basis. Assuming a truck engine of 350 kW uses approximately 30 g, and that the mass of PGM needed is linearly correlated with installed engine power, a marine engine of 6000 kW would then need approximately 500 g. A catalyst manufacturer similarly estimates a need for approximately 500 g Pd at an exhaust gas flow of 30 000 m³/h.

The withdrawal of metals from the earth's crust can be argued to be unsustainable. Using it for different technical applications causes it to disperse in the technosphere and can make it significantly more difficult for future generations to use the metal. According to one evaluation model that is used in life cycle assessment studies, resource depletion is for this reason valued highly (Steen, 2016). According to this model the Pd and Pt catalysts used need to be able to treat the exhausts for 5.1 and 5.7 years respectively to have a positive environmental impact (IVL, 2015). That is, after approximately three years, the value of avoided environmental impacts from methane emissions are higher than the value for elemental depletion. Rhodium is scarcer than the other two, and the Rh-based catalyst would have to work for more than 150 years to be beneficial from an environmental perspective according to the model. Assumptions include an annual LNG consumption of 4 500 tonnes, a slip of 3.5%, and 500 g PGM in the catalyst. Other evaluation models do not assign the long-term perspective a similar importance. As a consequence, the elemental depletion has fewer relative values in those evaluation models.

A sustainable use of scarce metals requires well-functioning recycling processes. Catalysts from trucks have been reported to be worn down during use, but the recycled material from catalysts used in vehicles is still an important contributor to

the 120 tonnes of palladium and platina that were recycled in 2018. The recycling in 2018 corresponded to approximately 30% of the primary production (US Geological Survey, 2020; Emilsson Dahllöf, 2020). According to a web article published by Thermo Fisher Scientific, the recoverable amounts of Pt, Pd, and Rh can range from 1-2 grams for a small car to 12-15 grams for a big truck (Thermofischer, 2014). The amount of PGM, the metal loading, used in the catalysts in cars varies from 1 g for the smallest vehicles to 15 g for the largest most powerful, and is on average 4-5 grams (Johnson Matthey, 2012).

The price for Rhodium has risen steadily since the beginning of 2018. The Palladium price also appears to have an increasing trend, while the price for Platinum has fallen slightly since 2015, see Figure 4.

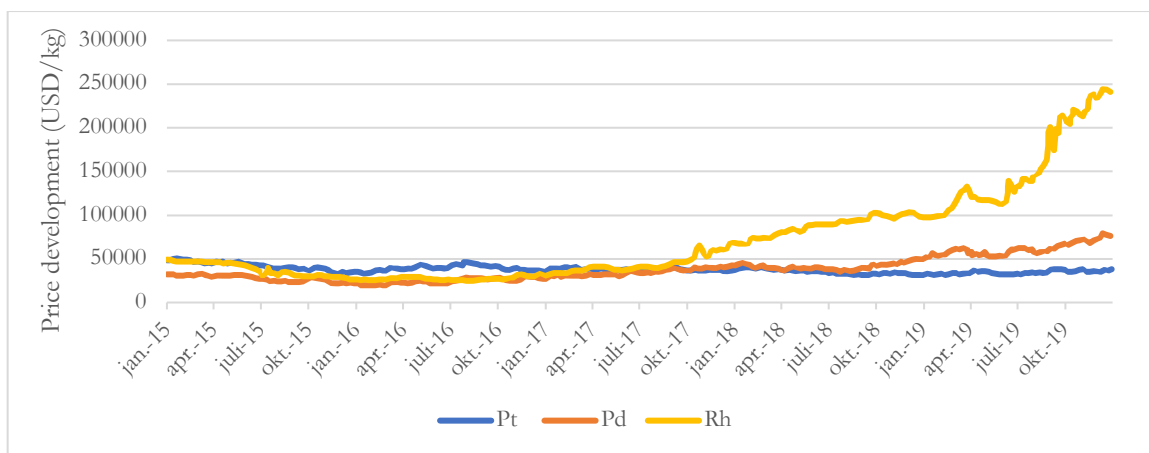


Figure 4. Price development for Pt, Pd, and Rh, unit USD/kg.

Sustainability issues connected to the non-thermal plasma technology studied here are expected to mainly be associated with the high need for energy to create the plasma. The extents of these are not explored in detail in this work.

6 Tests of methane oxidation in Daphne Technology's R&D Facility

Due to the environmental effects from methane slip from LNG-powered ships, Daphne Technology has investigated methane removal from exhaust gas (on a laboratory scale at their R&D Facility in Lausanne, Switzerland) with its patented (EP3356018B1) catalyst-free gas purification system (Figure 5 a and b). As the main component of this system, the Daphne Reactor generates high-energy electrons to initiate the breakdown of pollutant gases, akin to NTP-induced gas cleaning.

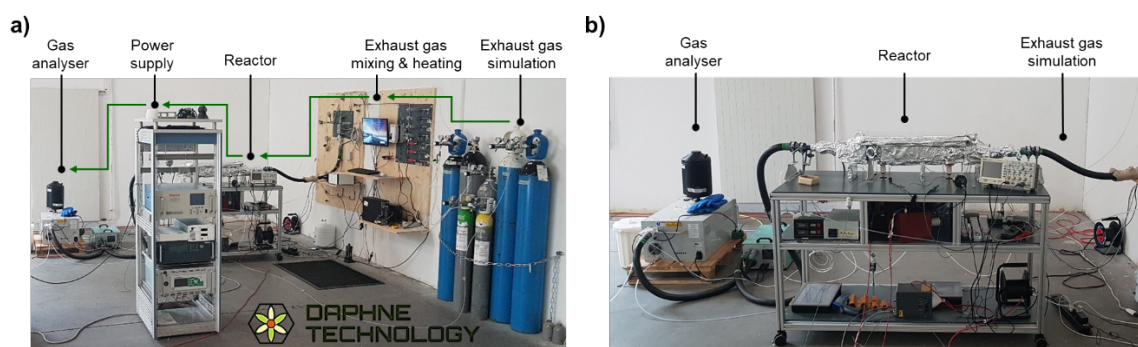


Figure 5 a) Custom in-line, continuous testing setup developed at Daphne Technology. b) Highlight of the Daphne Reactor with gas analyzer for exhaust gas purification.

Daphne Technology has developed a customized and continuous through-process system that monitors exhaust gas compositions, which is used to monitor pollutant breakdown with its patented reactor (Figure 5 a). An exhaust gas chemical profile from an engine (including humidity and temperature) is first replicated via mixing of individual gases (exhaust gas simulation). The simulated exhaust gas passes through Daphne’s Reactor (that is powered by a high-voltage power supply) and a multicomponent FTIR gas analyzer records the concentrations of the individual gas species.

A typical composition of exhaust gas from a hypothetical 500 kW LNG-fuelled engine (exhaust flow rate of 3500 kg/h) is shown in Figure 6a, whereby a methane slip of 4.1-6.9 g/kWh is equivalent to 585-986 ppm(m). Daphne replicated this exhaust gas mix at their R&D Facility (Figure 6b), passed 4 L/min of it through their reactor at 190 °C, and monitored the breakdown of methane and concomitant product formation with a multicomponent FTIR gas analyzer (as depicted in Figure 5). By varying the voltage applied to the reactor (equivalent to varying the power inputted into the exhaust gas), they observed up to 835 ± 20 ppm(v) or 3.1 ± 0.1 g/kWh of methane removed from the exhaust gas (Figure 6c).

As expected, the main components of methane oxidation via the reactor were carbon monoxide and carbon dioxide (Figure 6d). The low exhaust gas temperature used in the experiments (190 °C) highlighted that the reactor did not require high temperatures for operation, in opposition to current methane oxidation catalysts; there is no minimum temperature requirement for the reactor to function and additional experiments have shown that the methane removal efficiency increases with increased temperature. Furthermore, the reactor is not ‘poisoned’ by high amounts of water (>10% v/v) or SO₂ (the reactor breaks down SO₂).

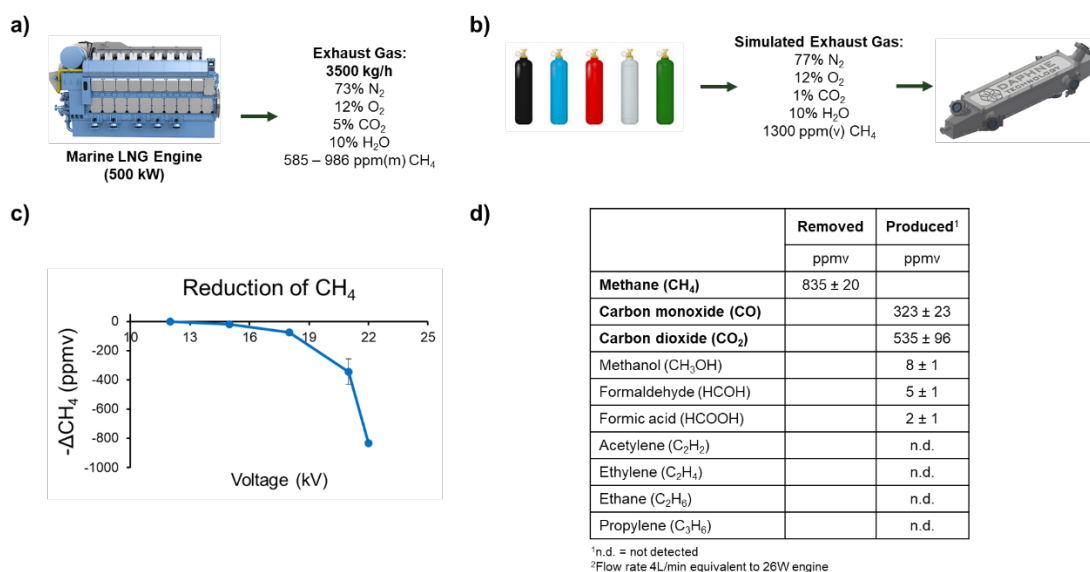


Figure 6 a) Exhaust gas composition from a hypothetical 500 kW LNG engine (exhaust gas flow rate of 3500 kg/h). b) Replication of the exhaust gas composition at Daphne Technology. c) Graph of methane oxidation with the Daphne Reactor. d) Gas concentrations recorded from a multicomponent gas analyzer from methane oxidation with the Daphne Reactor.

A scale-up of their continuous through-process system and reactor has also been developed at Daphne's facility in Gothenburg, Sweden (Figure 7). Built into an open-sided, 20' shipping container, the system is capable of handling exhaust gases at flow rates exceeding 70 m³/min. At present, the system is connected to an 18 L Caterpillar diesel engine (Type 3408 B; 330 kW at 1500 rpm) running with high sulphur fuel oil, and has demonstrated simultaneous removal of sulphur oxides (SO₂) and nitrogen oxides (NO_x) from exhaust gas. The system is being modified to include methane slip in exhaust gas to monitor methane oxidation.



Figure 7. Scaled-up design (left) and construction (right) of Daphne's custom through-process exhaust gas monitoring system with Reactor to break down pollutant gases.

7 Case study on a low-pressure dual fuel engine

An existing gas-fuelled ship with a 4-stroke low pressure dual fuel engine was used as the basis of a case study to estimate the approximate cost and technical feasibility of a catalyst installation to reduce methane emissions. The vessel chosen was the *M/T Fure West*.

The *M/T Fure West* is a 17 557 DWT product tanker with length overall (LOA) of 144 m and beam of 21.5 m (see Figure 8). The operator is the Furetank shipping company. Furetank currently has three LNG dual fuel vessels in service and two under construction. The other two LNG vessels in service, *Fure Valo* and *Fure Ven*, are newbuilds brought into service in 2018 and 2019 respectively. They each have single 9L34DF Wärtsilä 4-stroke engine, with 4500 kW installed power. The two vessels under construction, *Fure Vinga* and *Fure Viten*, will also have 9L34DF Wärtsilä 4-stroke engines with 4500 kW installed power. The Wärtsilä 9L34DF, a medium speed low-pressure dual fuel engine, is used by other ship owners in the Gothia Tanker alliance, including Thun Tankers and UniTankers.

The *M/T Fure West* was built in 2006, and was converted to LNG operation in 2015/2016 as part of the project LNG CONV. The vessel's original MaK M43C engine was converted to an MaK 7M46DF engine that can operate on either gaseous or liquid fuels (Markström et al., 2017). The engine is a 4-stroke low pressure dual fuel with a maximum power output of 6300 kW at 500 rpm. The M46DF engine requires injection of a small amount of diesel fuel (maximum 5%) for ignition when operating in gas mode. IMO tier III emission limits are met in gas mode and Tier II emission levels are met when the engine is in diesel mode.



Figure 8. A photo of *M/T Fure West* with the LNG tanks digitally rendered (source: Kalantari et al., 2016).

Vessel particulars for *M/T Fure West* are shown below in Table 12.

Table 12. Selected Vessel Particulars of the M/T Fure West.

Vessel Particulars:	
Main Dimensions:	
Length Over all (LOA)	144 m
Breadth	21.5 m
Depth	12.5 m
Machinery:	
Main Engine	MaK M46DF: 6300 kW medium speed 4-stroke dual-fuel diesel with MDO pilot fuel ignition, fitted with SCR for NO _x reduction
Auxiliary Engines	3 x 910 kW (MDO)
Fuel Capacity:	
LNG	500 m ³
Distillate fuel oil	112 m ³

7.1 Exhaust Gas Characteristics for the case study engine

Exhaust gas temperature and flow at varying engine loads for the MaK M46DF in gas mode are shown in Table 13.

Table 13. Exhaust Gas Temperature and Flow for the MaK M46DF Engine in Gas Mode (Caterpillar Motoren GmbH, 2016).

Power/ Torque (%)	100	75	50	25
Exhaust Flow (kg/h)	33682.1	26438.5	17759.1	9628.6
Temperature °C	346	382	409	450

Tests on Fure West give an approximate flow of 9 500, 15 000, 26 000, and 31 000 m³/h at 26, 50, 72, and 93% engine load respectively (personal communication, Furetank). Corresponding mass flows are 12 000, 20 000, 33 000, and 40 000 kg/h, in order of ascending engine loads.

7.2 Catalyst System Description

The catalyst system used for the case study is a palladium catalyst. Methane oxidation catalysts are appropriate for use with lean burn gas engines, because oxygen is needed in the reaction (Majewski and Jääskeläinen, 2020). Although the palladium catalyst is considered the most active of the methane oxidation catalysts, they should be operated at temperatures of around 500 °C to achieve a high methane conversion (Majewski and Jääskeläinen, 2020; Stenersen and Thonstad, 2017). There is, however, ongoing research to assess how to measure and optimise performance of the palladium catalysts in the lean burn gas engine exhaust typical temperature range (Nitta and Yamasaki, 2019). Good CH₄ removal performance has been exhibited in the 350 to 400 °C range with a palladium catalyst (Nitta and

Yamasaki, 2019). Palladium catalysts are very sensitive to sulphur and will be deactivated by even trace amounts in the exhaust gas (Majewski and Jääskeläinen, 2020; Stenersen and Thonstad, 2017).

7.3 Cost Assessment Components

Life cycle costs for ships typically include investment costs (design, construction), operating costs, and end of life costs including scrapping and recycling. Costs considered for this overview assessment of a methane catalyst installation on the *M/T Fure West* were limited to those associated with investment (CAPEX) and operation (OPEX) related to the catalyst. Life termination costs were excluded from the analysis. There are currently no methane oxidation catalysts commercially available or installed on ships. Thus, the cost estimates for the equipment components are based on extrapolation from other catalyst applications (gas engines in automotive and stationary power applications) and should be considered very approximate.

7.3.1 CAPEX Cost Estimates

CAPEX costs for the methane oxidation catalyst could include the following:

- Detailed system design and approval for placement on board the ship
- Catalyst component costs (catalyst, housing, insulation)
- Catalyst installation costs at a shipyard, including piping, ducting, and if necessary, strengthening of structural supports due to weight and placement
- Auxiliary system such as a heater to increase exhaust gas temperatures if determined necessary by the catalyst manufacturer.

Of the above costs, only the methane oxidation catalyst and system installation costs were estimated at this time, as described below:

Methane Oxidation Catalyst

According to information from catalyst suppliers, the cost for a palladium-based catalyst sized to treat the emissions from an LNG-powered lean burn engine with a maximum exhaust gas flow of 30 000 m³ per hour can be estimated to about 30 000 Euro. The dominant cost contributor is the Pd metal cost itself, which is currently on a high level and is subject to fluctuations over time. Further, this estimate was based on a linearly scaled manufacturing cost for a comparable methane-powered lean burn engine for trucks.

A second cost estimate was calculated based on costs presented in CIMAC's position paper on gas engine aftertreatment systems (CIMAC, 2017). These estimates were developed for stationary, 4-stroke natural gas engines up to 3 MW. The cost for oxidation catalysts were stated as follows:

- Aftertreatment component costs: 5-10% of engine cost
- Aftertreatment installation costs: 1-3% of engine cost (CIMAC, 2017).

The component costs include catalyst, housing, and insulation. Using an installed kW price of 627 USD/kW hour (Wärtsilä, 2017) for a medium gas engine

(Wärtsilä, 2017), and the case study engine power of 6300 kW, the cost of the oxidation catalyst is as follows:

- Low (5% for component costs and 1% for installation cost): 208 000 EUR
- High (10% for component costs and 3% for installation costs): 450 565 EUR

For a marine installation, it is expected that the costs for components and installation would be higher than for a land-based installation. Ships at sea are subjected to wind and waves and the equipment must be able to operate reliably under specified pitch, roll, and range of angles of inclination. Thus, the higher estimate from above is expected to be reasonable to use in the cost estimate. The difference between the estimate by a catalyst manufacturer and CIMAC position paper is believed to illustrate the difficulties in estimating costs for products not yet commercially available on the market.

7.3.2 OPEX

OPEX costs for a methane catalyst installation would include the following:

- Catalyst maintenance costs – cleaning and replacing. CIMAC (2017) estimates that this should be done every 10 000 to 20 000 hours.
- Increased fuel costs due to:
 - Requirement to use 0.001% S fuel for the pilot fuel rather than the cheaper 0.1% S fuel, due to catalyst sensitivity to sulphur
 - Fuel penalty due to catalyst operation (catalyst regeneration, heating if required, etc.)
- Training costs for catalyst operation

For this case study, only the increased fuels costs and fuel penalty were estimated for the OPEX.

Annual Increased Fuel Costs for Pilot Fuel

To avoid catalyst poisoning, fuel with a lower sulphur content is needed for the approximately 5% pilot fuel used when operating the engine in gas mode. During 2019, the M/T Fure West had the following fuel consumption in the main engine (Gustafsson personal communication):

- LNG: 1 420 502 kg
- MDO: 477 456 kg

Based on an average 5% pilot fuel needed for ignition when the engine is in gas mode (Gustafsson personal communication), 71 205 kg of pilot fuel is used annually.

Possibilities within the Swedish market for fuel with a suitably low sulphur content include MK 1 diesel fuel (Swedish environment class 1 diesel), which is a distillate fuel with less than 10 ppm sulphur (0.001%), which is used for road vehicles and also for the Swedish Road Ferries vessels. Preem also produces a product called “Gas Oil Minima” that has a maximum sulphur content of 10 ppm. European directives for inland waterway vessels also require a maximum sulphur

content in fuel of 10 ppm, thus this fuel quality is available widely, although not always produced solely as a product for the marine market.

Using data from The Swedish Transport Administration (2020), MK1 is estimated to cost 6288 SEK per tonne while MDO is 4080 SEK per tonne (based on 2017 prices). This is a differential of 214 EUR per tonne.

Thus, annual additional fuel costs from using 0.001% S pilot fuel are as follows:

- Option 1: MK1 is used only for the 5% pilot fuel: 15 212 EUR
- Option 2: MK1 is used for pilot fuel plus liquid fuel operation: 102 260 EUR

Fuel penalty for catalyst operation: Periodic changes in temperature and exhaust gas composition are necessary for catalyst regeneration. Research for automotive applications is directed towards finding methods that can be employed with minimal impact on fuel penalty (Kinnunen et al., 2017). Data on fuel penalty for methane oxidation catalyst for use with a marine dual fuel engine similar to the case study could not be found. An assumption of 1% was used in the operating cost estimate. This 1% was applied to the total amount of fuel used, resulting in an estimated fuel penalty cost of 7500 EUR.

7.3.3 Cost Data Summary

The estimates for investment costs and annual operational costs are summarized in Table 14.

Table 14. Cost data summary.

Cost categories	Costs (EUR)
Investment Costs	
Methane Oxidation Catalyst	450 000
Annual Operational Costs	
Differential for lower S pilot fuel	102 260
Fuel penalty for catalyst operation (regeneration)	7 500

8 Conclusions and recommendations

We have not been able to identify any commercially available method that in its present state can be used to efficiently abate methane emissions in the exhaust gases from marine LNG engines. However, activities are on-going at catalyst manufacturers to develop methane oxidation catalysts for marine applications. Another technology that we have studied in detail for this work is based on non-thermal plasma.

Literature and discussions with catalyst manufacturers indicate a deactivation of the catalysts over time in the prevalent exhaust gas conditions of marine engines. The plasma technology studied here is efficiently reducing methane in laboratory tests but has high energy requirements for the plasma generation. Further development of this technology is planned.

The particulars of marine exhaust gas that make it difficult to use methane catalysts are high sulphur content, high water content and low temperatures. The use of “very low sulphur” or “no-sulphur” pilot fuel in dual fuel engines would be one step towards introducing methane aftertreatment on ships, and scheduled regeneration of the catalysts by elevated temperatures and rich (or stoichiometric) combustion conditions would be needed.

The sustainability issues associated with the considered treatment technologies are the use of critical raw material in oxidation catalyst and the energy needed for efficient oxidation of methane in the plasma technology.

Our case study shows that the investment costs for an oxidation catalyst on a 6300 kW engine could be around 450 000 euro and that operational costs are approximately 110 000 euro per year.

Besides the development of technologies mentioned above, we suggest that future work on the subject involves detailing a catalyst regeneration process in the exhausts of marine LNG engines. This is a crucial step for any future demonstration project. We also propose that further work involves studies on potential regulations and incentives to reduce the methane emissions from ships, in order to increase interest in aftertreatment of methane emissions.

9 Referenser

EG/595/2009, 2009, EUROPAPARLAMENTETS OCH RÅDETS FÖRORDNING (EG) nr 595/2009 av den 18 juni 2009 om typgodkännande av motorfordon och motorer vad gäller utsläpp från tunga fordon (Euro 6) och om tillgång till information om reparation och underhåll av fordon samt om ändring av förordning (EG) nr 715/2007 och direktiv 2007/46/EG och om upphävande av direktiven 80/1269/EEG, 2005/55/EG och 2005/78/EG

American Petroleum Institute, 2015. Liquefied Natural Gas (LNG) Operations – Consistent Methodology for Estimating Greenhouse Gas Emissions, Version 1.0 prepared by Levon LLC.

Anderson M., Salo K. and Fridell E. 2015. Particle- and gaseous emissions from an LNG powered ship, *Environmental Science & Technology* (49), pp. 12568-12575.

Banks C, Turan O., Incecik A., Theotokatos G., Izkan S., Shewell C. and Tian X., Understanding ship operating profiles with an aim to improve energy efficient ship operations, Low carbon shipping conference, London 2013.

Baresic, D., Smith T., Raucci, K., Rehmatulla, C., Narula, N. and Rojon, I. 2018. LNG as a marine fuel in the EU: Market, bunkering infrastructure investments and risks in the context of GHG reductions, UMAS, London.

Bengtsson S., Fridell E. och Andersson K., 2012. Environmental assessment of two pathways towards the use of biofuels in shipping., *Energy Policy* 44 (2012) 451-463.

Brynolf, S., Fridell, E., Andersson, K., 2014. Environmental assessment of marine fuels: liquefied natural gas, liquefied biogas, methanol and bio-methanol. *Journal of Cleaner Production* 74, 86-95.

Caterpillar Motoren GmbH & Co. KG. 2016. Emission Test Report Parent Engine MaK M46DF.

Chu, Paul K.; Lu, XinPei, CRC Press **2013**, Low Temperature Plasma Technology: Methods and Applications.

CIMAC, 2014. Methane and Formaldehyde Emissions of Gas Engines, CIMAC Position Paper 04/2014.

CIMAC WG 17, 2017. Gas Engine Aftertreatment Systems. CIMAC Position Paper 05/2017. International Council on Combustion Engines.

de Wit J., Johansen K., Hansen P., Rossen H., and Rasmussen N., 2003. Catalytic emission control with respect to CH₄ and CO for highly efficient gas fueled decentralized heat and power production, Danish Technology Centre and Haldor Topsoe, available at https://www.dgc.dk/sites/default/files/filer/publikationer/C0001_catalytic_emission_control.pdf

European Commission, 2017. Study on the review of the list of Critical Raw Materials – Criticality Assessments, by Deloitte Sustainability, British Geological

Survey, Bureau de recherches Géologiques et Minières, and Netherlands Organisation for Applied Scientific Research (TNO)

Huan, T., Hongjun, F., Wei, L., and Z. Guoqiang. 2018. Options and Evaluations on Propulsion Systems of LNG Carriers. IN Propulsion Systems, edited by A. Serpi and M. Porru.

ICCT, 2017, Greenhouse gas emissions from global shipping, 2013-2015, by Olmer N., Comer B., Roy B., Mao X., and Rutherford D.,

IEA-AMF, 2020, Technology Collaboration Program (TCP), Annex 51: “Methane Emission Control”.

IMO, 2018. Note by the International Maritime Organization to the UNFCCC Talanoa Dialogue: Adoption of the initial IMO strategy on reduction of GHG emissions from ships and existing IMO activity related to reducing GHG emissions in the shipping sector.

IMO, 2020. 4th IMO GHG Study - Final report, prepared by Faber et al. for the IMO, MEPC 75/7/15.

IPCC, 2013. Climate Change 2013: The Physical Science Basis. Contribution of Working Group I to the Fifth Assessment Report of the Intergovernmental Panel on Climate Change [Stocker, T.F., D. Qin, G.-K. Plattner, M. Tignor, S.K. Allen, J. Boschung, A. Nauels, Y. Xia, V. Bex and P.M. Midgley (eds.)]. Cambridge University Press, Cambridge, United Kingdom and New York, NY, USA, 1535 pp.

ISWG-GHG 7/3, Further consideration of concrete proposals to reduce methane slip and emissions of volatile organic compounds (VOCs), Proposal to include all greenhouse gases emitted from ships including methane in the EEDI, Submitted by FOEI, WWF, Greenpeace International, Pacific Environment and CSC, 7 Feb 2020.

ISWG-GHG 7/3/1, Further consideration of concrete proposals to reduce methane slip and emissions of volatile organic compounds (VOCs), Information and proposal for the reduction of methane slip from ships, submitted by SGMF, 7 Feb 2020.

IVL, 2015. Environmental Priority Strategies (EPS), EPS version 2015d, Web data resource: <https://www.ivl.se/english/startpage/pages/our-focus-areas/environmental-engineering-and-sustainable-production/lca/eps.html>. Accessed 2020-02-25.

Johnson H. and L. Styhre, 2015. Increased energy efficiency in short sea shipping through decreased time in port, Transportation research Part A 71, 167-179.

Johnson Matthey, 2012, PGM loading and recycling rates in autocatalysts, web page accessed 2020-08-17 at <https://www.technology.matthey.com/resources/view-questions-answers/pgm-loading-recycling-rates-autocatalysts/>

- Kalantari, J. (ed.). 2016. Activity 7 – Compilation and Evaluation of Results. Report from Pilot LNG project - LNG Bunkering Infrastructure Solution and Pilot actions for Ships operating on the Motorway of the Baltic Sea.
- Kimpton K. and Brown M., 2010, Investigations on new acceptable EU limits for gas quality. Influence on the performance of new and installed gas appliances. Study Project, GASQUAL DELIVERABLE D1.3. Future Gas Profiles.
- Kinnunen, N.M., Hirvi, J.T., Kallinen, K., Maunula, T., Keenan, M., and M. Suvanto. 2017. Case study of a modern lean-burn methane combustion catalyst for automotive applications: What are the deactivation and regeneration mechanisms? *Applied Catalysis B: Environmental* 207, pp. 114-119.
- Le Fevre C.N., 2018. A review of demand prospects for LNG as a marine transport fuel, the Oxford Institute for Energy Studies, OIES PAPER: NG 133
- Lehtoranta K., Murtonen T., Vesala H., Koponen P., Alanen J., Simonen P., Rönkkö T., Timonen H., Saarikoski S., Maunala T., Kallinen K., and Korhonen S., 2016. Natural Gas Engine Emission Reduction by Catalysts, *Emiss. Control Sci. Technol.*, DOI 10.1007/s40825-016-0057-8.
- Lehtoranta K., Aakko-Saksa P., Murtonen T., Vesala H., Kuittinen N., Rönkkö T., Ntziachristos L., Karjalainen P., Timonen H., and Teinilä K., 2019. Particle and Gaseous Emissions from Marine Engines Utilizing Various Fuels and Aftertreatment Systems, *CIMAC* 2019/399.
- Lehtoranta K., Aakko-Saksa P., Murtonen T., Vesala H., Ntziachristos L., Rönkkö T., Karjalainen P., Kuittinen N., and Timonen H., 2019a. Particulate Mass and Nonvolatile Particle Number Emissions from Marine Engines Using Low-Sulfur Fuels, Natural Gas, or Scrubbers, *Environ. Sci. Technol.* 2019, 53, 3315–3322.
- Lipsith, G. 2019. Under pressure: Competition over dual-fuel concepts intensifies. *Riviera Maritime Media Ltd.* Available: <https://www.rivieramm.com/opinion/opinion/under-pressure-competition-over-dual-fuel-concepts-intensifies-55388> Accessed: 20200401
- Majewski, W.A., and H. Jääskeläinen. 2020. Methane Oxidation Catalysts. *Diesel Net.* Available: https://dieselnet.com/tech/catalyst_methane_oxidation.php.
- MAN Diesel & Turbo, 2015. Exhaust Gas Emission Control Today and Tomorrow Application on MAN B&W Two-stroke Marine Diesel Engines.
- MAN Diesel & Turbo, 2015a. ME-GI Dual Fuel MAN B&W Engines - A Technical, Operational and Cost-effective Solution for Ships Fuelled by Gas.
- MAN. 2020. Lower the pressure on your capital cost. Copenhagen: MAN. Available <https://www.man-es.com/marine/products/megi-mega/me-ga>.
- Marintek, 2010. Emission factors for CH₄, NO_X, particulates and black carbon for domestic shipping in Norway, revision 1, by Nielsen J.B. and Stenersen D. for Klima og forurensningsdirektoratet, Report no 222232.00.02.

- Markström, L., Örtberg, A., Andersson, A., Forsman, N., Ellis, J., and O. Lundbäck. 2017. ENVISWITCH Sustainable environmental switch to LNG machinery in existing fleet. Deliverable D1.3 Final Report. SSPA: Göteborg.
- Matsumoto, Takao; Wang, Douyan; Namihira, Takao & Akiyam, Hidenori, **2012**, *Non-Thermal Plasma Technic for Air Pollution Control*.
- McKinsey & Company, 2019. web-article: Forced boil-off gas: The future of LNG as a fuel for LNG carriers, by Nafie Bakkali and Loukas Ziomas, available at <https://www.mckinsey.com/industries/oil-and-gas/our-insights/forced-boil-off-gas-the-future-of-lng-as-a-fuel-for-lng-carriers>
- Monks, Paul S. 2005. *Chem. Soc. Rev.*, **34**, 376–395
- Moon and Woo, 2014. The impact of port operations on efficient ship operation from both economic and environmental perspectives, *Maritime Policy & Management*, 41, 5, 444-461.
- Moreau, M., N. Orange, and M. G. J. Feuilloley. 2008. Non-thermal plasma technologies: New tools for bio-decontamination. *Biotechnology Advances* **26** (6):610–617.
- Mörkkåsa Sandvik H., 2016. Catalysis for Control of Methane Sip in Marine Machinery – using a Palladium based Catalyst, PhD thesis NTNU Department of Chemical Engineering.
- Nitta, Y., and Y. Yamasaki. 2019. Evaluation of effective active site on Pd methane oxidation catalyst in exhaust gas of lean burn gas engine. ICEF2019-7152. Proceedings of the ASME 2019 Internal Combustion Engine Division Fall Technical Conference. ASME.
- Nylund I., Alder R., Hirose T., Umemoto Y., and Yamada T., 2016. The 2-stroke Low-Pressure Dual-Fuel Technology: From Concept to Reality, CIMAC 2016, Paper 233.
- Pavlenko N., Comer B., Zhou Y., Clark N., and Rutherford D., 2020. The climate implications of using LNG as a marine fuel, ICCT working paper 2020-02.
- Raj A., 2016. Methane Emission Control, *Johnson Matthey Technology Review*, 60 (4) 228-235.
- Roosjen S., and Meyer F., 2020. Low temperature methane oxidation for industrial and maritime lean-burn gas engines: An experimental study
MANUSCRIPT IN PREPARATION
- Scholtz, Vladimir, Jarmila Pazlarova, Hana Souskova, Josef Khun, and Jaroslav Julak. 2015. *Nonthermal plasma — A tool for decontamination and disinfection*. *Biotechnology Advances* **33** (6, Part 2):1108–1119.
- Schuller O., Kupferschmid S., Hengstler J., and Whitehouse S., 2019. Life Cycle GHG Emission Study on the Use of LNG as Marine Fuel – Final report, for SEA\LNG Limited, and Society for Gas as a Marine Fuel Limited (SGMF).

Sea-lng.org, 2020. <https://sea-lng.org/why-lng/global-fleet/> accessed August 2020.

Sharafian, A., Blomerus, P., and W. Mérida. 2019. Natural gas as a ship fuel: Assessment of greenhouse gas and air pollutant reduction potential. *Energy Policy* 131, pp. 332-346.

Shine K., 2009. The global warming potential-the need for an interdisciplinary retrieval; an editorial comment, *Climatic change* (2999) 96:467-472.

Steen B., 2016. Calculation of Monetary Values of Environmental Impacts from Emissions and Resource Use - The Case of Using the EPS 2015d Impact Assessment Method, *Journal of Sustainable Development*; Vol. 9, No. 6; 2016.

Stenersen, D. and O. Thonstad. 2017. GHG and NOx emissions from gas fueled engines. Trondheim: Sintef.

Takamura, N., Wang, D., Seki, D., Namihira, T., Yano, K., Saitoh, H., Akiyama, H. **2012**. *International Journal of Plasma Environmental Science & Technology*, Vol.6, No.1, 59-62.

Thermodis, 2014. web-article: Platinum Group Metal Recovery from Spent Catalytic Converters Using XRF, by Stephen Dietz, available at <https://www.thermodis.com/blog/metals/platinum-group-metal-recovery-from-spent-catalytic-converters-using-xrf/>

Thomson H., Corbet J. J., and Winebreak J. J., 2015, Natural gas as a marine fuel, *Energy Policy* 87 (2015) 153-167.

Tractebel Engineering, 2015. CNG for commercialization of small volumes of associated gas, for World bank group energy & Extractives and GGFR, available at: <http://documents.worldbank.org/curated/en/210571472125529218/pdf/104200-V2-WP-CNG-commercialization-PUBLIC-Main-report-REPLACEMENT.pdf>

The Swedish Transport Administration (Trafikverket), 2020. Analysmetod och samhällsekonomiska kalkylvärden för transportsektorn: ASEK 7.0. Kapitel 14 Operativa trafikeringkostnader för godstransporter.

Tu, X and Whitehead J. C., *Applied Catalysis B: Environmental*, 125 (2012) 439– 448

Uniongas, 2020. <https://www.uniongas.com/about-us/about-natural-gas/Chemical-Composition-of-Natural-Gas>, accessed 2020-05-11

U.S. Geological Survey, 2020. Mineral commodity summaries 2020: U.S. Geological Survey, 200 p., <https://doi.org/10.3133/mcs2020>

Ushakov S., Stenersen D., and Einang P.M., 2019. Methane slip from gas fuelled ships: a comprehensive summary based on measurement data, *Journal of Marine Science and Technology* 24, 1308-1325.

WIN GD, 2020. X-DF2.0 Technology, web page accessed 2020-09-11, available at <https://www.wingd.com/en/technology-innovation/engine-technology/x-df-dual-fuel-design/x-df2-0-technology/>

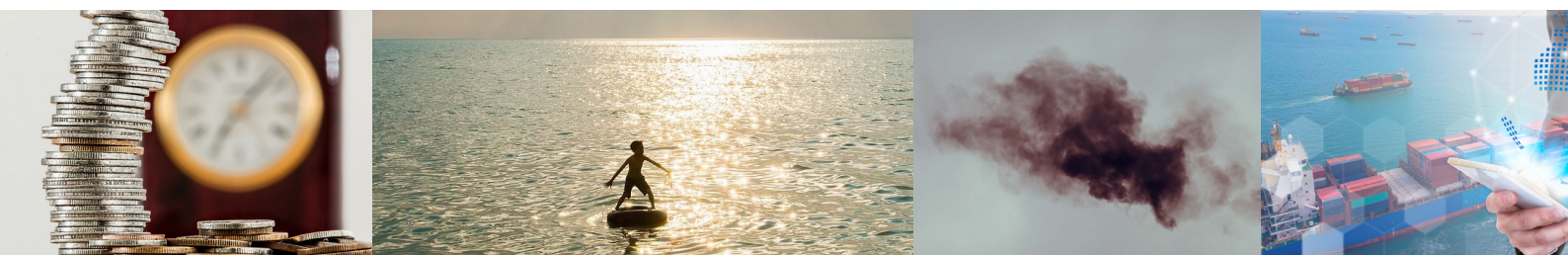
Winnes H., Brynolf S., Hjort A., and Yaramenka K., 2020. LNG och LBG som fartygsbränsle, IVL report to be published autumn 2020.

Wärtsilä. 2019. Wärtsilä 34DF Product Guide. Wärtsilä Finland Oy.

Yaramenka K., Fridell E och Åström S., 2019. Environmental assessment of Sweden-related LNG fleet in the Baltic Sea and the North Sea – Emissions to air and external costs, För Energigas Sverige, IVL rapport C369.

Lighthouse samlar industri, samhälle, akademi och institut i triple helix-samverkan för att stärka Sveriges maritima konkurrenskraft genom forskning, utveckling och innovation. Som en del i arbetet för en hållbar maritim sektor initierar och koordinerar Lighthouse relevant forskning och innovation som utgår från industrin och samhällets behov.

Lighthouse – för en konkurrenskraftig, hållbar och säker maritim sektor med god arbetsmiljö



LIGHTHOUSE PARTNERS



LIGHTHOUSE ASSOCIATE MEMBERS

