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Emissions countermeasures for low-speed two-stroke marine ammonia engines

Exhaust Gas Aftertreatment Solutions & CCS

Takaaki MAKINO, MITSUI E&S Co., Ltd.

Ryo Wakayama, MITSUI E&S
Nozomu Hattori, MITSUI E&S
Hans-Philipp Walther, MAN Energy Solutions
Mathias Moser, MAN Energy Solutions

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

Ammonia as marine fuel is one of the most promising candidates for achieving GHG-free emissions in the international shipping sector. Mitsui E&S and MAN Energy Solutions have conducted the world's first full-scale test of an ammonia engine (Mitsui-MAN B&W 7S60ME-Cxxxxx) mid-2024. There has been limited studies on the composition of exhaust emissions from low-speed two-stroke marine ammonia engines, however, the measures to reduce emissions such as nitrogen oxides (NO_x), unburned ammonia slip and nitrous oxide (N₂O) which has a high GHG factor must be considered before conducting this ammonia engine test.

The MAN HP-SCR (selective catalyst reactor) has been selected as the optimal emission and by-product (i.e., ammonia water) reduction technology for the ammonia engine. The double catalyst layer design has been applied for its ability to have various catalysts installed adapting to the actual composition of exhaust emission from the ammonia engine. Basic research has been conducted in accordance with various emission scenarios.

1 INTRODUCTION

1.1 Background

Climate change, driven by global warming, has already begun to impact human life. To mitigate climate change, urgent reductions in greenhouse gas (GHG) emissions are required across all societal sectors, including the maritime industry. The International Maritime Organization (IMO) updated its GHG Reduction Strategy in July 2023 during the Marine Environment Protection Committee (MEPC 80) meeting. This revised strategy includes several enhanced targets and measures to address GHG emissions from international shipping.

The IMO remains committed to reducing GHG emissions from international shipping and aims to phase them out as soon as possible. This is part of a broader effort to promote a just and equitable transition in the maritime sector. The strategy aims to reduce the carbon intensity of international shipping by at least 40% by 2030, compared to 2008 levels. Additionally, it sets an enhanced common ambition to achieve net-zero GHG emissions from international shipping by or around 2050. By 2030, the strategy targets the uptake of zero or near-zero GHG emission technologies, fuels, and/or energy sources to represent at least 5%, striving for 10% of the energy used by international shipping.

Potential carbon-neutral fuels include hydrogen, ammonia, biofuels, and e-fuels. Hydrogen, due to its low energy density, is generally considered suitable only for short-sea shipping. Biofuels, which can utilize existing engine and fuel tank infrastructure, are promising as drop-in fuels for existing ships, though cost and supply volume remain challenges. E-fuels (excluding e-ammonia) also benefit from compatibility with existing infrastructure, but securing carbon-neutral carbon sources is a challenge. Ammonia is expected to be cheaper to produce and capable of larger-scale production compared to biofuels and e-fuels. However, it requires new engines, fuel tanks, and supply systems, as well as the establishment of a new bunkering network.

Each fuel type has its advantages and disadvantages, and it is unlikely that any single fuel will dominate the market. However, ammonia, with its lower production costs and higher supply capacity, may become the predominant marine carbon-neutral fuel.

1.2 Ammonia Engine Emissions

Though NH_3 is a promising candidate for marine carbon-neutral fuel, attention must be paid to its exhaust gas emissions. Unlike heavy fuel oil,

ammonia mainly consists of nitrogen, making its combustion byproducts uncertain. Ammonia slip in exhaust gases is also a concern, requiring specific measures. The main components of concern are NO_x , N_2O , and NH_3 . The current issues for each component are explained below.

1.2.1 NO_x emissions

NO_x emissions include thermal NO_x , produced by the oxidation of atmospheric N_2 , and fuel NO_x , produced by the oxidation of nitrogen in the fuel. Both types of NO_x can be generated from ammonia fuel combustion, potentially increasing NO_x emissions compared to conventional fuels. Studies by Zhou et al. have shown that NO_x concentrations in two-stroke low-speed diesel engines operating on ammonia can be lower than those operating on heavy fuel oil under certain conditions [1]. Rodriguez et al. have shown that in four-stroke medium-speed engines, NO_x concentrations increase with higher ammonia ratios in fuel mixtures [2].

1.2.2 N_2O emissions

In two-stroke low-speed diesel engines, the amount of N_2O generated during ammonia operation has been reported by Li et al. [3]. This case also considers the co-combustion of heavy fuel oil and ammonia. The trend reported indicates that N_2O concentrations increase with higher ammonia ratios. N_2O has a high global warming potential, and even small amounts require countermeasures. The report compares N_2O levels in high-pressure injection dual-fuel engines and low-pressure injection dual-fuel engines, showing that high-pressure systems can reduce N_2O more effectively. Post-combustion reduction of N_2O using catalysts is challenging, requiring high temperatures for effective conversion. Coq et al. have demonstrated that Fe-Zeolite catalysts can reduce N_2O emissions more effectively at lower temperatures when a reducing agent (NH_3) is present [4].

As a preliminary study, we measured the catalytic performance of an N_2O decomposition catalyst sample in the same manner as described in Figure 2. We assumed two cases of gas composition. In case 1, the inlet gas contained 1000ppm NH_3 , 600ppm NO , 100ppm N_2O , 10% O_2 , and N_2 as the balance gas; Gas hourly space velocity (SV) was 25000 h^{-1} . In case 2, NH_3 concentration was changed to 700ppm. According to the results shown in Figure 1, high operating temperature ($>450^\circ\text{C}$) is still required for the effective N_2O decomposition even when NH_3 is present as a reducing agent.

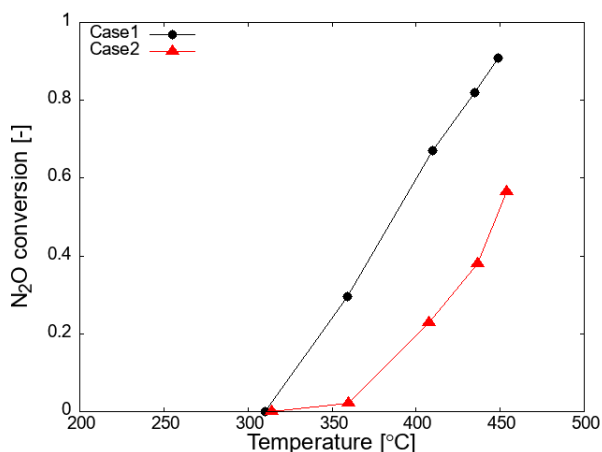


Figure 1. Catalytic performance of N₂O decomposition catalyst.

1.2.3 NH₃ emissions

Exhaust gases from ammonia-fueled engines may contain ammonia slip. Xu et al. conducted co-combustion tests of ammonia and heavy fuel oil in four-stroke medium-speed engines, reporting cases where ammonia slip concentrations reached approximately 10000ppm [5]. The amount of ammonia slip can vary significantly depending on the injection method and engine speed. Nevertheless, high concentrations of ammonia slip, as reported, necessitate countermeasures.

1.3 Strategy for emissions

Our approach to addressing these issues raised above is as follows:

NO_x: During the design phase of the exhaust gas treatment reactor, it was difficult to predict the amount of NO_x. Therefore, the reactor was enlarged to increase the amount of catalyst that can be installed, ensuring that excess NO_x can be treated even if it exceeds expectations.

N₂O: Post-treatment reduction is challenging, and thus the engine development will focus on optimizing combustion conditions to prevent N₂O emissions during ammonia combustion.

NH₃: The primary approach is to reduce ammonia slip through combustion optimization. However, the application of ammonia slip catalysts (ASC) was also considered in parallel. This report focuses on addressing ammonia slip using ASC. The oxidation reaction of ammonia on ASC can generate significant amounts of N₂O as a by-product under certain conditions, necessitating the selection of appropriate catalysts for practical use.

1.4 Objective

A MAN B&W 7S60ME model engine, for the first deployment of MAN ES' ammonia dual-fuel two stroke engine, will be built by Mitsui E&S. The largest-ever selective catalytic reduction (SCR) catalytic converter, cluster 5 double layer (DL), produced by MAN ES will be installed for aftertreatment. Detailed design specifications are provided in Chapter 3.1. To mitigate various risks, particularly the potential for significant NH₃ slip, ASC will be incorporated during the first engine operation. This study examines the catalytic performance of ASC to select the most suitable catalyst for the SCR reactor. The optimal configuration of SCR catalyst and ASC was also determined through numerical considerations.

2 ASC EVALUATION

2.1 Experimental setup

A cylindrical quartz-glass (26 mm i.d.) was used as the reactor to mount the catalyst inside, with the gap between the catalyst and reactor wall filled with quartz wool (Figure 2). The catalyst temperature was measured using a thermocouple in contact with the catalyst. The feed gas consisted of NH₃, NO, O₂, and balance N₂, with the concentration of each component adjusted by a mass flow controller. An FTIR gas analyzer (Best Sokki; Bex-2000FT) was installed to measure the concentration of NH₃, NO, NO₂, and N₂O in the inlet and outlet gases, respectively. The reactor was heated to the desired temperature with an electric furnace equipped with a thermostat.

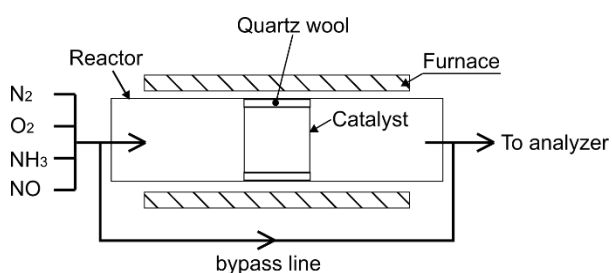


Figure 2. Schematic diagram of experimental setup for the catalytic performance test.

2.2 ASC performance test

2.2.1 Procedure

The catalytic performance measurements of ASC samples were conducted under atmospheric pressure in the temperature range of 225-430°C, and SV of 20000-120000 h⁻¹. Regarding the feed gas composition that simulates the exhaust emissions from ammonia engine combustion, we assumed three scenarios where NH₃ slip is 1000, 2000, and 3000ppm, with NO emission ranging

from 0-600ppm. In all cases, the O₂ concentration was maintained at a constant 15%.

ASC samples were purchased from several catalyst manufacturers, and all samples were characterized under the conditions mentioned above to select the appropriate one in terms of NH₃ conversion and N₂O production.

2.2.2 Results

In this section, we present the experimental results of the selected catalyst for the actual engine test. The experimental conditions are shown in Table 1.

Table 1. Inlet gas composition of ASC performance test. Conditions (unless specified): SV = 20000 h⁻¹, O₂ = 15%, H₂O = 0%, N₂ = balance.

Composition No.	NH ₃ [ppm]	NO [ppm]
1	1000	600
2	2000	600
3	3000	600
4	1000	300
5	1000	0
6	2000	0
7	3000	0

Figure 3 illustrates the N₂O formation and the amounts of NH₃ slip at various temperatures under constant NO conditions. Under a 1000ppm NH₃ inlet condition, NH₃ slip at the ASC outlet remained below the detectable level (<1ppm) over the whole temperature range. Conversely, for the 2000ppm and 3000ppm NH₃ inlet conditions, the NH₃ slip amount increased significantly at low temperatures around 225°C, while it stayed low at higher temperatures above 250°C. Regarding N₂O formation, it generally decreased with increasing temperature, except at 225°C, where a slight drop was observed. Additionally, the amount of N₂O formation showed a roughly proportional relationship to the inlet NH₃ concentrations.

Figure 4 gives the results under constant inlet NH₃ conditions with varying NO inlet concentration of 0, 300, and 600ppm. The influence of NO concentration on NH₃ slip at the ASC outlet is negligible above 250°C. However, at the low temperature of 225°C, an increase in NH₃ slip was observed in the low inlet concentration of NO. Additionally, the presence of NO in the inlet gas affects the amount of N₂O formation, with higher NO concentrations leading to increased N₂O production.

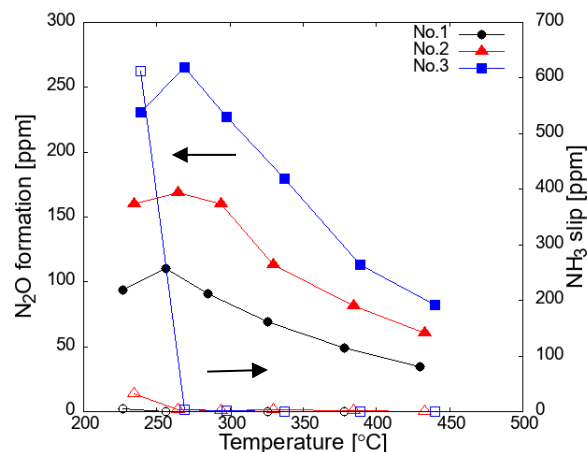


Figure 3. Inlet NH₃ concentration dependence of N₂O formation (solid symbols) and NH₃ slip (open symbols). Numbers in figure correspond to those in Table 1.

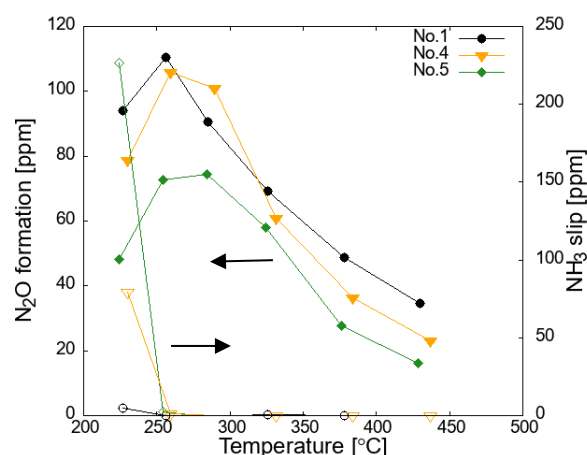


Figure 4. Inlet NO concentration dependence of N₂O formation (solid symbols) and NH₃ slip (open symbols). Numbers in figure correspond to those in Table 1.

2.2.3 Discussion

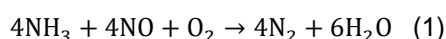
Recently, various types of multi-function ASC have been proposed, including dual-layer structures consisting of SCR and ammonia oxidation layers to enhance N₂ selectivity, thereby reducing production of NO_x and N₂O. Consequently, ASC catalytic performance needs to be considered in terms of both SCR and ammonia oxidation functionalities. Sukumar et al. has developed a dual-layer ASC 1D-1D (pseudo 2D) model to predict outlet gas concentrations [6]. Dongwei et al. improved the dual-layer ASC kinetic model by incorporating the intermediate product NH₃NO₃ as a source of N₂O [7].

In this study, we focused on four reactions eq. 1-4 related to NH₃ decomposition and N₂O formation to simplify understanding. According to the test

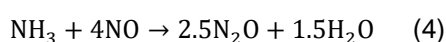
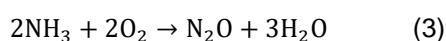
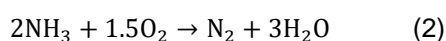
results, an increase in NH₃ slip around 225°C was observed in compositions No. 2-5. This behavior indicates that ammonia oxidation reactivity diminished in the lower temperature range below 250°C, while SCR reactivity remained. The decline in N₂O production with increasing temperature above 250°C is likely caused by the faster N₂ production reaction rate (eq. 1, 2) compared to that of N₂O production (eq. 3). Regarding the N₂O source, generation from NH₃ (eq. 3, 4) and NO (eq. 4) will explain the experimental results of inlet NH₃ and NO dependence.

Due to the low NH₃ consumption capability in lower temperature range, ASC should be utilized in the exhaust conditions above 250°C in practical use.

SCR functionality in ASC:



Ammonia oxidation functionality in ASC:



2.3 Numerical consideration

Considering that the concentrations of inlet NH₃ or NO affect the amount of N₂O formation in ASC, installing SCR catalyst in the first layer, with ASC in the second layer, is expected to be an ideal configuration for the Cluster 5 DL reactor. Therefore, we will focus on SCR-ASC sequence as the catalyst configuration in the following chapters. If the volumetric ratio of second layer ASC to the first layer SCR ($r_{A/S}$) is set smaller, N₂O production will be reduced, while NH₃ slip increase. Thus, it is desirable to determine the appropriate $r_{A/S}$ value to meet both NH₃ and N₂O emission requirements.

2.3.1 SCR model

The performance of the SCR catalyst was investigated in the same procedure as described for the ASC above. NH₃ decomposition capability was evaluated by k_{SCR} defined in eq. 5, where η_{SCR} represents the NH₃ conversion of SCR, based on the first-order reaction rate for simple estimation. The temperature dependence was determined by Arrhenius plots. It should be noted that since the k_{SCR} value depends on the NO inlet concentration, correction coefficient of NO is required to predict the wide range of NO inlet composition.

$$k_{\text{SCR}} = -SV \times \ln(1 - \eta_{\text{SCR}}) \quad (5)$$

2.3.2 ASC model

The performance of the ASC was considered in two perspectives: NH₃ decomposition and N₂O production. The NH₃ decomposition capability was assessed using k_{ASC} defined in eq. 6 in the same manner as for the SCR. Regarding N₂O, its production amount in relation to the amount of NH₃ decomposition is depicted in Figure 5. Due to its proportional dependency, we propose the N₂O production model in eq. 7, where α_M is proportionality factor on decomposition amount of M (NH₃ or NO).

While the concentration of NO affects the amount of N₂O production, considering the SCR-ASC configurations and the excessive inlet concentration of NH₃ relative to NO, the amount of NO entering the ASC is expected to be quite low. Therefore, the second term in Eq. 7 can be considered negligible.

$$k_{\text{ASC}} = -SV \times \ln(1 - \eta_{\text{ASC}}) \quad (6)$$

$$\Delta C_{\text{N}_2\text{O,ASC}} = \alpha_{\text{NH}_3} \Delta C_{\text{NH}_3,\text{ASC}} + \alpha_{\text{NO}} \Delta C_{\text{NO,ASC}} \quad (7)$$

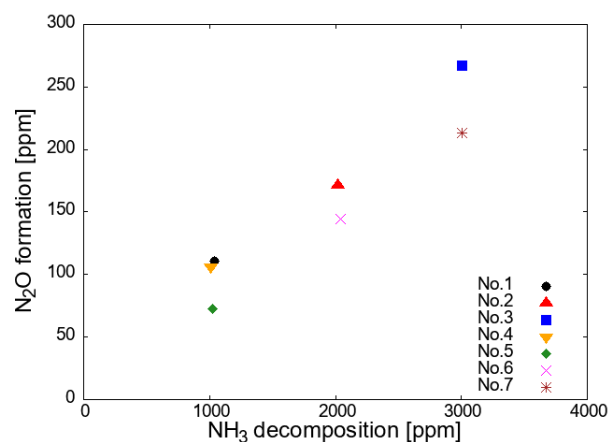


Figure 5. N₂O production dependence on NH₃ decomposition of ASC at approximately 260°C. Numbers in figure correspond to those in Table 1.

2.3.3 Optimization of configuration

According to eq. 5-7, NH₃ slip and N₂O formation during passing through the SCR-ASC system can be described by eq. 8 and 9.

Figure 6 shows one of the performance estimation results. The labels on lines represent the amount of N₂O produced or NH₃ slip at the SCR-ASC outlet in ppm. As the $r_{A/S}$ value increases, NH₃ decreases while N₂O production increases. Due to this trade-off relationship, it is essential to strike a balance.

After several numerical considerations, the $r_{A/S}$ value was ultimately set to 0.4 for the actual engine test.

$$C_{\text{NH}_3,\text{out}} = C_{\text{NH}_3,\text{in}} \exp\left[-\frac{k_{\text{SCR}}(1-r_{A/S})}{SV_{\text{total}}}\right] \times \exp\left[-\frac{k_{\text{ASC}}r_{A/S}}{SV_{\text{total}}}\right] \quad (8)$$

$$C_{\text{N}_2\text{O},\text{out}} = \alpha_{\text{NH}_3} C_{\text{NH}_3,\text{in}} \exp\left[-\frac{k_{\text{SCR}}(1-r_{A/S})}{SV_{\text{total}}}\right] \times \left(1 - \exp\left[-\frac{k_{\text{ASC}}r_{A/S}}{SV_{\text{total}}}\right]\right) \quad (9)$$

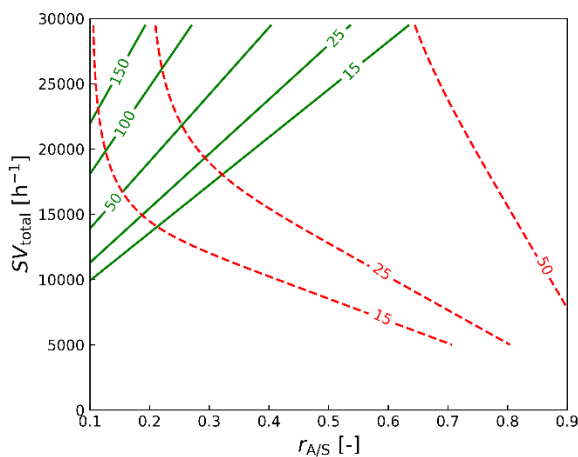


Figure 6. Numerical estimation of NH_3 slip (solid line) and N_2O production (dashed line). The boundary condition is composition No. 1 at 260°C .

2.4 SCR-ASC performance test

To validate the estimation results, the performance of the SCR-ASC configuration was evaluated. The experimental setup is illustrated in Figure 7. The $r_{A/S}$ value was set to 0.4. SV_{total} was controlled at 12000 h^{-1} (with the SV of SCR catalyst alone at 20000 h^{-1} , and that of ASC alone at 30000 h^{-1}). Inlet gas compositions No. 1-3 as detailed in Table 1, were used for this demonstration.

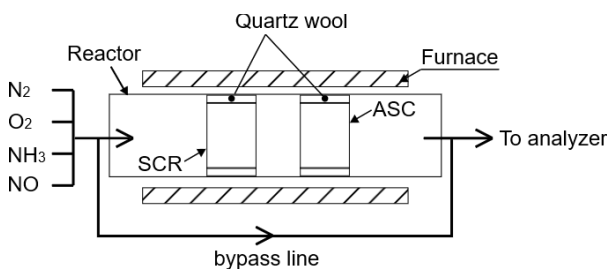


Figure 7. Schematic diagram of experimental setup for the SCR-ASC performance test.

Figure 8 presents the result of the combined configuration test. In comparison to the results of the ASC performance tests (Figure 3), the amount of N_2O formation decreased in all cases. Notably, for composition No. 1 at approximately 260°C , both NH_3 slip and N_2O formation were below 25 ppm , aligning with the predictions from numerical considerations.

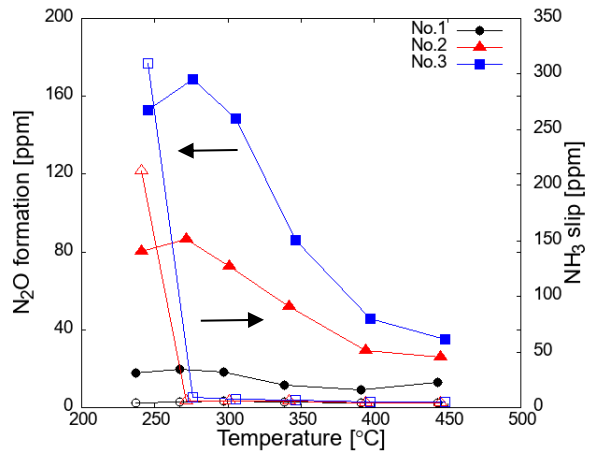


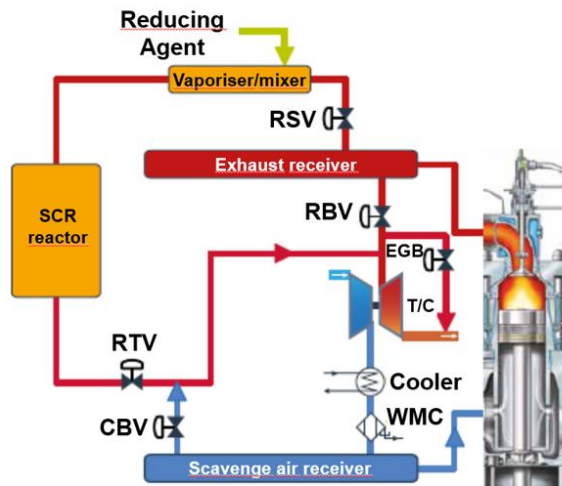
Figure 8. N_2O formation and NH_3 slip in the SCR-ASC test. Numbers in figure correspond to those in Table 1.

3 ACTUAL ENGINE TEST

3.1 SCR System Design

Considering catalytic aftertreatment systems, SCR is the most common technology for large engines. The emission regulations by IMO focus on NO_x and SO_x . The latter is typically controlled either by the sulfur content of the fuel or Scrubber technology. Consequently, NO_x remains the only emission for further treatment and besides exhaust gas recirculation (EGR) SCR has a considerable market share.

Catalytic reactions typically require a certain process temperature to be active, the so-called light-off temperature. As the exhaust gas temperatures for 2-stroke engines are comparably low, additional measures are likely necessary for heating up the exhaust gas for low pressure SCR applications. A viable alternative is high pressure SCR systems where the reactor is installed before the turbine. This leads not only to higher temperatures but also elevated pressures at higher engine loads. Consequently, the reactor needs to be designed for this. A typical system layout for a high pressure (HP) application is depicted in Figure 9.



RBV	Reactor Bypass Valve
RSV	Reactor Sealing Valve
RTV	Reactor Throttle Valve
CBV	Cylinder Bypass Valve
EGB	Exhaust Gas Bypass Valve

Figure 9. System overview and integration of a high pressure SCR system

3.1.1 Overview over MAN SCR-HP

The exhaust aftertreatment system applied on the test bed is an optimized version of the MAN SCR-HP, applying a double layer reactor design. This system provides a versatile basis for emission reduction. MAN only offers high pressure SCR systems for its 2-stroke engines due to the more compact installation and more suitable boundary conditions for SCR operation. For other suppliers the option remains to develop and apply suitable lower pressure systems.

The MAN SCR-HP system consists of

- SCR reactor including urea mixing pipe and soot blowers
- SCR catalyst honeycombs
- Pump module and dosing unit for urea supply
- Compressed air reservoir module
- MAN SaCoS SCR Control Unit

3.1.2 SCR system design

In the following sections a more detailed insight into the fundamental design of the system will be given as well as further insights into the actual system applied on the test bed.

3.1.2.1 Fundamental system design

The reactor on the Ammonia test engine is based on the second generation of MAN SCR-HP. This system is available in different cluster sizes to match different engine outputs.

The design is optimized for mixing uniformity after the Urea dosing and has a well proven internal sealing concept. For standard SCR applications on Diesel engines these two aspects are important to achieve a robust NO_x reduction performance. If one or both aspects are not optimal the result is likely NH₃ slip either through a by-pass or at those parts of the reactor where there is excess NH₃ compared to NO_x at the inlet of the honeycombs.

The main characteristics of the reactor design are

- Very compact outer dimensions
- Integrated mixing pipe
- Reverse flow for minimum piping length between engine and SCR systems
- Versatility concerning direction of outlet pipe connection
- Stainless steel for maximum service robustness and lifetime



Figure 10. Picture taken from MAN ES press release [8]

3.1.2.2 Specific design features of Cluster 5 DL

The applied Cluster 5 DL reactor is the largest SCR reactor yet that has been supplied by MAN ES (Figure 10). The fundamental layout is based on the requirements for Diesel operation. Ammonia specific adaptations are described in Chapter 3.1.3. When scaling the former smaller cluster variants, special focus was put on finding a suitable foot design for the reactor. Not only was it necessary to

deal with the increased static and dynamic loads. Due to the overall size of the reactor an optimized approach to dealing with thermal elongation had to be found.

3.1.3 Ammonia specific considerations

At the time when the cooperation between Mitsui and MAN ES was agreed upon no test data of an Ammonia engine was available. Therefore, the chosen system had to be versatile enough to deal with different scenarios concerning engine exhaust emissions.

The major emission components considered at that time were NO_x , NH_3 and N_2O . It was not clear, which concentrations were to be expected, and which reduction rates had to be achieved.

SCR honeycombs provide a good basis for aftertreatment, as the two harmful emission species NO_x and NH_3 react with each other and form harmless N_2 and H_2O . MAN SCR honeycombs are a well proven technology. From intensive laboratory testing it is known that N_2O formation is not relevant in the typical temperature range for an MAN SCR-HP application on a 2-stroke engine.

The fundamental capabilities of the reactor in terms of flow uniformity and internal sealing described in Chapter 3.1.2.1 also provide an ideal basis for high conversion rates during NH_3 operation. Especially when there is excess NH_3 in the engine raw emissions, the reduction rate can be close to 100%. The actual value is obviously dependent on other boundary conditions, mainly temperature and SV.

By choosing a DL type reactor one spare layer is reserved for additional catalyst materials. Both Mitsui and MAN ES are investigating further options. Depending on the outcome of the engine tests, further catalyst material may also be applied for service operation. As already described in Chapter 2, an ASC is considered especially for the test bed and possibly later service operation of the ammonia engine.

3.2 Preparation

A series of arrangements are currently underway for the full-scale test of the ammonia engine at the Mitsui E&S site. The ASC selected in Chapter 2 has been installed in the second layer of cluster 5 DL, with a volumetric ratio set to 0.4. An FTIR gas analyzer has also been installed to measure the exhaust gas concentration. Exhaust gases are collected from three sampling ports: the reactor inlet, between the SCR layer and ASC layer, and the reactor outlet. Commissioning of the engine in ammonia operation will take place soon and the

exhaust gas of ammonia combustion and its aftertreatment result will be clarified in the near future.

4 CONCLUSIONS

The catalytic performance of ASC was evaluated to select a suitable catalyst for the cluster 5 DL reactor. The methodology of optimizing its volumetric ratio to SCR catalyst was presented, determining the ratio to be 0.4 for this SCR-ASC system. Numerical predictions were consistent with experimental validation of SCR-ASC performance tests. The ASC for the actual engine test has already been installed in the reactor, and its demonstration is scheduled to take place shortly.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

GHG: Greenhouse Gas

IMO: International Maritime Organization

MPEC: Marine Environment Protection Committee

E-fuels: Electrofuels

NO_x : Nitrogen Oxides

N_2O : Nitrous Oxides

SO_x : Sulfur Oxides

SV: Space Velocity

ASC: Ammonia Slip Catalyst

SCR: Selective Catalytic Reduction

EGR: Exhaust Gas Recirculation

DL: Double Layer

HP: High Pressure

SaCoS: System of engine control

η_x : NH_3 conversion efficiency of catalyst X

k_x : Rate constant of NH_3 decomposition of catalyst X

$\Delta C_{\text{N}_2\text{O},\text{ASC}}$: Amount of N_2O formation at ASC

$\Delta C_{\text{M},\text{ASC}}$: Decomposition amount of M (NH_3 or NO) at ASC

α_{M} : Proportionality factor of N_2O formation to decomposition amount of M

$C_{\text{NH}_3,\text{in}}$: NH_3 concentration at the inlet of SCR-ASC system

$C_{\text{NH}_3,\text{out}}$: NH_3 concentration at the outlet of SCR-ASC system

$C_{\text{N}_2\text{O},\text{out}}$: N_2O concentration at the outlet of SCR-ASC system

$r_{\text{A/S}}$: Volumetric ratio of ASC to SCR

SV_{total} : Space Velocity based on total volume of SCR and ASC

6 ACKNOWLEDGMENTS

This work was partly supported by New Energy and Industrial Technology Development Organization (NEDO) Green Innovation Fund project.

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