Development of a Nitrogen-enrichment/Humidification Membrane System for NO_x Emission Reduction in a Marine Diesel Engine*

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2016 年から IMO の 3 次規制が始まるため、早急に船用ディーゼル機関における NO_x 低減技術を開発する必要がある。著者らは NO_x を低減するために NHM (窒素富化・加湿膜) システムの開発を行っている。NHM システムは、酸素分子と水分子が窒素分子よりも早く通過するという性質を持つポリマーガス分離膜で構成されており、酸素濃度が低く加湿された給気をエンジンに供給するため、燃料油中に含まれる硫黄分影響を受けない。このシステムを 103kW/2400rpm の船用高速 4 ストローク機関に接続し、負荷率 75, 50, 25 % における NO_x の低減効果を明らかにする実験を行った。その結果 NO_x の値は通常の運転状態よりも 80% 以上減少し、1.9 g/kWh 以下となった。

1. Introduction

Diesel engines are noteworthy heat engines from the standpoint of carbon dioxide emission reduction because they have high thermal efficiency. On the other hand, marine diesel engines need countermeasures against atmospheric pollution because they emit NO_x and SO_x due to the presence of sulfur in fuel oil. The NO_x emission standards set forth by IMO (International Marine Organization) for ECAs (Emission Control Areas) are shown in Table 1. The Tier II standards are in effect as of January 1, 2011, and the Tier III standards are tentatively scheduled to go into effect on January 1, 2016. The real starting date of Tier III is subject to a technical review to be concluded 2013, and the starting date could be delayed.⁽¹⁾

As NO_x reduction technologies for marine diesel engines, EGR (Exhaust Gas Recirculation), SAM (Scavenging Air Moisture), DWI (Direct Water Injection), emulsion fuel, SCR (Selective Catalytic Reduction), etc. have been proposed. Each creates certain challenges and offers certain features, as shown in Table 2.^{(2), (3)} Among these technologies, EGR and SCR have been thoroughly investigated. EGR is a standard technology in automotive diesel engines, but an exhaust gas scrubber is probably necessary in marine diesel engines to remove sulfur in the

exhaust gas. SCR is after treatment technology for the exhaust gas. The NO_x is highly decomposed to nitrogen and water by ammonia generated from aqueous urea using a vanadium based catalyst, a zeolite based catalyst, or the like.⁽⁴⁾ SCR is an effective method for four-stroke engines that have high temperature exhaust gas. On the other hand, the activity of SCR set up in two-stroke engines is low, because the temperature of the exhaust gas is low. Therefore, SCR placed before a turbocharger in order to utilize the high temperature of the exhaust gas, or a burner placed before the SCR in order to heat the exhaust gas is proposed. It is necessary to blow out soot periodically, because it accumulates in an SCR reactor. Details of the catalyst life are not clear because there are few reports. The control of SCR may require caution, because ammonia leaks in certain cases.

In this paper, the authors propose a Nitrogen-enrichment / Humidification Membrane (NHM) system as a key tool for super clean marine diesel engines. This technology is a way of controlling the composition of the intake air for a diesel engine using a polymer membrane that has selective permeability with respect to oxygen and water vapor. In other words, the intake air oxygen concentration and humidity, when adjusted properly by the NHM system, can reduce NO_x formation. This is because the reduced oxygen concentration and the higher heat capacity due to the high humidity can be expected to reduce the flame temperature in the cylinders of the diesel engine, resulting in a lowered rate of NO_x formation reaction.

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2. Development of the NHM system

Fig. 1 is a block flow diagram of the NHM system. In this system, the NHM module is installed between the turbocharger and the diesel engine and controls oxygen concentration and humidity in the intake air. A key distinguishing feature of the NHM system is that it is a clean technology because only air and water are used for reduction of NOx. The NHM module has a polymer membrane which has been newly developed by Asahi Kasei Chemicals Corporation. The polymer membrane has a gas permeation mechanism which is a gas dissolution-diffusion mechanism. As shown in Figure 2, the flux of gas i , F_i , in the membrane is represented as the product of gas permeability J_i , the area of the membrane S , and the difference of the partial pressure ΔP_i between the primary side and the secondary side. The gas permeability J_i is the product of C_i , which is the coefficient in Hnry's law, and D_i , which is a diffusion coefficient. Gas i dissolves into the membrane from the primary side, where partial pressure is high, and moves to the secondary side, where partial pressure is low, and then is released from the membrane. The form of the membrane is a flat-sheet type or a hollow-fiber type. When air is fed into the primary side of the membrane, oxygen passes through faster than nitrogen, resulting in nitrogen-enriched air, NEA, at the primary side. Oxygen-enriched air, OEA, is released from the secondary side. When water is fed into the secondary side of the membrane, water vapor moves toward the primary side with the difference of the partial pressure between the two sides. Thus the air on the primary side is humidified. A trial of using nitrogen-enriched air supplied by a membrane module in a diesel engine has already been reported by Stookey, Nemser, Keating, and Milhus.^{(5) - (8)} They reported that the membrane module for supplying nitrogen-enriched air was effective for NOx reduction.

The NHM system, which can effect an increase in humidity in addition to decrease in oxygen concentration in the intake air, is similar to a combination of EGR and water technology such as emulsion fuel or DWI.⁽⁹⁾ The mechanism for decreasing oxygen concentration is removing oxygen, unlike in EGR, in which the mechanism is dilution of intake air with exhaust gas. In EGR, carbon dioxide and a small amount of water vapor due to combustion are added to the intake air. In the NHM system, the concentration of nitrogen, oxygen, and water vapor in the intake air are controlled. Moreover, acidic wastewater isn't generated, unlike in EGR, which needs a water scrubber.

Table 1. MARPOL Annex VI NOx emission limits⁽¹⁾

Tier	Ship construction date on or after	Total weighted cycle emission limit (g/kWh) n = engine's rated speed (rpm)		
		n < 130	n = 130-1999	n ≥ 2000
I	2000.1.1	17.0	45 · n ^{-0.2}	9.8
II	2011.1.1	14.4	44 · n ^{-0.23}	7.7
III	2016.1.1	3.4	9 · n ^{-0.2}	2

Table 2. NOx reduction technologies

NO _x reduction technologies		Features	Challenges
Combustion control	NHM	Oxygen reduction and humidification	Coordination with turbocharger Heating system for water
	HAM	Use of sea water	Influence of sea water
	Emulsion	Adding water in fuel	Increase in viscosity of fuel
	DWI	Water injection in cylinders	Erosion of nozzle for water injection
	EGR	Recirculation of exhaust gas	Acidic waste water
After treatment	SCR	Reduction of NO _x with ammonium	Generation of acidic ammonium sulfate, influence of particulate matter, cost of aqueous urea, ammonia leakage

Fig. 1. Block flow diagram of NHM system

Fig. 2. Mechanism of the gas separation membrane

3. Experiment

In the experiment, the gas separation membranes, the membrane elements (cartridges), and the membrane modules that were used were created by Asahi Kasei Chemicals Corporation. Figure 3 shows a process flow diagram of the NHM system in the experiment. The nitrogen-enrichment and the humidification were carried out separately. Eight hollow-fiber elements having 10 m² of membrane surface each or eight flat-sheet elements having 7.5 m² of membrane surface each were used for the nitrogen-enrichment, and four hollow-fiber elements having 10 m² of surface each were used for the humidification. The specifications of the test engine connected to the NHM equipment are given in Table 3. The intake air was fed by an engine compressor that was separate from the test engine. Pressure from the compressor provides the driving force for gas separation in the nitrogen-enrichment unit. In practical use, the engine compressor should be replaced with a turbocharger installed in the diesel engine. The intake air was dried at a dew point of -20 °C with a dryer after leaving the compressor. The air coming out of the nitrogen-enrichment unit was heated with an electric heater and then fed into the humidification unit. This heater can be omitted in practical use because the temperature of the intake air can be controlled with an intercooler downstream of the turbocharger. The latent heat of the water for humidification was supplied using the sensible heat of circulating water. The equipment can supply air the humidity of which is controlled to be from an absolute dry condition to an approximately 100% RH condition, and the oxygen concentration is controlled to be from 18% to 21% on a dry air basis. Oxygen concentrations were measured with galvanic cell type oxygen sensors, JKO-25, produced by JIKO. NO_x concentrations were measured with chemiluminescence method NO_x analyzers CLM-107 produced by SHIMAZU, and EXSA-240CL produced by HORIBA.

4. Results and Discussion

4.1 Evaluation of the NHM system The influence of oxygen concentration and humidity in the intake air upon the NO_x concentration in the exhaust gas was investigated under conditions of 75%, 50%, and 25% engine loads. Equivalent ratios of oxygen to fuel were controlled to be at 1.6–4.3, as shown in Figure 4. The results suggested that the rates of NO_x formation decreased remarkably, falling to

Fig. 3. Process flow diagram of the NHM

Table 3. Test engine specifications

Fuel		Gas oil
Type		S4M-MTK
Capacity	kW	103
Speed	rpm	2400
Cylinder bore	mm	110
Piston stroke	mm	125
P _{me}	MPa	1.08

Fig. 4. Rates of excess oxygen

Fig. 5. Relationship between NO_x formation and O₂ concentration

approximately 1.9 g/kWh. Figure 5 shows that the oxygen concentration in the humidified air is relevant to NO_x formation, and the Tier III standards can be met by the NHM system. The dots at an oxygen concentration of around 21% are standard data for the test engine. The reduction rate was more than 80% compared to these standard data. The plotted points in Figure 5 show significantly different values. The upper line indicates the influence of dry air where the temperatures are about 30 °C and the concentrations of water vapor are approximately 2.0 mol% and the lower line indicates the influence of high humidity where the temperatures are about 70 °C and the concentrations of water vapor are approximately 15 mol%. These experimental results indicate that the target of the oxygen concentration in the intake air is probably between 17-18%, and humidified air is more effective for NO_x reduction than dry air. The latter result probably indicates the effect of increasing the heat capacity due to humidification. Figure 6 explains the relationship between NO_x formation and water fuel ratio at 75% load. The line in Figure 6 indicates the effect of humidity on NO_x formation.

The area below the line shows the effect of nitrogen-enrichment. Humidification without nitrogen-enrichment can reduce NO_x, but the combination of nitrogen-enrichment and humidification is a more effective method of NO_x reduction.

Intake balance and latent heat of the water should be listed as the key factors for practical implementation of the NHM system. Figure 7 depicts the intake balance. When the amount of air fed to the membrane modules, the amount of oxygen-enriched air released from the nitrogen-enrichment unit, and the amount of air leaving from the humidification unit are expressed as W_1 , W_2 , W_3 , and W_4 respectively, as shown in Figure 3, the intake balance is expressed as $(W_4 - W_1)/W_1$. Here, W_1 equals $W_2 + W_3$. A negative intake balance means lack of intake air compared to the amount of feed air at the entrance of the membrane modules, and a positive intake air balance means excess of intake air compared to the amount of feed air at the entrance of the membrane modules. Given the general features of a turbocharger, the intake balance is preferably more than -10%. A positive intake balance can be used under certain conditions of humidification.

4.2 The typical flow diagram of the NHM system on a vessel An outline of an engine system with the NHM system installed for practical use is shown in Figure 8. Air compressed by the turbocharger TC, is introduced into the

Fig. 6. Relationship between NO_x formation and water fuel ratio at 75% load

Fig. 7 Intake balance

Fig. 8. Outline of an engine system installed with the NHM

nitrogen-enrichment unit MM-1, via the intercooler, IC, at a specific temperature. Oxygen is removed to some extent by the gas separation membrane using the pressure provided by the turbocharger, so that it generates nitrogen-enriched air (NEA). Nitrogen-enriched and humidified air HA is introduced to the diesel engine from the humidification unit MM-2. The exhaust gas is introduced into the turbine of the turbocharger for recovery of energy. Heated water is circulated in the secondary side of the humidification unit MM-2, using a circulation pump CP. The fresh water FW,

which is supplied in the water tank WT, is heated by the heat exchanger HE. Fresh water FW is then introduced into the humidification unit MM-2. The latent heat of the water that evaporates in the humidification unit MM-2 is supplied by the sensible heat of the circulating water. Thereby, a temperature difference between the incoming and outgoing water is generated in the humidification unit MM-2. Since oxygen-enriched air of which the oxygen concentration is 25-28% is released, the amount of intake air is decreased by the amount of the OEA. Consequently, the amount the air increases is the amount of the humidification.

Under typical conditions, the intake balance, that is given as $[\text{Air} - (\text{NEA}, \text{HA})] / \text{Air}$, is controlled to be at more than -10% as described earlier, and accordingly a loss of intake air may be generated under specific conditions. Therefore, coordination of the NHM and turbocharger is important. Salt can't pass through the gas separation membrane, because only gas components can pass through the membrane, so that pure water vapor is fed to the engine. This point is a feature of humidification using a gas separation membrane. Moreover, the humidification can be conducted effectively because of the wide area of the membrane. Although it is theoretically possible to undertake nitrogen-enrichment and humidification using the same membrane modules, it should be decided whether a separated system for nitrogen-enrichment and humidification or a combined system for nitrogen-enrichment and humidification is advantageous, taking into account maintenance, life of the membrane modules, and ease of controlling operational conditions. Saturated steam pressure, which is given by Tetens' equation, is merely a function of temperature.⁽¹⁰⁾ Figure 9 makes it clear that the effect of diluting air by humidification decreases with the increase in total pressure of the system. Since the feed pressure of a turbocharger decreases with the decrease in engine load, the nitrogen-enrichment ability of the nitrogen-enrichment unit MM-1 decreases and the humidification effect of the humidification unit MM-2 increases. On the other hand, increase of the nitrogen-enrichment effect and decrease of the humidification effect result from an increase in the feed pressure under high load of the engine. Thus, nitrogen-enrichment and humidification are complementary to each other. In practical use, almost all the latent heat of the water vapor should be supplied by waste heat from the engine, by way of exhaust gas, an intercooler, coolant from the engine, or the like. When the combustion energy of fuel is given as 100, an example of heat balance with a 75%

Fig. 9. Water vapor pressure calculated from Tetens' equation

Fig. 10. Example of heat balance of a four-stroke engine at 75% load

engine load is shown in Figure 10. The authors are now investigating the feasibility of heat balances under each engine load. The blower B can be used in order to assist the pressure of the intake air if necessary. In this case, the energy consumption of the blower should be estimated. The NHM system is presumed to be usable as a NO_x reduction system for two-stroke engines as well as for four-stroke engines.

5. CONCLUSION

We conclude the following:

1. The experiment using a 100 kW four-stroke engine shows the effectiveness of the NHM system as NO_x reduction technology under a 75% load, a 50% load, and a 25% load.
2. The required oxygen concentration for achieving the level of Tier III in a four-stroke engine is predicted to be 17-18% oxygen.
3. Humidified air is more effective for NO_x reduction than dry air. This fact indicates the effect of increasing heat capacity due to humidification.
4. The combination of nitrogen-enrichment and humidification is an effective method of NO_x reduction.

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NOMENCLATURE

NHM	: Nitrogen-Enrichment / Humidification Membrane
IMO	: International Marine Organization
ECA	: Emission control area
F_i	: Flux of gas i [10^{-10} cm ³ (STP) / s cm ²]
J_i	: Permeability of gas i [Barrer],

	[10^{-10} cm ³ (STP) cm / s cm ² cmHg]
ΔP_i	: Difference of the partial pressure of gas i between the primary side and the secondary side of a membrane [cmHg]
t	: Thickness of the membrane [cm]
C_i	: Coefficient of H��nry's law
D_i	: Diffusion constant of gas i
NEA	: Nitrogen-enriched air
HA	: Humidified air
OEA	: Oxygen-enriched air
EGR	: Exhaust gas recirculation
SAM	: Scavenge air moisturizing
HAM	: Humidified air motor
DWI	: Direct water injection
SCR	: Selective catalytic reduction
W_1	: Amount of feed air to the nitrogen-enrichment unit
W_2	: Amount of air leaving from the nitrogen-enrichment unit
W_3	: Amount of oxygen-enriched air released From the nitrogen-enrichment unit
W_4	: Amount of air leaving from the humidification unit
TC	: Turbocharger
B	: Blower
IC	: Inter cooler
MM-1	: Membrane unit 1, Nitrogen-enrichment unit
MM-2	: Membrane unit 2, Humidification unit
DE	: Diesel engine
EG	: Exhaust gas
HE	: Heat exchanger
CP	: Circulation pump
WT	: Water tank
FW	: Fresh water
PI	: Pressure indicator
TI	: Temperature indicator
HI	: Humidity indicator