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Practical application study of an exhaust gas aftertreatment system for an ammonia diesel dual-fuel engine

Exhaust Gas Aftertreatment Solutions & CCS

Yuki Shimizu, DAIHATSU DIESEL MFG. CO., LTD.

Koichi Hirata, National Maritime Research Institute, National Institute of Maritime, Port and Aviation Technology
Yoichi Niki, National Maritime Research Institute, National Institute of Maritime, Port and Aviation Technology
Kazuyuki Kobayashi, DAIHATSU DIESEL MFG. CO., LTD.
Susumu Hikazudani, Kanadevia Corporation
Naoe Hino, Kanadevia Corporation
Yusuke Nishida, Kanadevia Corporation
Koichi Fujioka, Kanadevia Corporation

ABSTRACT

As countries around the world accelerate their efforts toward decarbonization, aiming to be carbon neutral by 2050, Japan's shipping industry is aiming to commercially operate "zero-emission ships" that do not emit greenhouse gases by 2028.

Hydrogen and ammonia (NH3) have attracted attention because they burn without emitting carbon dioxide and can be efficiently transported and stored as energy carriers. From the perspective of a fuel tank installation, NH3 has been considered as a main fuel for ship power and propulsion systems due to the higher energy density. However, the use of NH3 as fuel entails challenges to address, such as the development of a practical exhaust gas aftertreatment system for nitrogen oxides (NOx), unburned NH3, and nitrous oxide (N2O) emissions. For the exhaust gas aftertreatment system to be practical, it requires compactness and durability for sulfur oxides (SOx) for diesel mode operation.

This paper reports the results of various evaluation tests for the practical application of an exhaust gas aftertreatment system that efficiently reduces NOx, unburned NH3, and N2O, and that is compact in size.

In the beginning, exhaust gas characteristics were investigated with an NH3-fueled large single-cylinder engine. The low-pressure dual fuel type combustion was employed in the experiments. Gaseous NH3 was introduced in the intake air, and then the mixture of NH3 and air was ignited by a small amount of diesel pilot fuel in the cylinder.

As a result, it became clear that adjustments on the engine side were insufficient and that an exhaust gas aftertreatment system was necessary. Next, a catalyst performance evaluation using a stand-alone test apparatus and sulfur resistance evaluation during diesel operation were conducted to develop an exhaust gas aftertreatment system that can simultaneously reduce NOx, unburned NH3, and N2O, and SOx resistance. In addition, the exhaust gas aftertreatment system was applied to a low-pressure type NH3-fueled small single-cylinder engine, and a catalyst performance was evaluated in the actual exhaust gas. Based on these findings, we designed an exhaust gas aftertreatment system for a planned NH3-fueled large single-cylinder engine.

This study has shown that the developed exhaust gas aftertreatment system has a practical size and SOx resistance performance and can simultaneously reduce NOx, unburned NH3, and N2O.

1 INTRODUCTION

Efforts are currently underway around the world to reduce greenhouse gas emissions (GHGs) from various industries.

Ships are no exception, and Figure 1 shows the GHGs reduction strategy adopted at IMO_MEPC80 in 2023 [1], with enhanced targets compared to the 2018 adoption, including clear targets for the 2030 and 2040 phases.

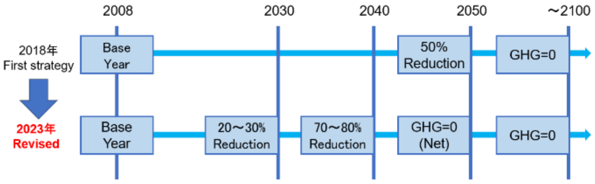

Figure 1. GHGs reduction load map

Therefore, a rapid response to GHGs reduction is needed on board ships.

One of the ways to reduce GHGs are to use methanol, ammonia (NH_3) and hydrogen (H_2) as fuels instead of conventional diesel fuel.

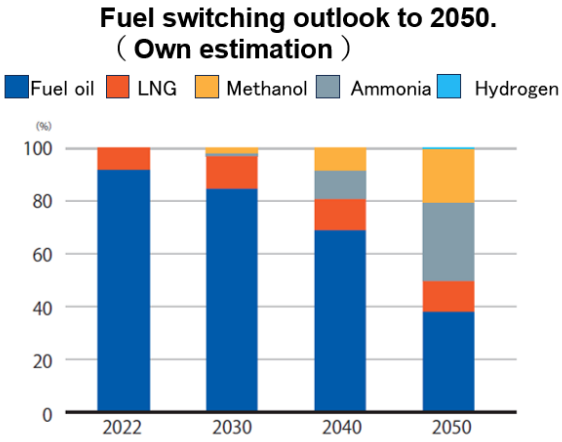

Figure 2. Fuel switching outlook

Figure 2 shows our own prediction of the future penetration rate of alternative fuels. Methanol is expected to spread in the market ahead of NH_3. We believe that the share of NH_3 will eventually exceed that of methanol, but not until after 2040.

NH_3 is easier to liquefy and has more energy per unit volume than H_2, so it has an advantage in terms of installation in fuel tanks, and research is progressing on its use in large two-stroke marine engines. In addition, NH_3 can be burned without CO_2 emissions unlike methanol and is effective for reducing CO_2 emissions from thermal power generation, industrial furnaces, ships, etc. However, NH_3 combustion has several challenges. It requires combustion stabilized by pilot fuel because it has a low adiabatic flame temperature and a low flame speed. NH_3 is difficult to burn stably as a single fuel in four-stroke engines. Furthermore, NH_3 combustion emits nitrous oxide (N_2O) with a global warming potential 275 times higher than that of CO_2 emissions.

This paper reports the results of various evaluation tests (NH_3 combustion characteristic test with a large single cylinder engine, Unit catalyst performance test of an exhaust gas after-treatment system, After-treatment system performance test with a small single cylinder engine) for the practical application of an exhaust gas after-treatment system that efficiently reduces NOx, unburned NH_3, and N_2O, and that is compact in size.

Also, the target concentration for NOx, NH_3, and N_2O emissions reduction was set as 10 ppm or less, which has less impact on human health and GHGs reduction.

2 VARIOUS EVALUATION TESTS RESULTS

2.1 LARGE SINGLE CYLINDER ENG. TEST

2.1.1 Specifications

NH_3 combustion characteristic was investigated with an NH_3 fueled large single cylinder engine (LSCE). Table 1 and Figure 3 show the specifications of the large single cylinder diesel engine and the outline of the test equipment. In the engine, NH_3 gas was mixed with the intake air by a gas admission valve. In the combustion chamber, dual fuel combustion using NH_3 and diesel fuel was carried out by injecting diesel fuel for ignition with an electronically controlled injector.

Table 1. Specifications of LSCE

Type	4-stroke, 1-cylinder
Bore/Stroke [mm]	285 / 390
Rated power [kW]	300
Rated speed [min^{-1}]	720
Diesel fuel injection system	Common rail type

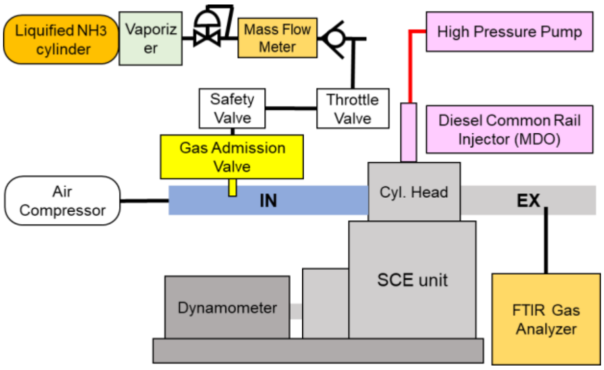

Figure 3. Outline of LSCE facility

2.1.2 Exhaust gas analyzer

The exhaust gases of both the large and small single cylinder engines were analyzed by a Fourier Transform Infrared Gas Spectrometer (FT-IR) and the concentrations were measured, respectively. In gas analyses, we simultaneously sampled and measured several gas components (CO_2, CO, NO, NH_3, N_2O) in high-temperature exhaust gas.

2.1.3 Engine operation condition

Engine operation condition was listed in Table 2.

Table 2. Engine operation condition

Speed [min^{-1}]	Brake power [kW]	EF_{NH3} [%]	λ
720	75	60	2
	150	95	1.2, 1.6
	225	95	1.2, 1.6
	300	95	1.2, 1.6

Here, EF is the energy fraction.

2.1.4 Engine operation method

Initially, the engine was started by motoring and then the diesel fuel was injected. After stable diesel combustion was achieved vaporized NH_3 was injected from a gas admission valve into the intake pipe. The mass of the supplied NH_3 and diesel fuel is adjusted to set the engine load. The engine speed and brake power are set to 720 min^{-1} and 75・150・225・300kW throughout the tests and was conducted while varying EF_{NH3} and λ.

2.1.5 Engine results

Figure 4 shows the exhaust gas temperature and emissions of diesel / NH_3 co-combustion were compared by λ.

When changing λ from 1.6 to 1.2, it found that NO, unburned NH_3 and N_2O were decreased due to the increase in exhaust temperature. However, target concentrations have not been achieved in both λ. Also, the high exhaust temperature of λ 1.2 was not in the practical range.

The result shown in Figure 4 is an example and not all the test results can be shown in this manuscript, but considering the results obtained from the series of experiments, it became clear that adjustment on the engine side was insufficient and that an exhaust gas after-treatment system was necessary.

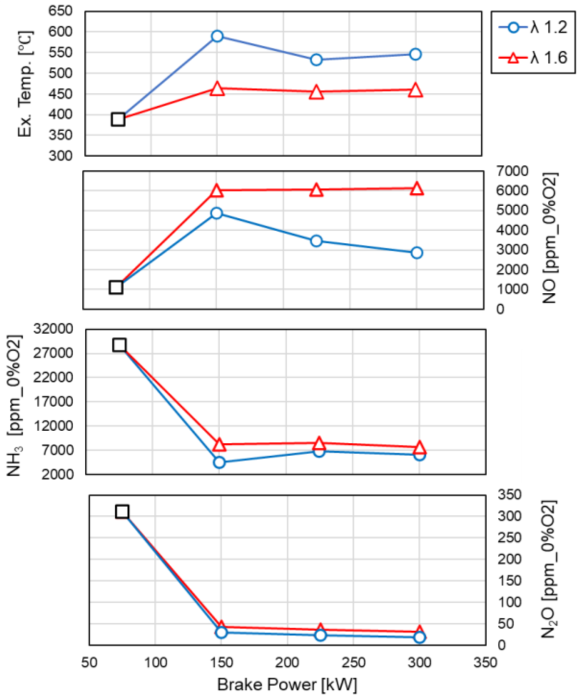

Figure 4. Exhaust gas temperature and emissions at different λ conditions for various loads

2.2 UNIT EVALUATION TEST OF AFTER-TREATMENT EQUIPMENT

2.2.1 Configuration of after-treatment equipment

Next, in response to the aforementioned exhaust gas performance test results, a reactor filled with three types of catalysts (DeNOx catalyst, NH_3 oxidation catalyst, and N_2O decomposition catalyst) as shown in Figure 5 was considered for the simultaneous reduction of NOx, unburned NH_3, and N_2O. As each catalyst is exposed to sulfur components in diesel mode, the catalyst amount was considered based on durability evaluation and degradation rate.

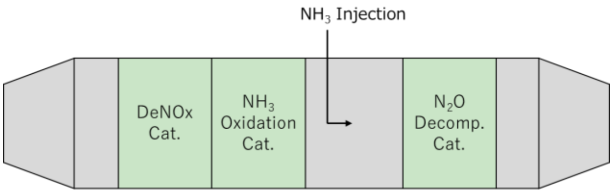

Figure 5. Configuration of after-treatment equipment

2.2.2 Catalysts used for evaluation

The DeNOx catalyst [2] and N_2O decomposition catalyst, both developed in Kanadevia, were used in combination with the NH_3 oxidation catalyst.

2.2.3 Catalyst evaluation equipment

The catalyst performance was evaluated using the equipment shown in Figure 6. The reaction gases were supplied from cylinders and the flow rates of each gas were controlled by mass flow controllers to mix them, simulating the exhaust gas composition. Water was introduced into the evaporator by a water injection pump, and the evaporated water vapor was mixed with the reaction gas and introduced into reactor. The catalyst samples were packed into the sample holder shown in Figure 7 (maximum size: 30 mm width × 26 mm height × 500 mm length) and evaluated.

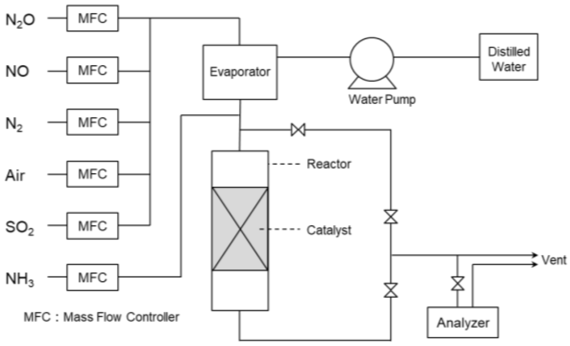

Figure 6. Overview of catalyst evaluation equipment

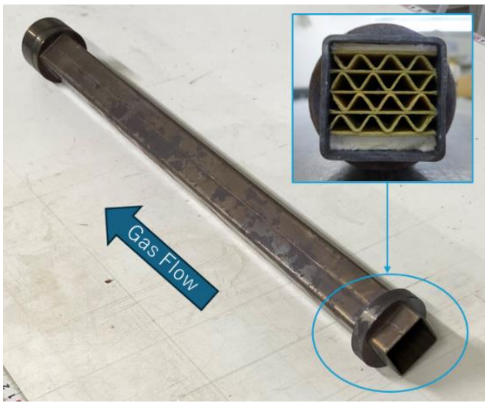

Figure 7. Appearance of the sample holder

2.2.4 Evaluation method

The initial performance (temperature dependence, SV dependence) of each catalyst individually, and the SO_2 durability and regenerability in case of degradation, were evaluated assuming diesel mode. Based on these results, the catalyst amount for efficient removal of NOx, NH_3, and N_2O when catalysts are combined as shown in Figure 5 was estimated, and reactor performance calculation and size selection were conducted.

2.2.5 Evaluation results of DeNOx catalyst performance

Figure 8 shows the performance curve of the fresh DeNOx catalyst at 200°C assuming diesel mode. From Figure 8, it is estimated that at SV < 7,000 h^{-1}, a NOx conversion > 90% is achieved under low-temperature diesel mode load conditions of 25%. Regarding durability, it has been confirmed that the performance degradation of the DeNOx catalyst after operating at 200°C for 28,000 hours in an actual land-based project is less than 10%. The DeNOx catalyst is confirmed to have high durability, but in this design, the amount of catalyst was set on the assumption that a 10% drop in performance would occur in diesel mode.

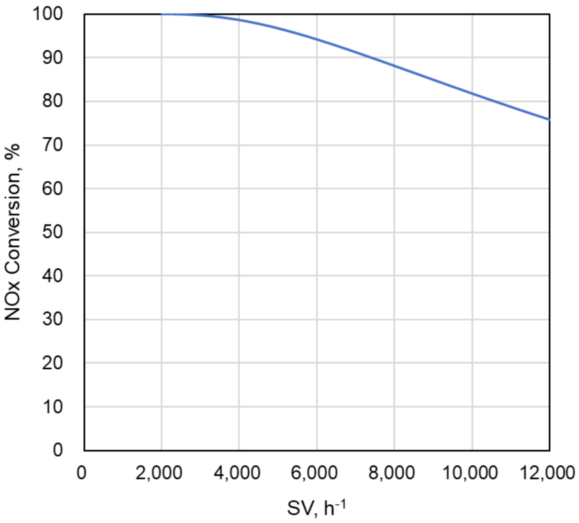

Figure 8. Performance curve of the DeNOx catalyst (Temperature: 200°C, NO: 100 ppm, NH_3: 100 ppm, O_2: 2.5%, H_2O: 10%)

2.2.6 Evaluation results of NH_3 oxidation catalyst

Figure 9 shows the temperature dependence of the NH_3 oxidation performance and N_2O by-production rate of the fresh NH_3 oxidation catalyst, and Figure 10 shows the SV dependence. From Figure 9, it was confirmed that the NH_3 conversion was approximately 100% in the temperature range of 280 to 360°C assumed in the NH_3 mode, which is sufficient performance. It was confirmed that the N_2O by-production rate tends to increase as the temperature increases (N_2O by-production rate: ($[N_2O]_{out}$ x $2/[NH_3]_{in}$) x 100). Figure 10 confirmed that NH_3 oxidation performance is sufficiently high in the SV range of 11,000 to 20,000 h^{-1}.

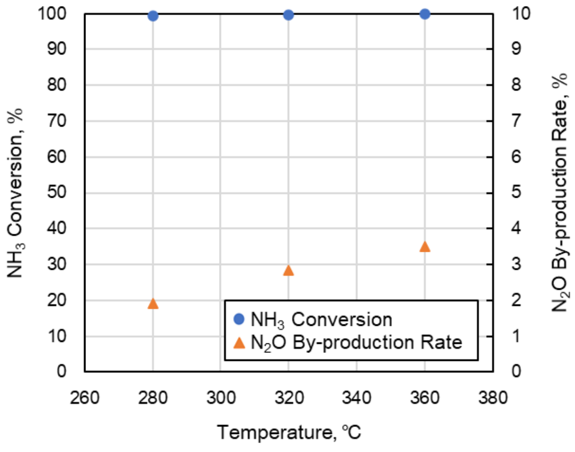

Figure 9. Temperature dependence of NH_3 oxidation catalyst performance (NH_3: 1,000 ppm, O_2: 12%, H_2O: 10%, SV:11,000 h^{-1})

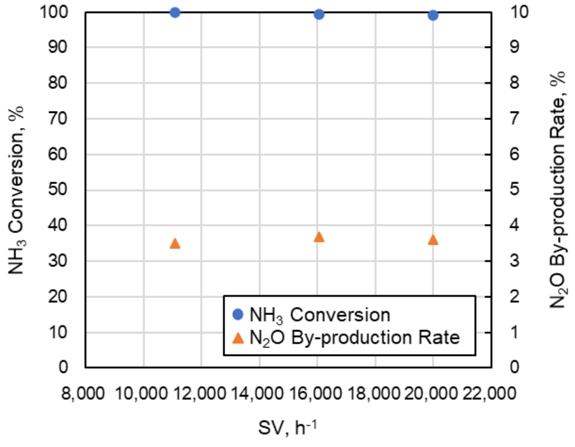

Figure 10. SV dependence of NH_3 oxidation catalyst performance (Temperature: 360°C, NH_3: 1,000 ppm, O_2: 12%, H_2O: 10%)

To evaluate the SO_2 durability of the NH_3 oxidation catalyst, an SO_2 exposure test was conducted at each temperature at 100 ppm, which is five times the assumed SO_2 concentration of 20 ppm in diesel mode, and the results are shown in Figure 11. It was confirmed that the NH_3 oxidation performance did not decrease at 350°C and the SO_2 durability was sufficiently high, but degradation was significant at temperatures below 300°C.

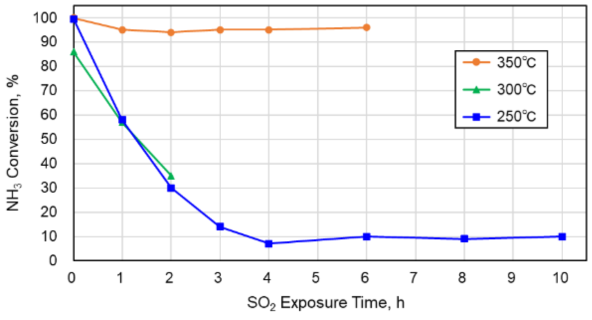

Figure 11. SO_2 durability results of the NH_3 oxidation catalyst (SO_2: 100 ppm, NH_3: 1,000 ppm, O_2: 12%, H_2O: 10%, SV: 11,000 h^{-1}, exposure and performance measurement temperatures are the same)

To verify the regeneration of degraded NH_3 oxidation catalysts, the NH_3 oxidation performance at each temperature after-treatment at 360°C for 1 hour for a sample saturated with degradation at 250°C is shown in Figure 12. At 250°C the NH_3 oxidation performance remains low, but at temperatures above 300°C, it was confirmed that the performance recovered to >95% after regeneration. From the exhaust temperature results in Figure 4, it was confirmed that the NH_3 oxidation catalyst is regenerable over the entire load range of the NH_3 mode.

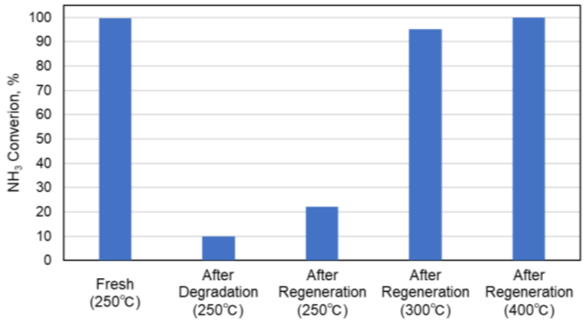

Figure 12. Post-regeneration performance of the NH_3 oxidation catalyst ([Performance measurement conditions] NH_3: 1,000 ppm, O_2: 12%, H_2O: 10%, SV: 11,000 h^{-1} [Regeneration treatment conditions] Temperature: 360°C, treatment time: 1h, NH_3: 1,000 ppm, O_2: 12%, H_2O: 10%, SV: 11,000 h^{-1})

2.2.7 Evaluation results of N_2O decomposition catalyst

Figure 13 shows the dependence of the conversions of N_2O, NOx, and NH_3 on the fresh N_2O decomposition catalyst on the amount of NH_3 injected. It was confirmed that the N_2O conversion improves with an increase in NH_3 injection amount. It was also confirmed that the DeNOx reaction proceeds on the N_2O decomposition catalyst, and that the DeNOx reaction is faster than the N_2O decomposition reaction, providing sufficient performance. Furthermore, as NH_3 was nearly 100% consumed under all NH_3 injection conditions, it was suggested that NH_3 oxidation reactions proceed on the catalyst, allowing for the removal of surplus NH_3 without leakage.

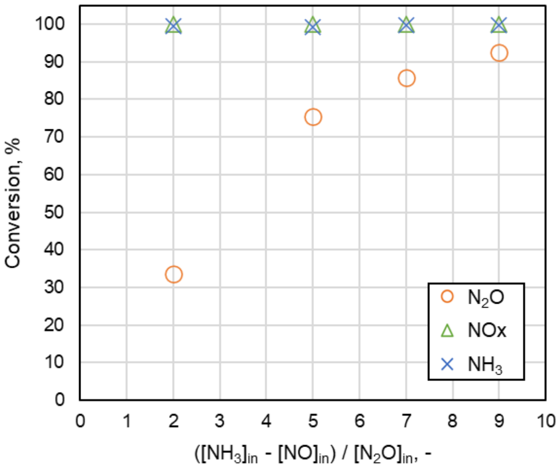

Figure 13. NH_3 injection amount dependence of N_2O, NOx, NH_3 conversions on the N_2O decomposition catalyst (Temperature: 400°C, N_2O: 100 ppm, NO: 1,000 ppm, O_2: 12%, H_2O: 10%, SV: 2,300 h^{-1})

To evaluate the SO_2 durability of the N_2O decomposition catalyst, an SO_2 exposure test was carried out at 100 ppm, which is five times the assumed SO_2 concentration of 20 ppm in diesel mode. The results are shown in Figure 14. The N_2O conversion did not decrease, and it was confirmed that this catalyst has SO_2 durability.

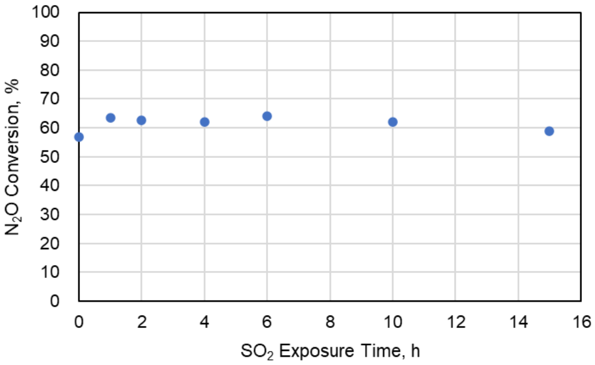

Figure 14. SO_2 durability results of the N_2O decomposition catalyst (Temperature: 250°C, N_2O: 100 ppm, SO_2: 100 ppm, O_2: 12%, H_2O: 10%, SV: 5,500 h^{-1})

2.3 SMALL SINGLE CYLINDER ENG. TEST

2.3.1 Specifications

The reactor configuration performance was evaluated in the actual exhaust gas with an NH_3 fueled small single cylinder engine (SSCE). Table 3 and Figure 15 show the specifications of the small single cylinder diesel engine and the outline of the test equipment. In the engine, liquefied NH_3 was mixed with the intake air by a modified gasoline direct injector. In the combustion chamber, dual fuel combustion using NH_3 and diesel fuel was carried out by injecting diesel fuel for ignition with an electronically controlled injector. More information about the engine can be found in the literature [3]. The exhaust gas from the SSCE is fed to the after-treatment system shown in Figure 16.

Table 3. Specifications of SSCE

Type	4-stroke, 1-cylinder
Bore/Stroke [mm]	112/110
Rated power [kW]	7.7
Rated speed [min^{-1}]	1500
Diesel fuel injection system	Common rail type

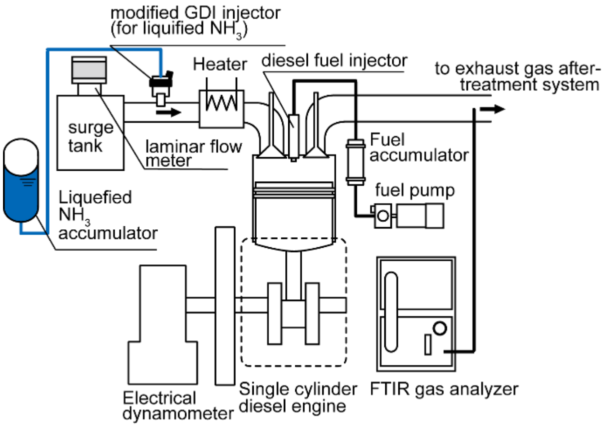

Figure 15. Outline of SSCE facility for after-treatment system test

2.3.2 Exhaust gas analyzer and sample positions

As for an exhaust gas analyzer, it is shown in 2.1.2. Figure 16 shows sample positions were set up before and after the catalyst.

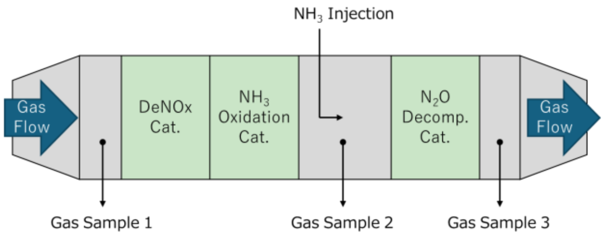

Figure16. Sample positions

2.3.3 Engine operation condition and history

Engine operation condition was listed in Table 4. Figure 17 shows the engine operation history. The engine was started by motoring and then the diesel fuel was injected. After stable diesel combustion was achieved, NH_3 gas was supplied to the intake air. The target NH_3 gas flow rate was injected into the intake pipe with a gas-injector. The mass of the supplied NH_3 gas and diesel fuel was adjusted to set the engine load. The engine speed and brake power were set to 1,500 min^{-1} and 7.9 kW throughout the tests. The tests were conducted while varying 19% and 68% of EF_{NH3}. Diesel / NH_3 co-combustion operation was performed after the reactor inlet temperature reached about 350°C. An amount of NH_3 gas equivalent to the sum of one stoichiometric amount of NOx and two stoichiometric amounts of N_2O was supplied upstream of the N_2O decomposition catalyst.

Table 4. Engine operation condition

Speed [min^{-1}]	Brake power [kW]	EF_{NH3} [%]
1500	7.9	19 / 68

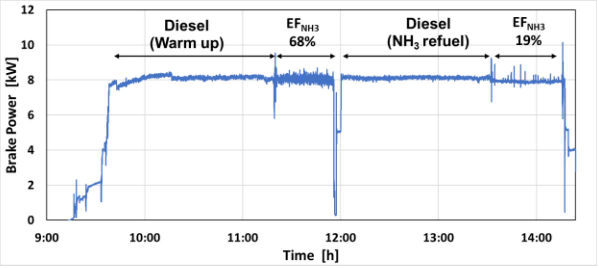

Figure 17. Engine operation history

2.3.4 Engine results

Figure 18 shows the comparison of the exhaust gas temperature and emissions at each sample position for the diesel / NH_3 co-combustion modes. The NH_3 concentrations at the inlet of the after-treatment system were approximately 4,600 ppm at 19% of EF_{NH3} and 11,800 ppm at 68% of EF_{NH3}. Regardless of EF_{NH3}, NH_3 was almost not emitted at Sample 2 (the downstream of the NH_3 oxidation catalyst) while NOx was also greatly reduced by the DeNOx reaction using unburned NH_3. Irrespective of EF_{NH3}, N_2O was approximately 70 ppm at Sample 1 (the inlet of the after-treatment system). The levels of N_2O for 19% and 68% of EF_{NH3} increased to approximately 110 ppm and 190 ppm at Sample 2, respectively. These increases in N_2O were probably due to the NH_3 oxidation reaction and its difference was caused by the difference in the NH_3 concentration at Sample 1. On the other hand, N_2O was almost not emitted regardless of EF_{NH3} at Sample 3 (the outlet of the after-treatment system).

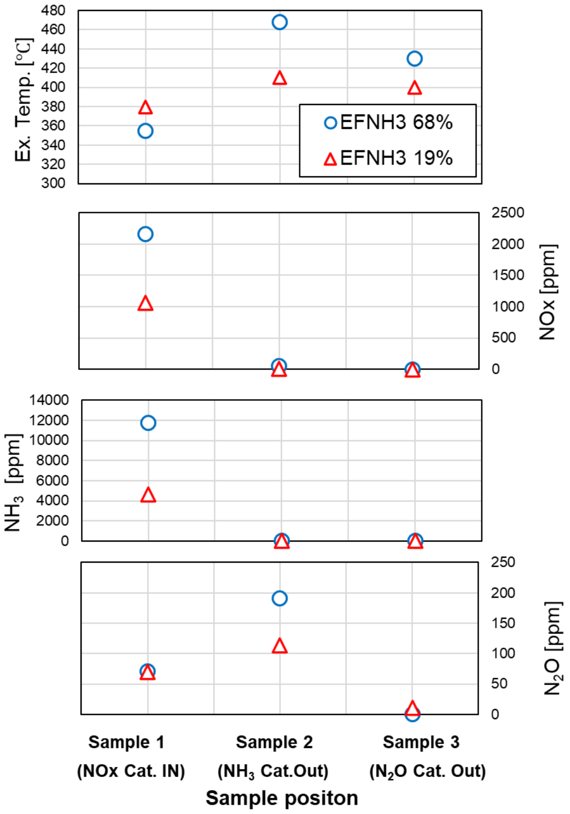

Figure 18. Exhaust gas temperature and emissions at each sample position for the diesel / NH_3 co-combustion modes

3 CONCLUSIONS

These results of the three types of catalysts indicate the possibility of simultaneously reducing NOx, unburned NH_3, and N_2O with the reactor configuration shown in Figure 5. Also, the target concentrations for each emission reduction were achieved at 10 ppm or less.

4 NEXT STEP

We designed and fabricated a prototype after-treatment system consisting of a DeNOx catalyst, an NH_3 oxidation catalyst, and an N_2O decomposition catalyst. Using this after-treatment system, we conducted performance test during diesel / NH_3 co-combustion by SSCE. We achieved a reduction of CO_2 emissions by diesel / NH_3 co-combustion and a reduction of environmentally hazardous substances in the exhaust gas by the after-treatment system. Based on the results of various evaluation tests, we made a trial calculation of the reactor size combining each catalyst for a 1,730kW diesel / NH_3 co-combustion engine. As a result of the trial calculation, the reactor size is shown in Figure 19. This is approximately 1.2 times larger than the size of Daihatsu SCR. As a next step, we will further optimize the amount of catalyst and NH_3 diffusion distance to reduce the size of the system. These results indicate the feasibility of an aftertreatment system that can simultaneously reduce NOx, NH_3, and N_2O with a practical size and SOx resistance. We will continue to work with related companies and research institutes to develop NH_3 combustion technologies and after-treatment system technologies to reduce GHGs and improve the marine and global environment.

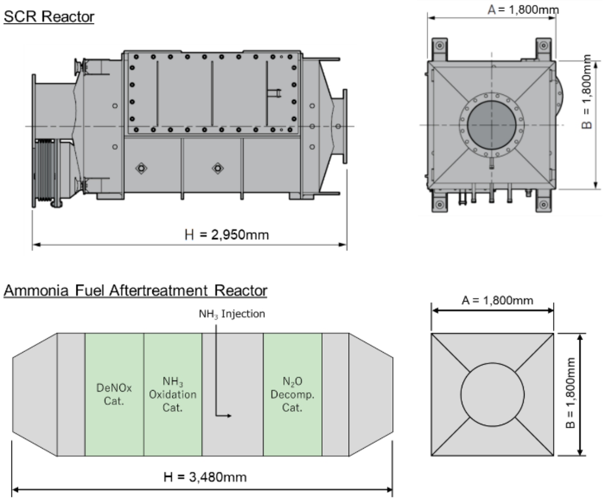

Figure 19. Reactor size for a 1,730kW diesel / NH_3 co-combustion engine reactor size

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

GHGs: Greenhouse Gas Emissions

NH_3: Ammonia

H_2: Hydrogen

CO: Carbon monoxide

CO_2: Carbon Dioxide

N_2O: Nitrous Oxide

NO: Nitric monoxide

NO_x: Nitrogen oxide

SO_2: Sulfur Dioxide

N_2: Nitrogen

H_2O: Water

O_2: Oxygen

LSCE: Large Single Cylinder Engine

SSCE: Small Single Cylinder Engine

FT-IR: Fourier Transform Infrared Gas Spectrometer

EF: Energy Fraction

SV: Space Velocity

6 REFERENCE

[1] IMO, 2023. IMO STRATEGY ON REDUCTION OF GHG EMISSIONS FROM SHIPS., MEPC 80/WP.12 Annex 1

[2] Murata, N., Kodama, T. and Hino, N. 2024. Marine SCR Evolution and Catalyst Technology for Ammonia Fuel~~.~~, *Journal of the JIME*, 59(3): 94-99.

[3] Niki, Y.~~,~~ 2023. Experimental and numerical analysis of unburned ammonia and nitrous oxide emission characteristics in ammonia/diesel dual-fuel engine~~.~~, *Int J Engine Research*, 24(9): 4190-4203.