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Green Ray project to develop solutions minimizing methane slip from LNG-fuelled engines

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Abstract

The use of LNG as a marine fuel is accelerating, driven by a well-developed supply infrastructure, a clear transition to cleaner fuels and significant air pollution and climate benefits. The issue of methane slip – unburned fuel escaping into the atmosphere from engines and across the production and supply chain – is seen as one of the main challenges to wider uptake.

A consortium including energy major Shell and technology group Wärtsilä has secured European Union funding to develop solutions minimizing methane slip from marine engines, advancing the environmental and climate benefits of LNG as a ship fuel.

The project group will develop on-engine technologies for low-pressure dual-fuel engines – both two- and four-stroke – as well as a novel catalytic aftertreatment concept. These solutions will be advanced to a high state of technology readiness, including demonstrators installed on two newbuilds and one retrofitted to an existing vessel.

Methane slip has become an important factor in ship owners' decisions about whether to use LNG fuel. With these promising technologies we aim to reduce the slip contributing directly to reduction of the total greenhouse gas emissions, opening this pathway to even wider segment of the maritime market.

Taking these solutions for newbuilds and retrofits to near commercial readiness will be an important step for the long-term viability of LNG as a marine fuel.

This paper will describe the key aspects of the four stroke on-engine technology and catalyst system development to date, the main challenges, and opportunities to optimize the solution space by exploring key considerations, design choices and integration aspects.

About the Green Ray Project

GREEN RAY is an Horizon Europe project aimed at minimising the methane slip from Liquefied Natural Gas (LNG) vessels to enable clean waterborne transport. By developing three innovative technologies for LNG engines that can be installed on new and existing ships, GREEN RAY is working to reduce the negative impact of waterborne transport and protect human and environmental health.

The goals of the project comprise assessing methane emissions from existing and new LNG vessels; developing technologies to reduce methane slip in two- and four-stroke LNG engines; developing an aftertreatment technology to further reduce methane slip; producing scenarios for shipping emissions and how GREEN RAY technologies can contribute to GHG emissions reduction; and enabling the utilisation of GREEN RAY results to maximise long-term research impacts.

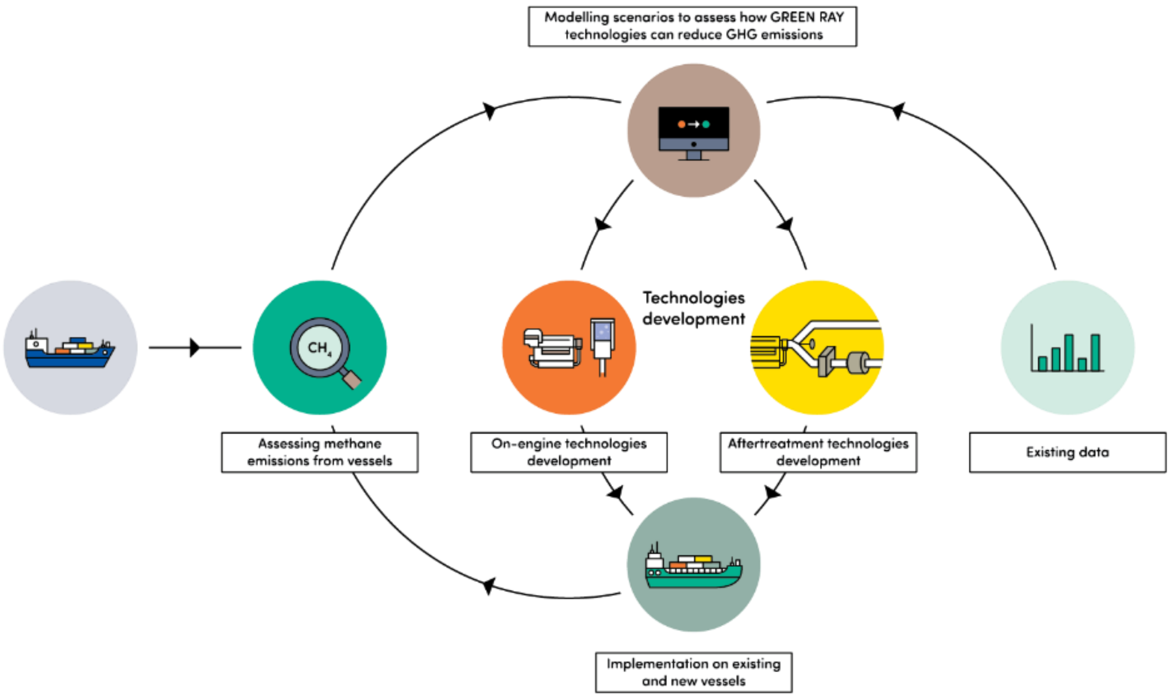


Figure 1: Green Ray Work Packages

To prevent methane slip, GREEN RAY will target low-pressure dual fuel concept, as this is the most popular LNG engine technology. To address the issue from multiple angles, the project will provide solutions to reduce methane slip in two- and four-stroke engines as well as tackling remaining methane slip through the development of an aftertreatment technology to convert the remaining escaping methane into a less potent greenhouse gas (GHG). These systems will help shipowners to reduce their greenhouse gas emissions as required by the IMO:

- Four-stroke engine: this engine will aim to enable methane slip reduction at all engine loads and to be applicable to the largest engines in the market involving cruise, ferry and gas carriers. Based on developments of the gas fuel system, liquid fuel injection systems, engine control, and engine charge air delivery system, GREEN RAY aims to significantly decrease methane emissions. This technology could provide a 40% overall reduction of methane slip.
- Two-stroke engine: GREEN RAY will develop a new LNG injection system that will significantly reduce methane slip by improving spray distribution and combustion behaviour compared to gas injection. This engine aims to significantly reduce methane slip from e.g., tankers and container ships. This could provide a 70% overall reduction methane slip.
- Methane Abatement Catalyst System: As a backstop for remaining methane emissions, GREEN RAY is developing a catalytic abatement system, comprising a high-capacity Sulphur Guard Bed and a low temperature Methane Oxidation Catalyst. This system will significantly reduce methane slip emissions – up to 95% - and reduce the methane slip to less than 1g/kWh.

The developed technologies will be demonstrated onboard two new ships and one retrofitted existing vessel. Partners will also contribute to the collection of climate data through the study of methane levels and reviewing the methane levels reported in the literature (Kuittinen et al. 2023). These data will allow for a more global assessment of GHG emissions from LNG marine fuel and will be combined with onboard experiments and modelling to provide a more comprehensive outlook of the climate impacts of marine transport. Ultimately, GREEN RAY can help make LNG a cleaner energy source as it spreads as an alternative fuel for the European and international maritime transport.

Green Ray has kicked off in June 2022 and is expected to run until May 2027.

**The GREEN RAY project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101056642.

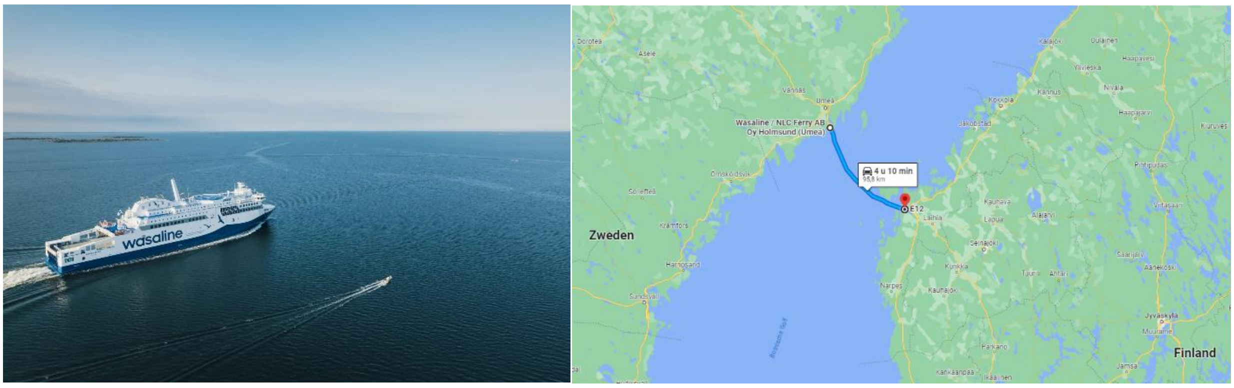
Medium speed engine improvements

Medium speed dual fuel gas engines successfully propel a large part of the LNG powered fleet. Combining fuel flexibility, high power density and low fuel consumption, they are often used in gas carriers, cruise ships, ferries, and other ship types.

To further reduce the methane slip of the larges medium speed gas engines, the Green Ray project builds upon results from a predecessor project: SeaTech. In the SeaTech project, sizeable emission reductions and ultra-high energy conversion efficiency were achieved by precisely controlling the auto-ignition of the fuel mixture at every operating point of the engine. Demonstrated on a medium bore engine in the SeaTech project, the technology will be scaled up to be applicable to Wärtsilä's large bore medium speed dual fuel gas engines during the Green Ray project.

As part of the assessment of current levels of methane emissions from shipping, a measurement campaign by project partner VTT was conducted on board of the Aurora Botnia ROPax vessel sailing between Vaasa, Finland and Umeå, Sweden.

Figure 2 M/S Aurora Botnia, photographed in the Vasa Archipelago and the route between Vaasa and Umea.



Aurora Botnia is a state-of-the-art ferry powered by 4 Wärtsilä 31DF dual fuel gas engines as part of a hybrid propulsion system. One of the installed engines was upgraded to incorporate the technology developed in the SeaTech project and emission measurements were conducted on that engine and on one of the non-modified 31DF engines. A full description of the measurements is available in (Lehtoranta, Kuittinen, Vesala, & Koponen, 2023).

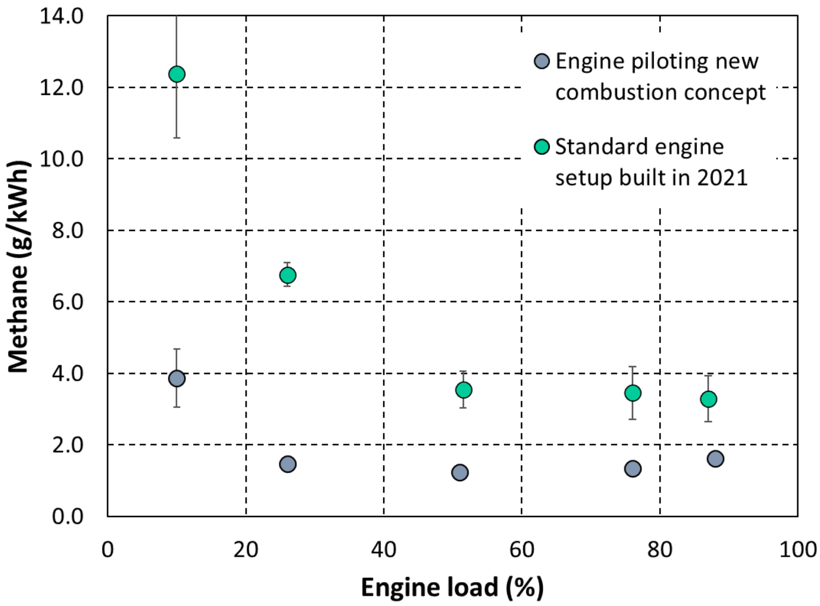


Figure 3 from [Lehtoranta, 2023], methane emissions measured on board Aurora Botnia for Main engine 4 (non-modified W31DF) and Main engine 3 (equipped with the technology developed in the SeaTech project)

Figure 3 contains the main results on measured methane emissions from both the non-modified engine (Main Engine #4, or ME4) and the engine equipped with the technology developed in the SeaTech project (Main Engine #3 or ME3). The achieved emission reduction is quite clear and sizeable, ranging from a 50% reduction at the highest loads measured up to 75% at lower loads.

The GREEN RAY project will further expand the applicability of this technology to larger engine sizes. During the first phase of the GREEN RAY project, different performance concepts have been developed and compared using real vessel operating data. A laboratory engine re-build is scheduled for Q4 2023, followed by extensive laboratory tests and development iterations during 2024. In the latter part of the GREEN RAY project, the developed technology will be brought to a pilot cruise vessel installation together with the GREEN RAY, partner Chantiers de l'Atlantique. In the end, emission measurements in real vessel operation will be performed by GREEN RAY partner VTT.

An economic and compliance perspective

With respect to methane emissions, the proposed EU's FuelEU Maritime is one of the most developed legislative packages. Under it, the maximum allowed carbon intensity of the fuel used is defined and it also it mandates the use of shore power for container and cruise ships in certain EU ports from 2030. Besides FuelEU Maritime, the EU's legislative bodies have introduced a revision to the Emission Trading Scheme (ETS) to start bringing shipping under the ETS from 2025 onwards, with a ramp up period to 2027.

If we focus on the ETS to investigate the value of reduced methane slip, it is important to note that the current legislative proposal requires that emission rights are bought for all emissions caused during voyages between EU ports and for 50% of emissions on EU in- or outbound journeys. CO2, methane and nitrous oxide emissions are in scope, with 100 year GWP weighting used to convert methane (25) and nitrous oxide (265) to CO2 equivalent as per Directive (EU) 2018/2001, Paragraph 4 of Part C of Annex V.

Default methane emission factors have been included in the legislative proposal for a number of engine types at an engine load of 50%. A percentage of the LNG fuel used has been defined to "slip" through the engine and for low pressure dual fuel engines, this "Cslip" value is equal to 3.1% of the LNG fuel mass used. Taking an average engine efficiency of 45% (+/-2%), this 3.1% equals between 4.75 and 5.25 g/kWh, so 5 g/kWh on average.

We can see from the measured data that both the standard engine and the engine equipped with the SeaTech technology are well below the 5g/kWh value at 50% load, coming in at 3.55 and 1.42 g/kWh respectively.

In an application that spends 4000 hours per year inside EU waters and running at an average load of 7500kW, this means the assumed (using the g/kWh standard emission factor) methane emission would be 150 tons of methane, equal to 3750 tons of CO2. For the upgraded engine though, the actual methane emission would only be 43 tons of methane, equal to 1065 tons of CO2. Assuming an EU ETS price of 90 €/ton (the average of 2022+2023 YTD), this translates into an annual saving of (3750-1065)*90 = €241.650,- for the purchase of ETS emission rights alone.

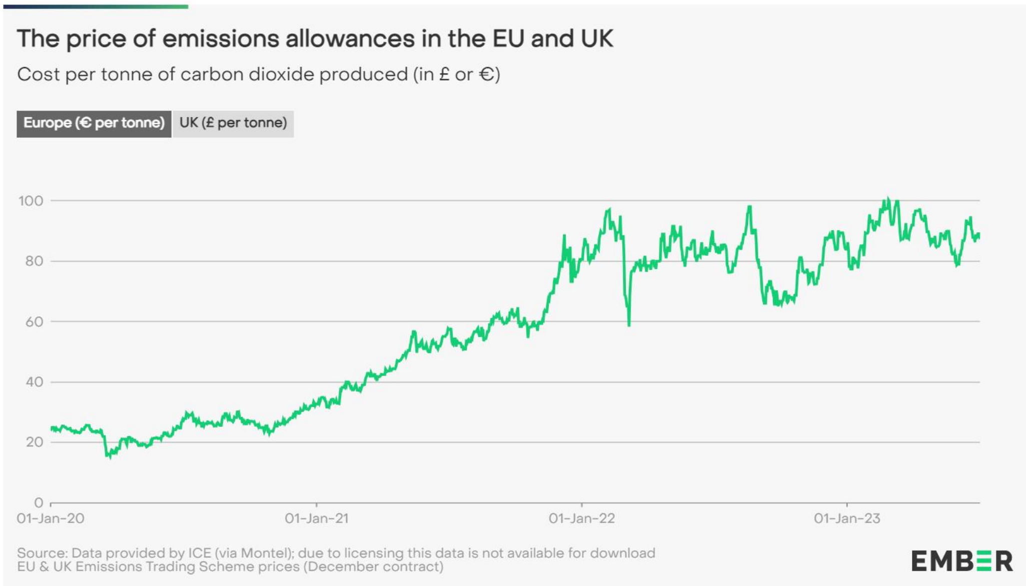


Figure 4 EU emission allowance prices, source: Ember.

Exhaust gas aftertreatment developments

The exhaust gas aftertreatment work package of the Green Ray project covers the development and deployment of methane abatement technology through oxidation of CH_4 to CO_2. The Methane Abatement Catalyst (MAC) System is the proprietary technology developed by Shell to oxidize non-combusted methane in exhaust of engines running on natural gas, enabling impactful reduction of methane emissions from the natural gas supply chain. The system is comprised of Sulphur Guard Bed (SGB) & Methane Oxidation Catalyst (MOC)

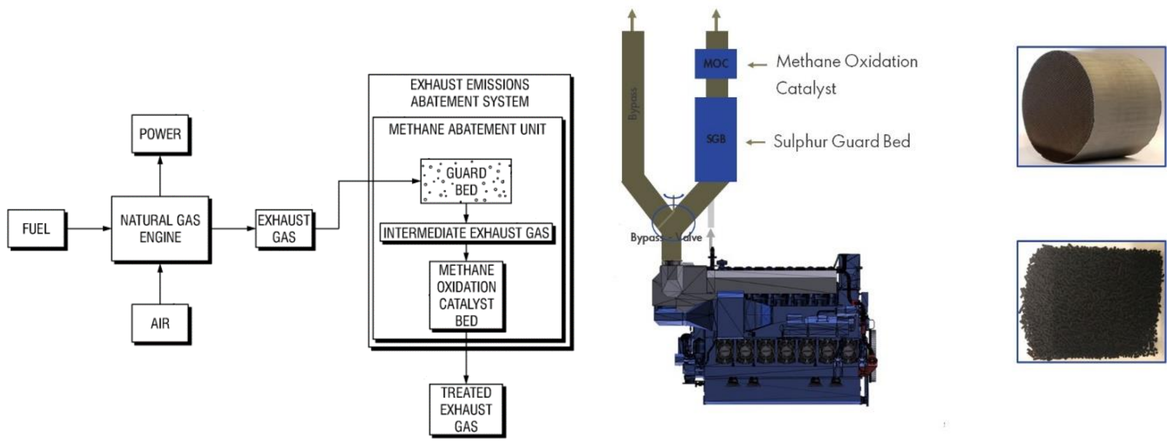
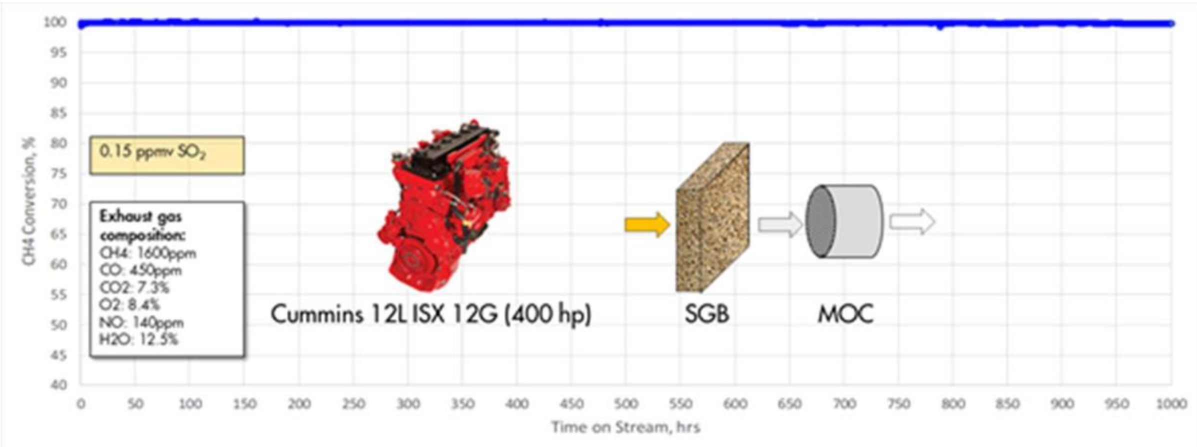


Figure 5: Schematic representation of the MAC System attached to a Wärtsilä 34DF engine (sketch as per WO2021262219A1)

The SGB integrated at the front end of the catalyst acts to preserve the MOC catalyst activity by removing catalyst poisons in the exhaust gas stream. The MOC is based on a honeycomb catalyst support coated with noble metals-based catalyst. The SGB removes SO_2 along with other catalyst poisons found in the pilot fuel, lube oil and LNG itself.

The initial development focused on stationary engines where it was demonstrated in a lean burn stationary engine laboratory test. The SGB combined with the MOC maintained >99% methane conversion during a 1000-hr engine demonstration (see figure below).



In addition, a field demonstration at one of Shell's facilities (Groundbirch Canada) using a slip stream from 320L, 4700hp engine was also completed. The MAC system achieved 96% CH4 conversion after 650 hrs of operation.

Figure 6: Groundbirch (Canada) stationary test rig in action.

The focus in GREEN RAY will shift the deployment of the MAC system to marine application. For such application, the MAC system has a potential to abate >80% of methane-slip emissions from LNG powered engines and reduce the methane slip to meet the upcoming

IMO regulations. The objective is to demonstrate and deploy the MAC system on LNG powered ships to abate methane slip in exhaust of engines running on natural gas and de-risk the technology in the marine sector.

The Green Project acknowledges that application in marine conditions is different from stationary conditions. There are many challenges to overcome such as more space constraints low temperature exhaust gas temperature and variable engine operation.

- Feasibility studies between Shell and Wärtsilä have concluded that the best place to install an after-treatment system is at the post-turbo location. A pre-turbo configuration where the temperature can reach up to 550°C has advantages for catalyst performance. However, these are outweighed by the many challenges to the installation of the catalyst in this configuration, including demanding conditions of high pressure and temperature, effect on engine transient operation and thermal management of the catalyst.
- Continuous improvements in LNG engine efficiency have resulted in lower exhaust temperatures post turbo charger (350-425°C). As methane is a highly stable molecule this requires a very active catalyst to lower the activation energy to break the C-H bond and subsequently oxidize it to CO_2. This imposes high requirements on catalyst activity in order to be able to sufficiently active at these lower temperatures.
  The MOC is highly sensitive to sulphur in the exhaust leading to fast deactivation of the catalyst without removal. Currently, there is no Sulphur resistant MOC catalyst with high activity available in the market that is able to withstand the long catalyst operation time required in Marine application. Shell's unique patented solution in GREEN RAY is to install the SGB upstream of the MOC to capture the sulphur prior to reaching the MOC. For the system to work, an SGB with high capture efficiency & capacity is required. The system needs to be compact with low pressure drop as to not impact the engine operation.

Shell has been actively developing the MAC system resulting in patented[1] SGB and MOC formulations that are state of the art when it comes to SO_2 removal and low temperature CH_4 conversion. Shell has taken major steps to address the above challenges and will continue to do that as part of the Green Ray project.

[1] US10512896B2 - Methane oxidation catalyst, process to prepare the same and method of using the same

US20220268191A1 - A methane oxidation catalyst and a method of making and using thereof

WO2021262219A1 - Exhaust gas emissions abatement system

Further development of the SGB and MOC will comprise of screening of new catalyst chemistries and optimization of its performance with small reactors under varying exhaust gas composition and reaction conditions. For this purpose, Shell will make use of 2 advanced test units in their laboratory, which were specifically built for the MAC project.

Figure 7: 16 reactors powder Test unit (left) & two cores test unit (right) at Shell Technology Center - Houston.

Latest R&D Developments and Project Progress

Since kick-off of the project significant improvements have been made with regards to the distribution of the PGM coating on the monolith base material of the MOC catalyst. Due to these improvements, Shell was able to embark on a series of experiments in their laboratories to evaluate the impact of hydrothermal ageing on the long-term stability of the catalyst. These ageing experiments were done on a custom-built test unit where engine conditions are mimicked using a mixture of synthetic gases. A hydrothermal durability study using 1”x3.5” catalyst cores was carried out at 425°C for 3000hrs (see Figure 5). During these tests the samples showed good thermal stability with an interpolated End or Run (EOR) conversion of 75% at 16000 hours of operation.

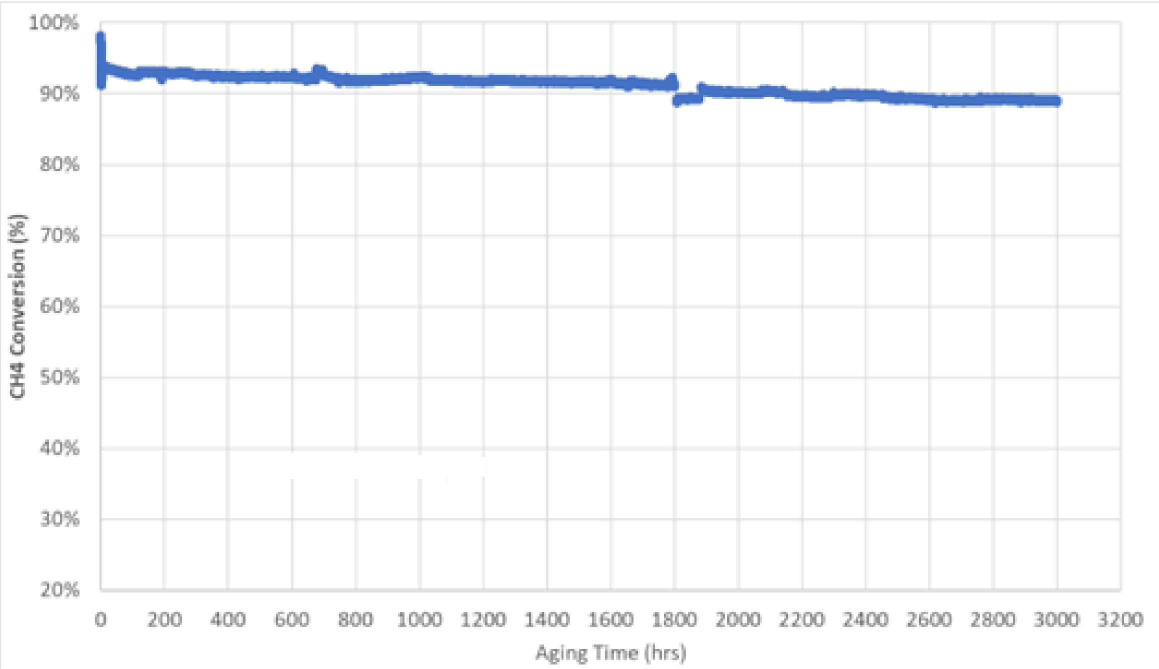


Figure 8: hydrothermal ageing with 10.5% H_2O of a 1”x3.5" sample at 425°C

Through further optimisation of the SGB recipe, great steps were made in the sulphur removal efficiency and capacity of the adsorbent. The SGB material in its actual form, together with the MOC cores have been tested together to evaluate the integrated system behaviour when exposed to SO2. These tests were done at accelerated conditions i.e. higher gas flows and higher SO2 concentrations than expected in practical applications.

These tests were stopped at 1380 hours of running when gradual reduction of conversion started. Considering that under real conditions SO2 is expected to be lower, and the gas velocity to be 4.3x lower, an operation time of approx. 16,000 hours is believed possible before a changeout is required, aligning well with the changeout frequency of the MOC Catalyst.

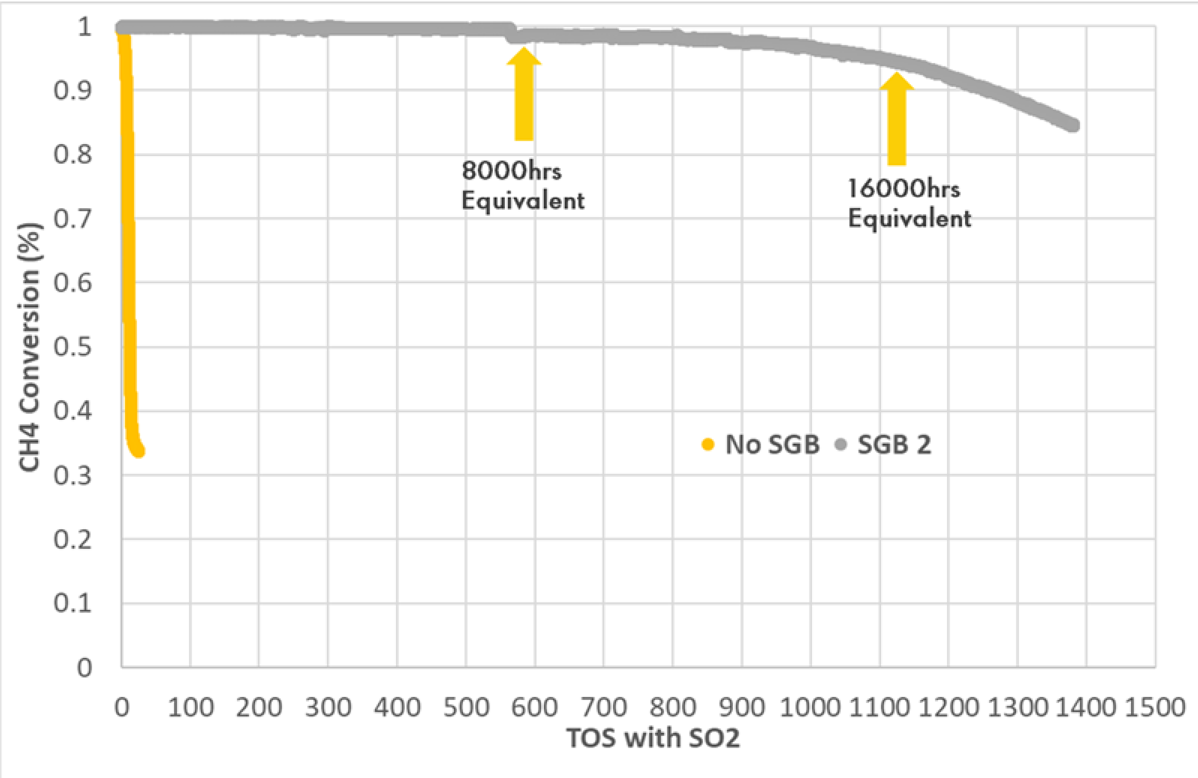


Figure 9: Accelerated sulfation test results,10.5% H_2O of a 1"x3.5" sample at 425°C

While further developments still ongoing with regards to further optimization of the MOC as well as SGB, the current recipes met the criteria to start with the catalyst scale-up in preparation of the lab tests at the Wärtsilä facilities in Vaasa. In preparation for Wärtsilä test, Shell has successfully scaled up the MAC system. The reactors (with catalyst) for the SGB and MOC have now been installed in Vaasa and start of testing is imminent. First results will be expected Q4 2023 and will form the basis for the design of the reactors for the on-board trial.

Optimized SGB and MOC catalyst candidates will be validated in Wärtsilä engine laboratory under real dual fuel engine exhaust conditions. Wärtsilä engine laboratories have the latest engine models and professional emission measurement capabilities to validate the new technologies, integrate the aftertreatment with engine operation and controls and secure the safety of the solutions before the field demonstration.

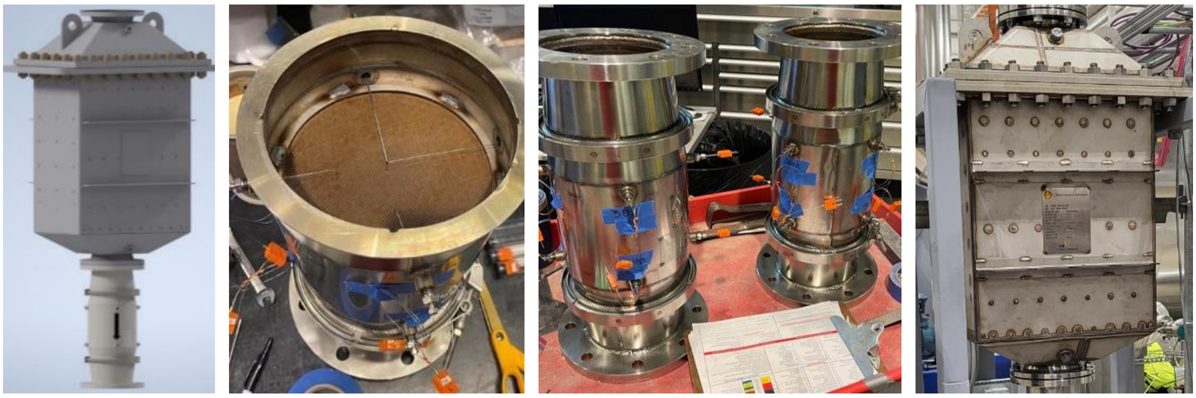


Figure 10: Vaasa (Finland) reactor design and experimental set-up

Preparations for the onboard tests have been started as well as these are planned to commence in 2025, implicating that in ship installation will happen in Q3/Q4 of 2024. A potential LNG carrier has already been identified using Wärtsilä 6L34DF engines for auxiliaries. The MAC system for this trial will take the full flow of one of these engines.

Integrated Performance Testing though Case Studies

The overall performance of the MAC system (average methane abatement) is determined by several factors that all need to come together:

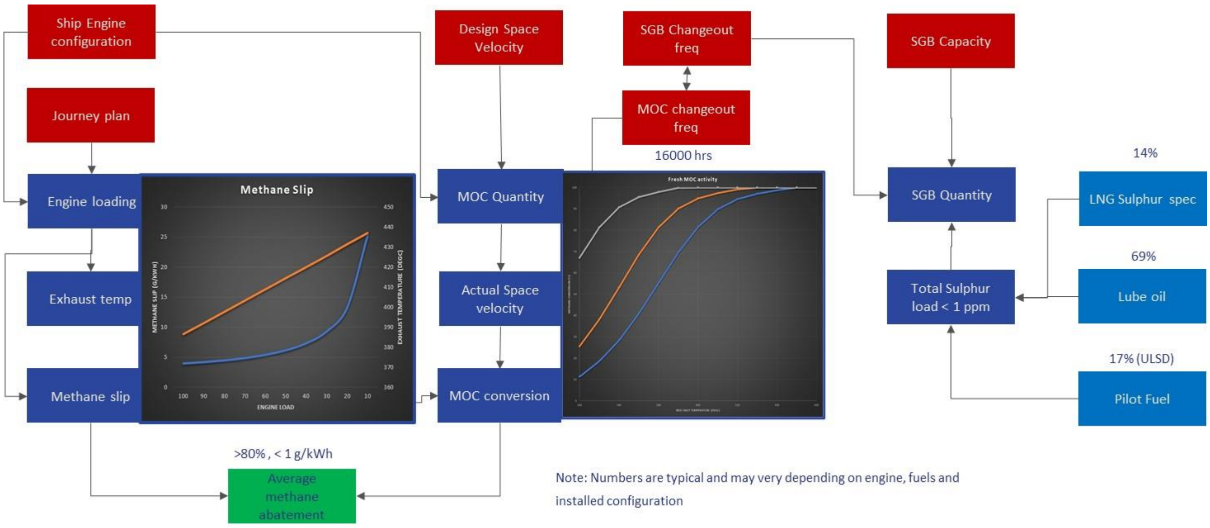


Figure 11: MAC System integrated model set-up

- **Ship Engine Configuration**. The configuration of engines (number and capacity) in combination with the journey plan will determine the average engine loading, but also the amount of catalyst that will be installed, assuming the system is designed for a 100% load.
- **Journey Plan**. See above. Determines engine actual power requirement based on vessel speed. The journey plan can be optimized to yield maximum utilization.
- **Design Space Velocity**. Criteria for sizing of amount of SGB and MOC catalyst. Together with the engine size this will determine the size of the reactor (amount of MOC catalyst)
- **MOC Change out frequency**. We are aiming for change out after 16000 hrs of operation (at 100%) accepting a certain degree of performance reduction at End of Run conditions.
- **SGB Capacity**. The capacity of the SGB material to contain sulphur. Together with the engine size, the required SGB Changeout frequency and the exhaust guess SO2 concentration, this will set the amount of SGB required.

- **LNG Sulphur specification, Lube oil and pilot fuel Sulphur content**. To keep the size of the SGB reactor reasonable (and/or the change out frequency) current assumption is to switch to ULSD pilot fuel. In that case the majority of sulphur is expected to come from the lube oil
- **Exhaust temperature**. The catalytic conversion of methane is strongly temperature dependent. The exhaust temperature is set by engine type and loading – typically higher at lower loads (and hence helping conversion)
- **Methane slip.** Methane slip is a strong function of engine load, with the lower load having a significantly higher slip.
- **Actual space velocity.** The actual engine load will usually be lower than 100% and hence gas velocities through the catalyst be lower (i.e. higher space velocity) resulting in a higher conversion.
- **MOC Conversion**. Start of Run conversion will be higher than End or Run conversions due to thermal ageing of the catalyst. Conversion will be determined by actual space velocity, temperature, and actual space velocity.

For the case study Shell and Wartila analysed an LNG carrier journey from Saguanay to Huelva based on two types of LNG carriers with different engine configurations:

- **New build**: 2S DM CONCEPT -174K LNGC. Main engines WinGD X-DF (LP) 2.1. Auxilary engines W34DF-C with GHG Reduction Package
- **Retrofit**: - DIESEL ELECTRIC – 174K LNGC. Gensets 2x W6L46DF + 2x W8L46DF

Table 1: Journey plan for Huelva to St Lawrence

Huelva to St Lawrence		Waiting at St. Lawrence	St. Lawrence	Whales speed limitation	Channelling Saguenay	Waiting	Loading	Channelling Saguenay	Whales speed limitation	St. Lawrence	St. Lawrence- Huelva	Unloading
Duration (Hours)	200	4	25	1	7.5	5.4	20	7.5	1	25	176	26
Speed (knots)	15	0	12	5	8	0	0	8	5	12	17	0

Using the integrated model approach as explained above, this resulted in the following outcomes:

Table 2: Results of Case study

Carrier	**New build**		**Retrofit**	
Engine	**WinGD X-DF (LP) 2.1**	**W34DF-C**	**W6L46DF**	**W8L46DF**
Average utilisation (%)	45%	9%	33%	34%
Methane slip @ full load (g/kWh)	4.0[1] (2.3 %)	4.0[1] (2.3 %)	4.0[1] (2.3 %)	4.0[1] (2.3 %)
Average methane inlet (g/kWh)	7.7	5.8	5.2	4.9
Average methane outlet (g/kWh)	0.8	0.7	0.6	0.6
Average conversion (%)	81	83	84	84
CO2e reduction per year (tCO2e/y) assuming 50% in European waters	7417	574	5829	7373
ETS value (@90 Euro/t) m$ per year	0.69	0.05	0.52	0.66

[1] Methane slip assumed to be 4 g/kWh for all engines, irrespective of type and make.

Key take aways from above are that assuming the vessel is 50% of its time in European waters and an average ETS price of 90 Euro per tonne of CO2, a saving of 0.7 to 1.1 million Euro per vessel per year can be realized for the purchase of ETS emission rights alone.

Initial installation costs and operational costs for catalyst replacement are currently indicating competitive CO2e abatement costs compared to ETS numbers.

Conclusions

- The Green Ray project is on track to deliver its 4 stroke engine improvements and aftertreatment solution
- Catalyst production for the MAC system can be successfully scaled up – a requirement for an impactful roll out of the technology.
- Rigorous testing on Wärtsilä engines commencing September 2023 – design of system for on boards trial has kicked off. Reporting out of measurement campaign as per Green Ray schedule

Powder unit Houston Shell	2 Core unit Houston Shell	Groundbirch Canada Shell	Vaassa Finland Wartsila	On board trial Shell chartered vessel
0.1 Nm3/hr	4.2 Nm3/hr	40 Nm3/hr slipstream	163 Nm3/hr slipstream	14000 Nm3/hr Full engine flow
N/A	DxL: 1" x 3.5" Single core	DxL: 4.16" x 3.5" Single core	DxL: 7.5" x 4.5" Single core	DxL: tbc Multiple cores

- MAC system success criteria seem achievable with current set-up – more rigorous modelling will be part of the Green Ray project
- Catalyst recipe development will be evergreen – R&D activities will continue to further optimize catalyst characteristics and aim to lower lifecycle costs.

Acknowledgements

Our Green Ray partners

This work was supported by the EU HORIZON project GREEN RAY (Grant number: 101056642).