

2025 | 074

From lab to machinery space: advances in methane slip catalyst technology and engine internal measures

Exhaust Gas Aftertreatment Solutions & CCS

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This paper has been presented and published at the 31st CIMAC World Congress 2025 in Zürich, Switzerland. The CIMAC Congress is held every three years, each time in a different member country. The Congress program centres around the presentation of Technical Papers on engine research and development, application engineering on the original equipment side and engine operation and maintenance on the end-user side. The themes of the 2025 event included Digitalization & Connectivity for different applications, System Integration & Hybridization, Electrification & Fuel Cells Development, Emission Reduction Technologies, Conventional and New Fuels, Dual Fuel Engines, Lubricants, Product Development of Gas and Diesel Engines, Components & Tribology, Turbochargers, Controls & Automation, Engine Thermodynamics, Simulation Technologies as well as Basic Research & Advanced Engineering. The copyright of this paper is with CIMAC. For further information please visit <https://www.cimac.com>.

ABSTRACT

With the 2023 IMO GHG Strategy, a further considerable step was made towards a climate-neutral future. Methane emissions have always been a topic in gas engine development. Originally reducing methane emissions was rather a side-effect of increasing combustion efficiency. The worldwide focus on global warming supported by monetary mechanisms like FuelEU Maritime opens the door for more sophisticated solutions. With the perspective to replace fossil-based LNG with bio- or electricity-based fuels containing methane, the methane emission will become the major climate impact of such fuels and therefore needs to be reduced to a minimum. MAN ES is taking several steps to further reduce the methane emissions of its engines. A general overview of the measures and their effects is presented in this paper.

Test bed results show that the latest versions of MAN ES DF engines can significantly undershoot the limits of FuelEU Maritime for the coming years. Detailed results are shown for the latest development steps of 35/44DF to 35/44DF CD and 51/60DF to 49/60DF. It is shown how different measures contribute to the overall methane emission reduction and that different approaches lead to similar results.

The methane catalyst development has made considerable progress with the first full-scale testing on an L23/30DF. The test results demonstrate that the high expectations from lab scale results can be met on the testbed. Furthermore, the catalyst performance was stable over the whole testing period, collecting more than 250 running hours under comparably harsh operating conditions. The testing setup is explained in detail as well as the impact of the pre-turbine catalyst setup on engine behavior. Several mitigation measures had to be taken to achieve stable operation. The impact on the engine dynamics will also be shown for both diesel and LNG operation.

Supporting the full-scale testing activities, MAN ES has also taken further steps to improve the pre-validation on lab-scale. A new ageing test bench for catalysts is shown in this paper. The test setup, methodology and test results are explained. Correlating the test results from the ageing test bed with full-scale tested honeycombs allows deeper insights into ageing and wear mechanisms and opens new pathways to further improve the system.

1 INTRODUCTION

With the 2023 IMO (International Maritime Organization) Greenhouse Gas (GHG) Strategy [1] a further considerable step was made towards a climate neutral future. Methane emissions have always been a topic in gas engine development. Originally reducing methane emissions was rather a side-effect of increasing combustion efficiency. The worldwide focus on global warming supported by monetary mechanisms like FuelEU Maritime [2] opens the door for more sophisticated solutions. With the perspective to replace fossil based LNG (Liquefied Natural Gas) with bio- or electricity-based fuels containing methane, the emission of unburnt fuel will become the major climate impact of such fuels and therefore needs to be reduced to a minimum. MAN ES is taking several steps to further reduce the methane emissions of its engines. A general overview of the measures and their effects is presented in this paper.

2 FUNDAMENTALS

The global warming potential (GWP) of an emission is normally measured in comparison to CO₂. As the lifetime of the chemical species is also relevant to assess the overall impact on the global climate, a common reference needs to be defined. The Intergovernmental Panel on Climate Change (IPCC) provides an extensive overview over relevant emission species and their climate impact. These are assessed on a 100-year time horizon. The latest factor for CH₄ is 29.8 which is also used for the calculations shown in this paper, see also Table 1.

Table 1: GWP factor of the most relevant emission species for combustion engines relative to CO₂ [3]

Species Name	Chemical Formula	GWP
Carbon Dioxide	CO ₂	1
Methane - fossil	CH ₄	29.8
Nitrous oxide	N ₂ O	273

In an effort to reduce the climate impact of combustion engines the overall GHG emissions need to be reduced. There are various examples that this has also become part of international regulations, e.g. the IMO GHG reduction strategy [1] or the Fuel EU Maritime Regulation [2]. Typically CO₂, CH₄ and N₂O are regarded as most relevant for engine emissions in general. This paper focuses on CH₄ reduction, yet also uses CO_{2eq} values to give a better overview over the overall engine emission behavior.

3 OVERVIEW OVER METHANE EMISSION REDUCTION MEASURES

High pressure fuel injection is regarded the most effective strategy towards reduction of methane emissions. The 2-stroke ME-GI engine types of MAN ES offer such a combustion setup. Unfortunately the application of such engines is not feasible in all market segments. Otto-cycle engines with Port Fuel Injection (PFI) still dominate especially the 4-stroke engine market. For those engines a further reduction of methane emissions is still required and feasible. The different approaches can be separated into engine internal measures and external treatment.

Engine internal measures

- Combustion chamber design
- Crevice volume reduction
- Combustion process

Control strategies

- Skip Firing
- Cylinder pressure based control

Aftertreatment solutions

- Selective Catalytic Reaction (SCR, as compensation for using the NO_x – CH₄ trade off)
- Methane Oxidation Catalysts (MOC) [4]
- Regenerative Thermal Oxidizer (RTO)
- Plasma [5]

Most aftertreatment solutions have still not reached a sufficient Technology Readiness Level (TRL) for use in shipping and there are serious doubts that they will ever be competitive. [6] MAN ES will present its approach in the following chapters.

4 ENGINE OPTIMIZATION

Having described the fundamental options for methane emission reduction, the following section will give a detailed insight into actual engine types and the reductions achieved with the latest technology upgrades. For this comparison current large bore Dual Fuel (DF) engines with PFI are chosen.

The two comparisons are obviously distinguished by bore size, the so called 3X bore size and the 4X/5X bore size. Still the major difference for the comparison of the two engine families is not their

size but rather their focus on different market segments.

While the engines are fundamentally suitable for different market segments, experience shows that the largest engine types are typically used for main propulsion and therefore a lot more focus is put on operating cost. While this is still the case for some projects with 3X engines, there is also a big focus on the application as auxiliary GenSets. Consequently the development of those engine types focuses even more on simplified and robust technology to keep the first cost as low as possible.

The former DF engine variants and their recently introduced successors are compared both considering CH₄ emissions as well as CO_{2eq}. Despite the fact that current discussions focus a lot on CH₄ emissions it must not be neglected that the overall GHG emissions are eventually relevant for the global warming.

4.1 Comparison of 35/44DF and 35/44DF CD

As mentioned before the 35/44 family is focused rather on the GenSet market with a high focus on first cost. The 35/44DF CD (CD: continuous development) is the latest version and a major part of its development process was to streamline the applied technologies. While the first version of the 35/44DF had a Common Rail (CR) system as main injection, the 35/44DF CD puts more focus on Gas Mode operation which justified the application of a conventional main injection. Sometimes the first version of the 35/44DF is therefore also referred to as 35/44DF CR.

The 35/44DF was well positioned in the market concerning its fuel consumption in both Diesel and Gas Mode. Yet when analyzing the overall performance of the engine it was clear that especially at part load the methane emission behavior was far from optimal. While this can be compensated to a certain extent by the operating pattern of the engine, it was clear that this had to be a focus topic for further development.

Consequently the optimization of the combustion setup was not only focused on maintaining a competitive specific fuel oil consumption (SFOC) and specific fuel gas consumption (SFGC) values but also a methane emission reduction especially at lower engine loads. At the same time the target was achieved to increase the overall Power Output of the engine. This helps reduce the number of installed cylinders on vessels with a certain power demand. Thus installation space, first cost and maintenance efforts can be kept to a minimum.

The achieved improvements are shown in Figure 1. A considerable reduction of methane emissions could be achieved over the whole load range with special focus on low load operation.

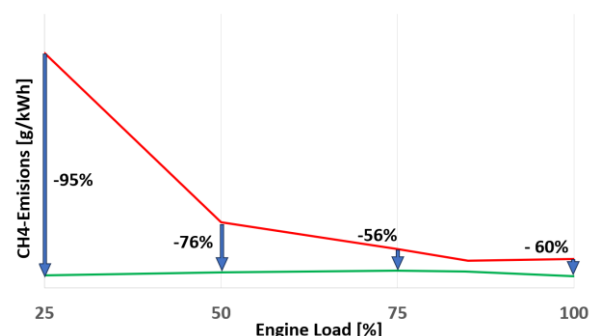


Figure 1. CH₄ Emission reduction for 35/44DF CD compared to 35/44DF

While the former 35/44DF shows a considerable increase in methane emissions towards lower loads, the 35/44DF CD maintains its low emission levels even down to 25% load.

The applied reduction measures consisted of

- Crevice volume reduction
- Skip Firing at low loads
- Optimized pilot injection strategy
- Cylinder-pressure controlled engine control with optimized parametrization
- SCR operation in Tier III Gas Mode

While cylinder pressure based control strategies were already used to a certain extent in the first version, the full potential was only used on the 35/44DF CD. This is due to the fact that this control strategy was an integral part of the development project from the early concept phase.

As part of the emission optimization also an SCR system is used. This decision was taken based on the fundamental results from combustion development. The engine showed a considerable potential to reduce the CH₄ emissions further when using the NO_x-CH₄-trade off. For operation in IMO ECA zones (ECA: emission control area) a fallback mode is still available where the engine is able to fulfill IMO Tier III requirements without SCR operation.

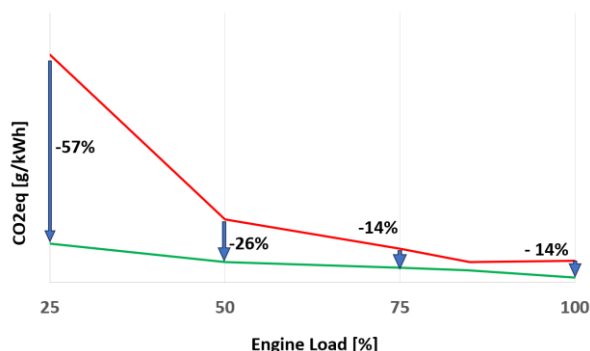


Figure 2. CO_{2eq} emission reduction for 35/44DF CD compared to 35/44DF

Despite focussing the combustion optimization rather on CH₄ emissions than fuel consumption and CO₂ reduction the overall CO_{2eq} emissions of the newer “CD” version are considerably lower than of the predecessor, as shown in Figure 2. Also here it can be seen that the biggest improvements were made in the low load range. Still there is an increase in the overall emissions towards lower loads, which is mainly due to increasing specific fuel consumption.

4.2 Comparison of 51/60DF and 49/60DF

When comparing 51/60DF and 49/60DF the differences between the underlying engines are much larger than the evolutionary update from 35/44DF to 35/44DF CD. The 49/60DF is a completely new engine type, with focus on considerably higher power output by both 2-stage turbo charger (TC) and a speed increase from 500/514rpm to 600rpm.

Being the typical choice for main engines on different types of vessels, the overall operating costs and especially fuel consumption are of highest importance. Still also in the development of this engine type a lot of effort was put into keeping the methane emission levels as low as possible. The results are shown in Figure 3.

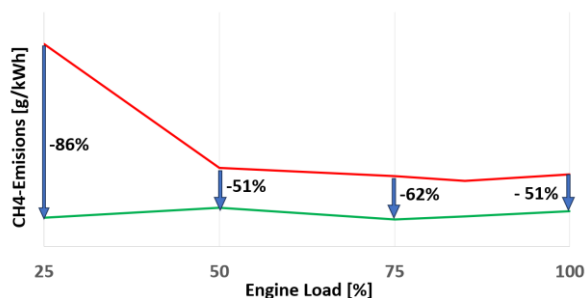


Figure 3. CH₄ emissions reduction of 49/60DF compared to 51/60DF

The major differences of the technology package of the 49/60DF comprise of:

- Crevice volume reduction
- Skip firing
- Cylinder pressure based control strategy
- Optimized pilot injection strategy
- 3-point VVT (variable valve train)

When optimizing the combustion setup it was found that the engine is operated close to different operation limits under different operating conditions, like the knocking limit or the peak firing pressure limit. Thus it was found that there is no potential left to use the NO_x-CH₄-tradeoff. Consequently the already very low CH₄ emissions could not be further reduced by applying an SCR. Still the emissions are on a similar level as those of the 35/44DF CD while fulfilling IMO Tier III requirements without aftertreatment.

The 3-point VVT is an enabler technology to optimize the engine operation in different load points. MAN ES chose to use this setup with a rather conventional mechanical solution due to robustness reasons. Other technologies with increased flexibility for the valve lift curves could provide further potential. Yet those solutions need to prove they are robust enough for the typical applications of those engines.

In Figure 4 the CO_{2eq} emissions of both engines are compared. The values of the 49/60DF benefit from both an improvement in fuel consumption as well as reductions in methane emissions. Again it can be seen that the gap widens at lower loads which correlates well with the methane emission improvements.

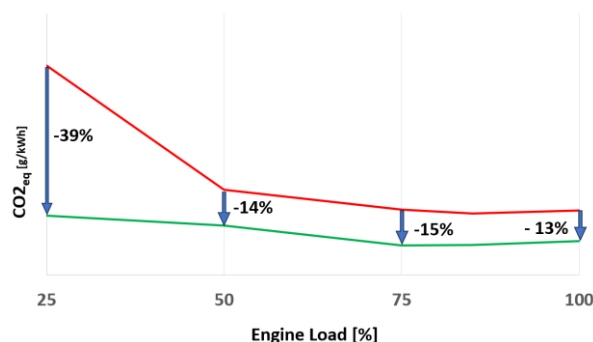


Figure 4. CO_{2eq} emission reduction of 49/60DF compared to 51/60DF

4.3 Communalities and differences between different engine types

When comparing the results for the 3X and the 4X/5X families some interesting trends can be identified.

- By engine optimization the emission of unburnt fuel can be kept to around 1.5% of the gaseous fuel consumption in the relevant load range. The lowest values for the discussed engines are even below 1%.
- SCR can be a technology to achieve these emission values. Yet depending on the fundamental combustion setup it could also be neither viable nor beneficial.
- Further reduction steps could be achieved yet the potential is more and more limited and the effort increases.

4.4 Further aspects for reducing engine out methane emissions

When reducing methane emissions is the major focus, further aspects should be considered. From test data it can clearly be shown that the operating mode of the engine has a considerable impact on engine emissions.

As shown in Figure 2 and Figure 4 the engine load plays a significant role. This can be used especially when operating several engines on a vessel. More and more ships also rely on more complex power systems including batteries. Optimizing the engine operation and shifting towards higher loads will not only lower the overall fuel consumption but also the methane emissions.

If the focus is on lowering methane emissions at lower loads engine operation with variable engine speed should be considered. Due to the reduced air mass flow the air-fuel-ratio becomes richer. This leads to a more complete combustion. The 49/60DF engine is available for applications with variable speed and even for Dual Fuel Diesel electric (DFDE) applications it can be applied using EPROX.

5 METHANE OXIDATION CATALYST DEVELOPMENT

Methane oxidation catalysts are an appealing solution to reduce the climate impact of engines run on methane based fuels. As there are no commercial solutions available MAN ES decided to develop such a system together with dedicated partners in the framework of the funded project IMOKAT II. [7] A continued technology monitoring with various suppliers is also part of the activities

to make sure the most effective technical solution is available for the end customer.

5.1 Fundamentals on testbed setup and catalyst elements

At the CIMAC congress 2023 in Busan the fundamental approach was already presented in detail [8]. The catalyst material identified in the underlying IMOKAT I funded project [9] was to be integrated into a reactor in a pre-turbine installation setup. At that stage the reactor was already manufactured and waited for final assembly at the test site in Frederikshavn.

In the meantime the whole test program was carried out and the setup is now disassembled and certain components are subject to further investigations. In the following the overall testbed setup will be described, followed by a summary of the major findings concerning both engine operating performance and catalyst performance and ageing.

5.2 Test bed setup

In order to achieve the required temperatures for the MOC the reactor was installed on engine. The target was to keep the installation space to a minimum. Especially the maximum height for the installation was limited to be able to install the whole setup into a ship. This led to an inclined mounting of the reactor, see Figure 5.

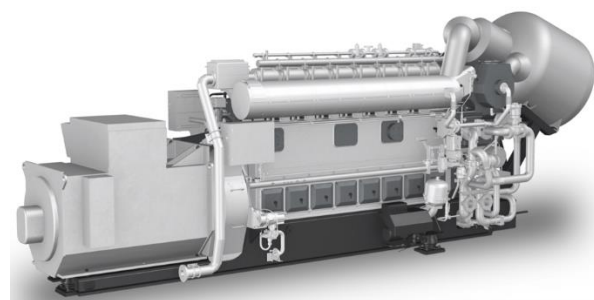


Figure 5. Rendering of the reactor assembly on engine

The weight of the additional components is supported by a dedicated console. The exhaust piping is modified so that a further by-pass flap could also be included. Again due to space restrictions it was not possible to include a full by-pass solutions. Instead a setup was chosen where either the full exhaust gas flow had to go through the reactor or an additional by-pass could be opened. Depending on the actual load point of the engine roughly 45...55% of the engine exhaust mass flow goes through the by-pass. The focus of the by-pass installation is obviously not on protecting the catalyst elements – which is not

deemed necessary – but on enhancing engine performance if required. The final installation on testbed is depicted in Figure 6.

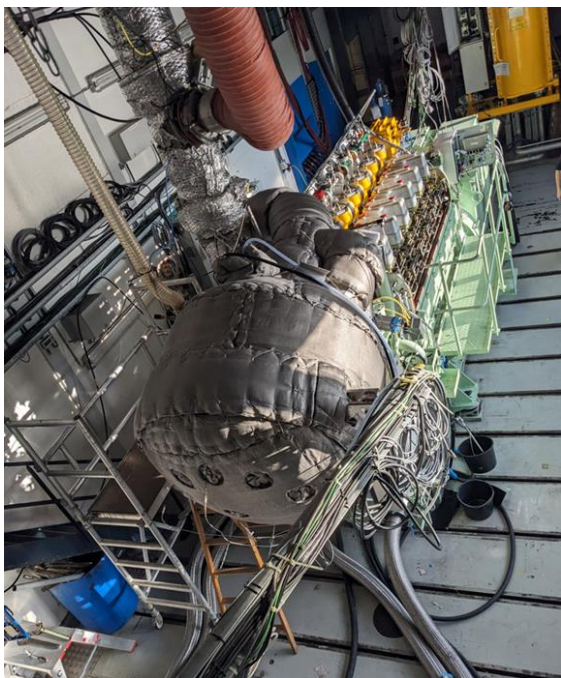


Figure 6. Test bed installation of an L23/30DF equipped with the pre-turbine MOC

5.3 Operational experience

Already with the first engine start up it became very clear that the MOC installation had a big impact on engine behavior. The reactor introduces high thermal inertia into the system. Consequently the TC is not in operation as usual when attempting to do load ramps or load steps.

An extensive learning phase followed to understand the new operating cycle of the engine including the oxidation catalyst. Especially during that period unexpected events led to manual or automatic shutdowns. This was mostly linked to the engine running at either very lean or rich conditions which both eventually result in very high exhaust gas temperatures – either from the combustion itself or from the oxidation of larger amounts of unburnt fuel gas.

In order to stress the catalyst material as much as possible and to get a most realistic test setup the catalyst honeycombs were installed from the very beginning. As shown by the results in this paper it can be stated that the catalyst robustness was surprisingly good while especially during the early phase the catalyst honeycombs were likely damaged.

As the L23/30DF engine is mainly used in GenSet applications operational robustness in general and stable engine speeds in particular were most in focus.

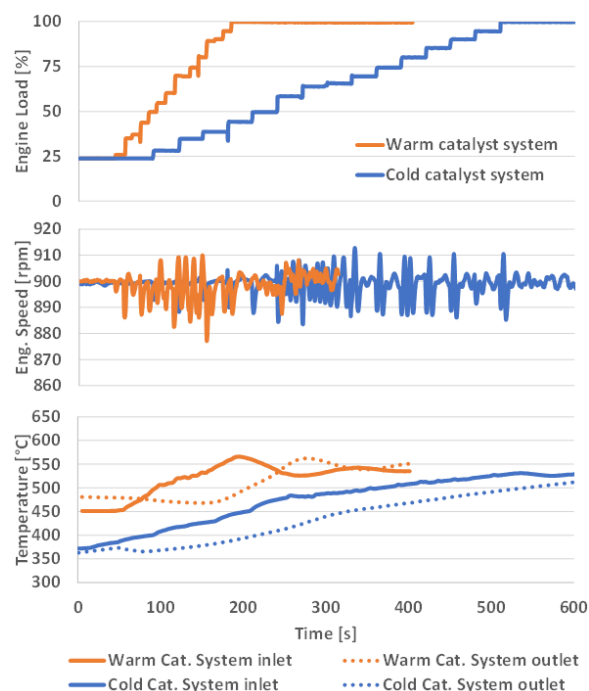


Figure 7: Comparison of engine and catalyst behavior during dynamic operation with cold and hot MOC.

As shown in Figure 7 there is a major difference in engine dynamics for warm and cold MOC. To achieve an acceptable start-up behavior the bypass needs to be fully open. Catalyst heating then took at least 25 minutes depending on the operating pattern of the engine. Due to the fundamental character of the test setup no effort was put into minimizing this heat up time. This will be subject to further optimization for following series development projects.

Once the reactor has reached the typical operating temperature no relevant drawbacks in engine dynamics compared to engine setups without MOC were found. The same load steps could be done as for the Type Approval of the very engine type and the fluctuations in engine speed were within acceptable margins.

The major learning concerning engine operation is the influence of the MOC on the air path of the engine. With the installed MOC the link between the exhaust ducts of the cylinders and the TC inlet is influenced by a new sub-system that can both reduce or increase the enthalpy of the exhaust mass flow. With the gathered data new models

are developed. These will not only help to optimize the overall system layout but also the corresponding control strategies for engine operation.

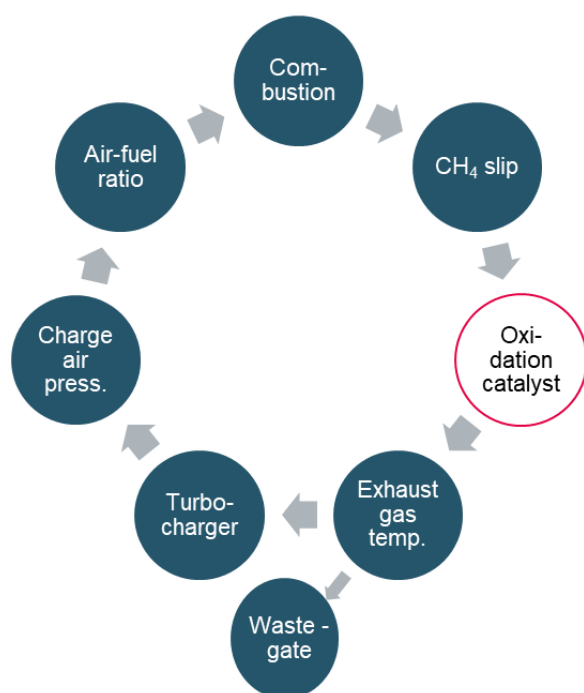


Figure 8: Scheme of the mutual influence of the Oxidation catalyst on the air-fuel ration control

5.4 Methane oxidation performance

5.4.1 Methane reduction rates

The fundamental performance of the catalyst elements was measured on a synthetic gas testbed prior to installing full size honeycombs at the testbed. The first measurement of conversion rates was only in focus after achieving stable enough running conditions of the engine. The first measurement was carried out after about 90 running hours and further measurements were done after approximately 120, 140, 200 and 270 running hours. As can be seen in Figure 9 a stable CH₄ reduction performance was achieved when comparing all measurements.

The slight differences in the measurement data for the different measurements are expected to be within the range of measurement accuracy. Unfortunately only one FTIR (Fourier Transform Infrared) was available for measurement and the sampling had to be switched. Consequently it was not possible to measure both inlet and outlet concentrations at the catalyst exactly at the same time.

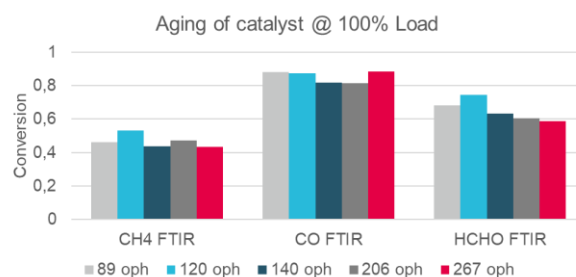


Figure 9: Reduction rates and ageing behavior of the MOC

This contributes to the overall inaccuracies of the measurements. After 206 h, 20% of the catalyst was replaced by new material, which entails higher CO conversion. For CH₄ conversion this effect disappears due to the above mentioned reasons in measurement accuracy.

5.4.2 Catalyst deterioration and ageing

As already indicated with the small decrease in HCHO oxidation performance obviously some ageing and deterioration effects took place. Although the overall catalyst performance was initially as expected and didn't decrease much over the testing period, some damages to the honeycombs could already be identified by visual inspection. For this inspection the honeycombs were cut open and it could be seen that there was a locally limited grey zone. Further tests with catalyst material from that zone showed a considerable deterioration of methane oxidation performance.

The reduction in oxidation performance could not be detected in the overall performance of the catalyst system due to the very limited size of the grey zone and the measurement uncertainties. It is difficult to assess how both the deteriorated zone itself and its impact on the whole system would evolve over a longer operation period. Therefore the development target is to completely avoid a formation of that zone.

Further investigations were therefore started and are still ongoing to better understand the underlying mechanisms. More details are described in chapter 6. The overall target is to understand the damage and wear mechanisms in detail to be able to adapt the engine operation accordingly. It was already possible to operate the test engine with the designed reduction rates for over 250 running hours.

Within the last 61 running hours of the testing program it could be demonstrated that even with

the research oriented and non-optimized test setup it was possible to avoid measurable damages to the catalyst elements. Therefore it seems a realistic development target to achieve a service lifetime of 6,000...12,000 hours.

5.4.3 Oxidation of HCHO and CO

Besides the reduction of methane the catalyst material is also capable of oxidizing CO and HCHO. The corresponding reduction rates are also shown in Figure 9. The CO oxidation behavior is also rather stable. Yet for the HCHO oxidation a declining tendency could be assumed. Nonetheless the major finding is that still after the whole operating time the catalyst is able to reduce the overall emissions of the engine although this would not be necessary from a regulatory point of view. It is assured that the MOC does not produce well-known harmful emission species while mainly oxidizing methane.

6 LABORATORY ANALYSES

The inhouse catalyst testing center allows for a further characterisation of the catalyst and its deactivation mechanisms. With different rapid aging methods, the longtime stability and critical operation conditions for each exhaust gas aftertreatment system can be identified.

6.1 Burner test rig

The goal of the burner test rig is to poison the catalyst under the most realistic conditions possible. For this purpose, EN 590 diesel is burned in a burner with a maximum output of 70 kW. Lubricating oil can be atomized and fed into the combustion chamber through a lance. This creates the combustion products that are typical for an engine. In order to increase the amount of poisons, the lube oil can be doped with different chemicals, e.g. triphenyl phosphate. To regulate the temperature inside the test rig, compressed air is supplied to the combustion chamber. In the main gas line, steam can be added at up to 10 kg/h and the particle size distribution of the exhaust gas is measured. The main gas line splits into four reactor branches, in which samples with a diameter of 72.4 mm and a maximum length of 300 mm are installed. The temperature inside each reactor is measured at four different positions with a type K thermocouple. Behind each reactor line, as well as in the bypass, there are flaps to individually adjust the volumetric flow. The exhaust gas composition is measured at several measuring points using an IAG FPS06 FT-IR.

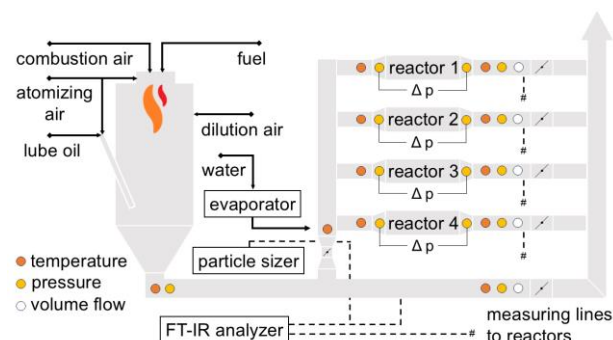


Figure 10: Schematic overview of the burner test rig.

6.2 Synthetic gas testbed

The activity of a drill core sample of the catalyst is measured in a synthetic gas testbed. CH₄, CO, NO, N₂ as a pure gas is dosed via mass flow controllers into a synthetic air gas stream, to obtain the desired testing conditions. Water is evaporated without a carrier gas and is added to the stream. The drilling core samples are placed inside a tubular furnace, which can be operated up to 750 °C and 5 bar(g). A type K thermocouple is placed 1 cm in front of the catalyst to monitor the inlet temperature and to assure same conditions between different experiments. Under the measured conditions no significant blind reaction takes place inside the reactor and an isothermal temperature profile in absence of a reaction is present. The composition after the reactor is measured with an IAG FPS06 FT-IR, while the feed concentration is determined via a bypass line.

6.3 Activity after the full engine test

The honeycombs from the full engine test have been analyzed regarding their activity and catalytic properties. Figure 11 shows the activity of the fresh catalyst compared to a sample, which was present in the reactor during the first operating hours (OPH) in which the engine parameters have been varied. During this operation time, the engine settings have been optimized and unusual conditions were present, which lead to a severe local deactivation of the catalyst. After the optimisation of the engine one set of honeycombs was replaced with fresh ones, which were analyzed after 61 OPH. Here only a minor decrease in activity can be seen, stating that the catalyst is stable under normal engine operation.

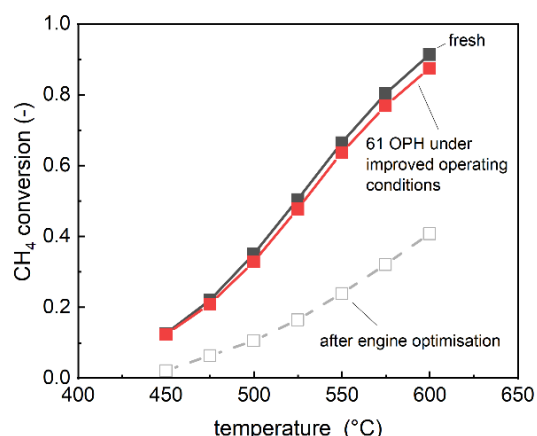


Figure 11: CH₄ conversion of the fresh and during the full engine test used catalyst. Feed: 1000 ppm CH₄, NO; 250 ppm CO; 10 vol.% H₂O, O₂; N₂ balance; 0 bar(g)

6.4 Hydrothermal aging at lab scale

To further investigate the long-term stability under hydrothermal conditions, aging at 550 °C with 1000 ppm CH₄ and 10 vol.% H₂O present in the feed was carried out on the synthetic gas testbed over 90 h. In Figure 12 the CH₄ conversion rates can be seen. During the first 40 h a slight increasing in the oxidation capacity is observed. During the remaining 50 h, no deactivation is seen, supporting the statement, that the developed system is stable during field operation.

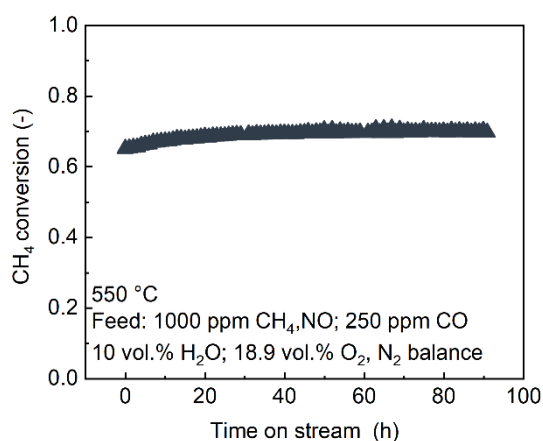


Figure 12: CH₄ conversion rate during hydrothermal aging of the catalyst at 550 °C.

To exclude any temperature hotspots inside the honeycomb, the temperature profile at different conditions has been investigated. Figure 13 shows, that at different space velocities and methane concentrations in the feed, the temperature almost follows a linear increase over the catalyst length. Under the tested conditions, local hotspots inside the catalyst can be excluded

and no local degrading due to high temperature should take place.

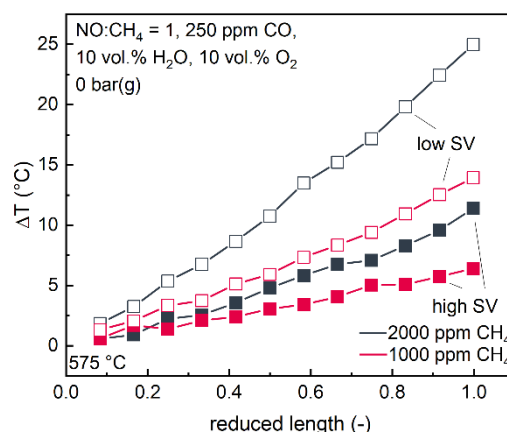


Figure 13: Temperature profile inside the honeycomb at different feed conditions.

6.5 Poisoning of catalyst elements

In addition to the hydrothermal degrading, several poisoning elements are a threat to the catalyst performance. Typically poisons, like sulphur or phosphor, are found in the fuel and lube oil. By using a sustainable, clean fuel, the amount of poisons entering the exhaust gas aftertreatment system can be reduced and therefore increase the lifetime of the used catalyst.

To assess the deposited poisons during the full engine test on the honeycombs, the elemental composition was analyzed via X-Ray Fluorescence (XRF). Figure 14 shows the concentration of Ca, P and S in their oxidic form, deposited on the catalyst after the full engine test. The highest amount of each element is found at the entry of the sample. From the elemental analysis of the fuel and lube oil it can be seen, that the found contamination mostly originates from lube oil combustion inside the engine.

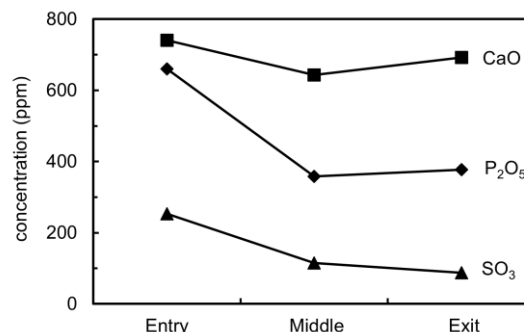


Figure 14: Deposited elements on a honeycomb after the full engine test.

The influence of various catalyst poisons on methane conversion cannot be assessed at this

stage. However, previous sulphur poisoning experiments have shown, that the activity of the MOC remains stable. [8] Moreover the full scale testing showed very stable performance over more than 250 running hours. Both laboratory studies and full scale testing will contribute to gain a better understanding on the poisoning stability of the chosen catalyst material. At present the indication is that it is well suited for engine operation with reasonable service intervals.

7 SUMMARY AND CONCLUSION

As demonstrated in this paper a vast range of measures is available to reduce the methane emissions of Otto-cycle combustion engines. While it is possible to combine several measures, some of them interact in a way that it doesn't seem reasonable to apply all of them on the same engine type. This is e.g. relevant when optimizing the combustion setup and hitting operational limits like the knocking limit or the peak pressure limit.

Some engine internal measures lead to increased engine emissions of other emission species. Typically the trade-off between CH₄ and NO_x emissions can be used as SCR provides a robust and well proven technology to reduce the latter.

A further step for engine internal optimization can be the switch to a Diesel-cycle combustion with direct high-pressure fuel injection. For certain market segments this is already applied. The solution is especially attractive when the fuel is available in liquid form – typically LNG – and the additional cost is compensated by the operational advantages of the combustion concept [8].

Dedicated aftertreatment solutions for methane are in discussion for many years now. Several approaches are documented based on Platinum group metals (PGM) based oxidation catalysts. [10] The major obstacles for large scale application are the high cost and the limited stability in typical engine exhaust conditions. While hydrothermal ageing already harms many catalyst materials the sulfur content in the exhaust resulting from fuel and lube oil seems to be the major obstacle. Approaches with sulfur trap installations have so far also only been realized in research applications.

In addition to other measures MAN ES continues the development of a PGM-free MOC based on the results of the funded projects IMOKAT I and IMOKAT II. The catalyst needs temperatures above 500°C for relevant conversion rates. Further it has been found that not only temperature has a significant influence. The optimal catalyst performance can only be achieved when optimizing further influence

parameters like pressure and other emission species.

With the full scale engine test it could be demonstrated that the catalyst system achieved stable reduction rates over more than 250 operating hours under harsh operating conditions. The achieved methane reduction rates were around 45%, while total reduction rates together with further engine optimization measures of up to 70% were reached.

When analyzing the catalyst samples after the test it was found that certain areas of the catalyst material were damaged. The characterization of these severed zones is still ongoing. The current working hypothesis includes local overheating due to oxidizing of very high methane peaks in certain operating conditions. Especially at the early phase of engine testing the dynamic operation of the engine was not yet adequately calibrated. During that period several methane peaks exceeding 10,000 ppm were recorded. Catalyst material that was only installed at the last phase of testing did not show any obvious damages or reduced oxidation performance at later laboratory tests.

To better understand the damage and wear mechanisms of the catalyst materials in general, MAN ES has set up a new testing device. The burner test rig is specifically designed to mix dedicated exhaust gas compositions and apply those at defined temperature levels. The overall goal is to find the key mechanisms and be able to test catalyst materials in accelerated testing schemes.

Overall it can be stated that different measures for CH₄ emission reduction have different maturity levels. With engine internal measures CH₄ emissions below 1.5% of the gaseous fuel consumption are achievable in the relevant load range and even below 1% for the best operating points. Many of the measures are also applicable in Retrofit. For an even further reduction the development of new technologies gets more and more challenging. MAN ES is thoroughly investigating different measures and those need to undergo profound validation schemes before they will be released to the market.

8 DEFINITIONS, ACRONYMS, ABBREVIATIONS

CH₄: Methane

CD: Continous Development

CO: Carbon Monoxide

CO₂: Carbon Dioxide

CO_{2eq}: Carbon Dioxide equivalent

CR: Common Rail

DF: Dual Fuel

DFDE: Dual Fuel Diesel Electric

ECA: Emission Control Area

EPROX: Propulsion system with variable speed Gensets

FTIR: Fourier Transform Infrared

GHG: Greenhouse Gas

GWP: Global Warming Potential

H₂O: Water

HCHO: Formaldehyde

IMO: International Maritime Organization

IPCC: Intergovernmental Panel on Climate Change

LNG: Liquefied Natural Gas

MAN ES: MAN Energy Solutions

MOC: Methane Oxidation Catalyst

N₂: Nitrogen

N₂O: Nitrous oxide or laughing gas

NO: Nitric oxide

OPH: operating hours

PFI: port fuel injection

PGM: Platinum Group Metals

SCR: Selective Catalytic Reduction

SFGC: Specific Fuel Gas Consumption

SFOC: Specific Fuel Oil Consumption

RPM: Revolutions Per Minute

RTO: Regenerative Thermal Oxidizer

TC: Turbocharger

TRL: Technology Readiness Level

VVT: Variable Valve Train

XRF: X-Ray Fluorescence

9 ACKNOWLEDGMENTS

The authors acknowledge the financial support of the German Federal Ministry for Economic Affairs and Climate Actions and the Projektträger Jülich (PtJ) for their support (project numbers: 03SX438A; 03SX535A). Furthermore, the authors acknowledge the joint work with the company Interkat Catalyst for developing the honeycombs.

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