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

Shimizu Atsushi*1, Ohno Hirokazu*1, Koizumi Yosuke*1, Maeda Kazuyuki*2, Yamanishi Dai*2

*1: Asahi Kasei Chemicals Corporation, 1-3-1, Yakoh, Kawasaki-ku, Kawasaki, Kanagawa, JAPAN 210-0863,
E-mail shimizu.ac@om.asahi-kasei.co.jp, Phone +81-44-271-2237
*2: National Fisheries University 2-7-1, Nagata-honmachi, Shimonoseki, Yamaguchi, JAPAN 759-6595,
E-mail kmaeda@fish-u.ac.jp, Phone +81-83-286-5111

Since the IMO Tier III standards are scheduled to come into effect at the beginning of 2016, the development of NOx reduction technologies is critical for marine diesel engines. The authors are developing an NHM (Nitrogen-enrichment / Humidification Membrane) system as a method to reduce NOx emissions. The NHM system is composed of polymeric gas separation membranes. Oxygen and water molecules can permeate the membranes faster than nitrogen molecules, so the system can feed SOx free, clean nitrogen-enriched and humidified intake air into an engine. The NHM system was connected to a four-stroke high-speed engine having a rated power of 103 kW and a rated speed of 2400 rpm. NOx concentration in the exhaust gas was measured under loads of 75%, 50%, and 25%. The results show a remarkable decrease in NOx to a value less than 1.9 g/kWh which represents an 80% reduction compared to normal operating conditions.

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 NOx and SOx due to the presence of sulfur in fuel oil. The NOx 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 NOx 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

Table 1  MARPOL Annex VI NOx emission limits(1)

<table>
<thead>
<tr>
<th>Tier</th>
<th>Ship construction date on or after</th>
<th>Total weighted cycle emission limit (g/kWh) n / engine's rated speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>2000.1.1</td>
<td>17.0 / 45.0 n=130 / 13.0 n=1999 / 9.0 n=2000</td>
</tr>
<tr>
<td>II</td>
<td>2011.1.1</td>
<td>14.4 / 44.0 n=130 / 13.0 n=1999 / 7.7</td>
</tr>
<tr>
<td>III</td>
<td>2016.1.1</td>
<td>3.4 / 9.0 n=130 / 13.0 n=1999 / 2</td>
</tr>
</tbody>
</table>

Table 2  NOx reduction technologies

<table>
<thead>
<tr>
<th>NOx reduction technologies</th>
<th>Features</th>
<th>Challenges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Combustion control</td>
<td>NHM</td>
<td>Oxygen reduction and humidification</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coordination with turbocharger</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Emission of sea water</td>
</tr>
<tr>
<td></td>
<td>HAM</td>
<td>Use of sea water</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Heating system for water</td>
</tr>
<tr>
<td></td>
<td>DWI</td>
<td>Water injection in cylinders</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Emission of nozzle for water injection</td>
</tr>
<tr>
<td>After treatment</td>
<td>SCR</td>
<td>Reduction of NOx with ammonium</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Generation of acidic ammonium sulfate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Influence of particulate matter</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cost of aqueous area, ammonium leakage</td>
</tr>
</tbody>
</table>

Translated from Journal of the JIME Vol.48,No.3  ©2013(Original Japanese)
exhaust gas. SCR is after treatment technology for the exhaust gas. The NOx 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 NOx 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 NOx formation reaction.

2. Development of the NHM system

Figure 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 \(\Delta P \_i\) between the primary side and the secondary side. The gas permeability \(J \_i\) is the product of \(C \_i\), which is the coefficient in Hénry’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 Mlhus.\(^{(5)-(8)}\) 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.

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. NOx concentrations were measured with chemiluminescence method NOx analyzers CLM-107 produced by SHIMADZU, 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 NOx 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 NOx formation decreased remarkably, falling to approximately 1.9 g/kWh. Figure 5 shows that the oxygen concentration in the humidified air is relevant to NOx 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.

Table 3 Test engine specifications

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Gas oil</th>
<th>S4M-MTK</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacity</td>
<td>kW</td>
<td>103</td>
</tr>
<tr>
<td>Speed</td>
<td>rpm</td>
<td>2400</td>
</tr>
<tr>
<td>Cylinder Bore</td>
<td>mm</td>
<td>110</td>
</tr>
<tr>
<td>Piston Stroke</td>
<td>mm</td>
<td>125</td>
</tr>
<tr>
<td>$P_{\text{in}}$</td>
<td>MPa</td>
<td>1.08</td>
</tr>
</tbody>
</table>
The area below the line shows the effect of nitrogen-enrichment. Humidification without nitrogen-enrichment can reduce NOx, but the combination of nitrogen-enrichment and humidification is a more effective method of NOx 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 air leaving from the nitrogen-enrichment unit, 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 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 \[\text{Air} - (\text{NEA,HA})/\text{Air},\] 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. 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% 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 NOx 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 NOx 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 NOx 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 NOx reduction.

6. Acknowledgments

This study was conducted under a grant from Ocean Policy Research Foundation assisted by a subsidy of speedboat racing promoted by The Nippon Foundation. We would like to thank Professor Koji Takasaki and Associate Professor Hiroshi Tajima of Kyushu University, who assisted our work from the theoretical point of view.

References


Nomenclature

NHM: Nitrogen-enrichment / Humidification Membrane

Translated from Journal of the JIME Vol.48, No.3 ©2013(Original Japanese)
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]
$\Delta P_i$ : Difference of the partial pressure of gas i between the primary side and the secondary side of a membrane [cmHg]
$\delta$ : Thickness of the membrane [cm]
$C_i$ : Coefficient of Hénry’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

Translated from Journal of the JIME Vol.48, No.3  ©2013(Original Japanese)