Development Design of Ammonia Decomposition System for Safe Operation of Ammonia Fuel to achieve Carbon Neutrality

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The use of ammonia as a fuel is expected to expand with the trends such as the commencement of demonstration of ammonia co-firing in the field of thermal power generation, and the development of ammonia-fueled engines in the field of marine vessels. The key factors for the demand expansion are considered to be: the safety of operation because of the use of toxic ammonia, the reasonable economic efficiency as an alternative to fossil fuel, and the environmentally conservative properties involving no generation of greenhouse gases (GHGs) or by-products that can lead to environmental destruction. The ammonia decomposition system, which is proposed by Mitsubishi Heavy Industries, Ltd. (MHI), employs its original catalytic technology and will be one of the means to satisfy these factors. However, the operation conditions of such systems and the requirement specifications have yet to be clarified. This report summarizes our system that can satisfy the factors, in addition to the specifications and features. Even in a project requiring the reduction of NOx by-products in the exhaust gas after ammonia is decomposed, the increase in the system size can remain at a minimum. Our system was also development designed in modules to make it transportable. We hope that this report will become a proposal for customers who are considering the use of ammonia as a fuel, and will lead them to determine their own system operation conditions and specifications required for ammonia gas or wastewater detoxification.

1. Introduction

In Japan, research and demonstration tests are in progress to expand the use of ammonia as a fuel toward achieving carbon neutrality by 2050. The Ministry of Economy, Trade and Industry (METI) has set the targets for the total amount of ammonia domestically introduced as a fuel for co-firing in thermal power generation and combustion in marine vessels: 3 million tonnes per year by 2030, and a 10-fold increase by 2050, which means 30 million tonnes per year (**Figure 1**)[(1)].

As ammonia gas is toxic, decomposition system is required to be equipped with an ammonia detoxifying system if the operation and maintenance are to be conducted safely. The system should also be less costly and environmentally compatible.

The major technologies for ammonia decomposition are: absorption in water, biological treatment, combustion of ammonia gas, and catalytic decomposition (**Table 1**). For absorption in water, water is required in large quantities to prevent the re-liberation that is associated with the heat of absorption. There is another issue of the costs for post-absorption wastewater treatment and industrial waste disposal. The biological treatment requires a large site area. Considering the costs incurred as well, we consider this treatment system difficult to be introduced in a simple way. When it comes to the combustion of ammonia gas, a pilot fuel for combustion is necessary, which involves the risk of generating gaseous by-products including GHGs. It is also challenging to completely burn low-concentration ammonia.

MHI has adopted catalytic decomposition, which can decompose low-concentration ammonia and generates no gaseous by-products or wastewater. In our design, the system will be equipped with a sub-system to treat ammonia-containing wastewater with the intention of allowing

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ammonia to be quickly absorbed in water in the case of emergency.

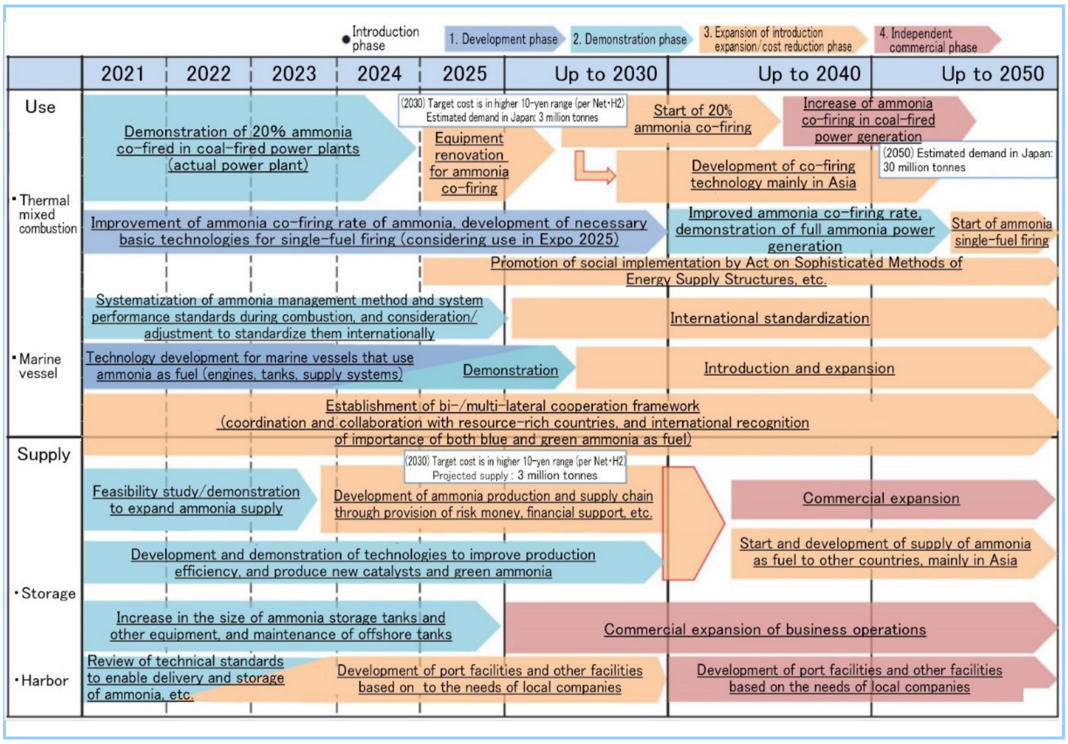

Figure 1 Road map for introduction of ammonia as fuel and its expansion in use (Agency for Natural Resources and Energy, METI)[1]

Table 1 Comparison of ammonia decomposition technologies

Method	Summary	Merit	Demerit
Absorption in water	Water or an acid is sprayed to allow ammonia gas to be absorbed as ammonia water.	・High responsiveness.	・Requires large quantities of water for high-concentration treatment. ・Requires wastewater collection and secondary treatment.
Biological treatment	The N content in water is nitrified/denitrified by microorganisms to enable it to be treated as sludge.	・Commonly applied method as the treatment of N content in wastewater from thermal power plants.	・Requires the retention time, and the site area needs to be larger than other methods.
Combustion of ammonia gas	Ammonia gas is decomposed by combustion in the burner.	・The equipment is compact and less costly. ・No wastewater.	・Currently at the stage of assessing if the low-concentration ammonia can be decomposed. ・Requires a gas for combustion (e.g., LNG) ・Generates gaseous by-products (NOx and others).
Catalytic decomposition	Ammonia gas is decomposed using a catalyst.	・Can be decomposed at low concentrations. ・No wastewater or gaseous by-products, and therefore no need for secondary treatment. ・Has past installation records for power plants and factories.	・As catalysts are consumables, they need to be replaced every few years.

As described later, we have a good track record of delivering this decomposition system. However, since we have not delivered it for ammonia co-firing at thermal power plants or for marine vessels, it is necessary to scale up the system capacity and change the specifications according to the installation site and type of application. Thus, MHI carried out development design to upgrade the whole system. We are also improving the catalysts, taking the reduction of environmental impact into consideration.

2. Characteristics of our catalyst for ammonia decomposition

MHI offers various catalyst products, including denitrification catalysts for power generation or industrial plants. Its original catalyst technologies feature prominently in our ammonia decomposition system as well.

As a mechanism of ammonia decomposition using a catalyst, an ammonia-containing gas is oxidatively decomposed on a catalyst by the following chemical reactions.

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \quad (1)$$
$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \quad (2)$$
$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \quad (3)$$
$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \quad (4)$$

In the case of using general oxidation catalysts containing oxidizing components such as platinum, decomposition of ammonia involves the production of not only nitrogen as shown in equation (1), but also by-products such as NOx and N_2O as shown in equations (2) to (4). The more ammonia is decomposed, the more by-products are produced. When a large amount of ammonia is decomposed using an oxidation catalyst, it is therefore necessary to add, downstream of the oxidation catalyst process, a means of purifying the exhaust gas containing by-product components such as NOx and N_2O. This results in the problems such as the increase in the system size and power consumption.

To address these problems, MHI has developed a catalyst that can work for both NOx removal (denitrification) and oxidative decomposition of ammonia (i.e., a multifunctional catalyst), and have made it available commercially. The multifunctional catalyst was originally developed for projects such as US heat recovery steam generators (HRSGs), whose exhaust gas had a high CO concentration. Based on this catalyst that realizes both CO oxidation and denitrification, we have improved to make it applicable to ammonia decomposition as well.

Figure 2 shows the ammonia decomposition reaction model of our multifunctional catalyst. A pore in the catalyst contains the first component that participates in denitrification, and the second component that takes part in ammonia oxidative decomposition is distributed at intervals. When ammonia enters the catalyst with such a structure, some of it is adsorbed onto the first component at the entrance of the pore, while some other of it advances further into the pore and is decomposed on the second component, producing NO as shown in equation (2). The produced NO collides with the adsorbed ammonia in the process of diffusing out of the catalyst, to be reduced to non-toxic N_2 as shown in equation (5).

$$NH_3 + NO + 1/4O_2 \rightarrow N_2 + 3/2H_2O \quad (5)$$

As indicated by the mechanism above, ammonia can be decomposed on our multifunctional catalyst to give N_2 without generating NOx. Moreover, as ammonia is oxidized to N_2 by the reaction written above, it is advantageously unlikely to produce intermediates of ammonia decomposition such as N_2O, as in equation (4).

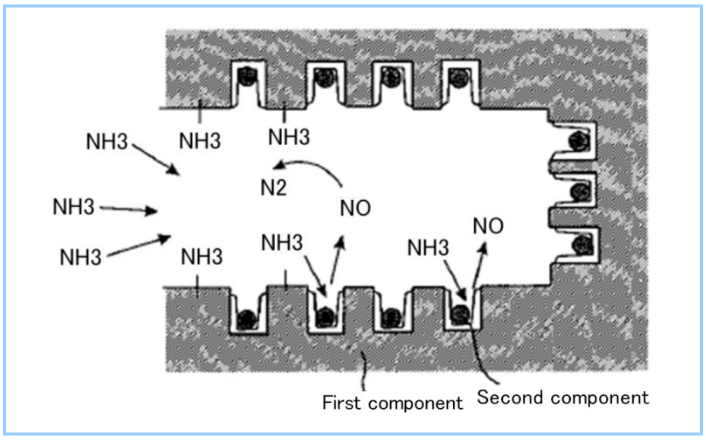

Figure 2 Reaction model for our multifunctional catalyst [2]

Figure 3 compares the results of our multifunctional catalyst and a typical oxidation catalyst. It clearly indicates that, with the use of our multifunctional catalyst, the production rate of by-products such as NOx and N_2O can be decreased to practically zero, while the decomposition rate of ammonia as high as that of the oxidation catalyst is maintained.

These characteristics of the catalyst allow the system size to be kept to a minimum even in a project requiring the reduction of by-product NOx emissions in the exhaust gas after ammonia is decomposed. We have also made a transportable version of the system available commercially, as described in the later sections.

As more and more amount of ammonia is promoted for use as a fuel in society, the quantity of ammonia to be treated is expected to increase. As described earlier, since there is a correlation between the amount of ammonia treated and that of by-products produced, more stable performance is required if the concentrations of ammonia and by-products are to be kept low. In recent years, despite our catalyst having already achieved high performance in both ammonia decomposition and denitrification, we are further improving it to have the capability of decomposing the N_2O by-product in trace amounts, and will obtain a patent for it. The global warming potential of N_2O is extremely high (about 300 times higher than CO_2). With regard to the exhaust gas from the engines of NH_3 fueled ships and transport ships, the importance of taking measures is also emphasized. We will accelerate the development of our catalyst technologies to realize more superior properties of environmental conservation and further social contribution.

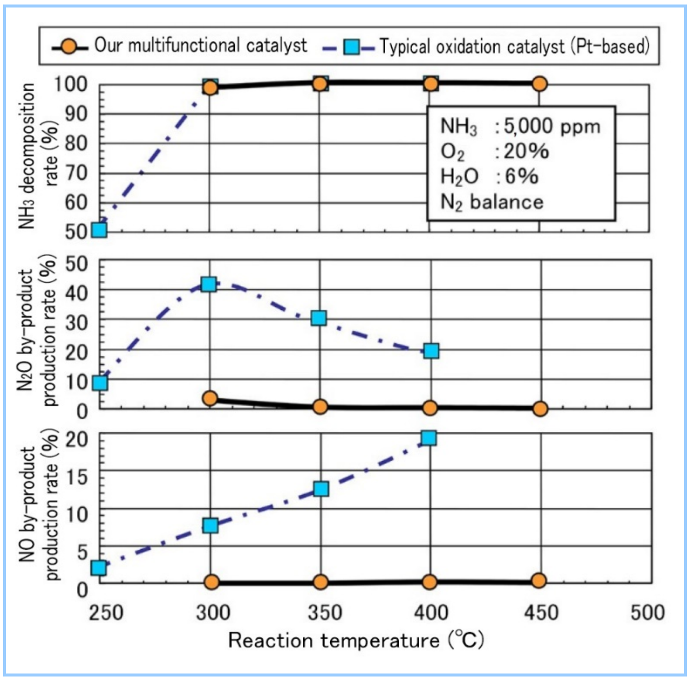

Figure 3　Comparison of our multifunctional catalyst and typical oxidation catalyst

3. Summary of our system and application

Let us present the system configuration and process flow diagram (**Figure 4**). In order to keep the ammonia decomposition reaction going, it is necessary to keep the temperature high in the reactor (with a catalyst bed). Therefore, before the system is started, the heater is turned on to increase the temperature in the system. Once ammonia gas, which needs to be detoxified, is fed, the heat generated by ammonia decomposition is recovered by the heat exchanger for the purpose of heating the gas at the reactor inlet. In this way, the reaction can continue without operating the heater. During normal operation, therefore, there is almost no need to use power for anything other than the air fan, making energy-saving operation possible. Meanwhile, if an excessive concentration of ammonia is fed into the reactor, the temperature in the system also increases excessively because of the heat of the reaction, resulting in thermal degradation of the catalyst. To avoid that, the ammonia concentration at the reactor inlet is required to be controlled appropriately. Specifically, the concentration is kept under control using the air fan to provide dilution air. This also leads the ammonia concentration in the system to be kept below the explosion limit, enabling safe operation with long-term stability.

Next comes the application of the system (**Figure 5**). The expected settings in which the system is in operation include the thermal power plants introducing ammonia co-firing or single-fuel firing, and the marine vessels equipped with an ammonia storage facility and/or an ammonia-fueled engine. For example, it is necessary to safely purge and detoxify ammonia gas, when a periodic inspection on the ammonia storage tank is performed. That is to say, the conduct of ammonia slip treatment of engine exhaust gas or boil-off gas (BOG) treatment is needed to detoxify ammonia. For marine vessels, we also expect the on-board operation of the system.

Meanwhile, in the event of an emergency in which leakage occurs because of a problem such as a fire, it is necessary to quickly treat large quantities of ammonia gas. There is a concern that the catalytic system cannot handle such sudden treatment, because it requires pre-heating before the system start-up. Although absorption in water is often employed for sudden ammonia treatment, the work and cost of post-absorption wastewater treatment become an issue. In our system configuration, a stripping tower is installed before the stage of the reactor system in which ammonia is detoxified. It therefore becomes possible to treat ammonia gas as well as ammonia-containing wastewater.

In the case of large decomposition capacity, the system will also increase in size and therefore, we offer a normal stationary type. Depending on the decomposition capacity of the system, however, we can arrange a transportable type. If the type of application does not necessitate the constant operation of the system, the transportable system can be operated wherever and whenever needed. The actual application examples are given in a later chapter.

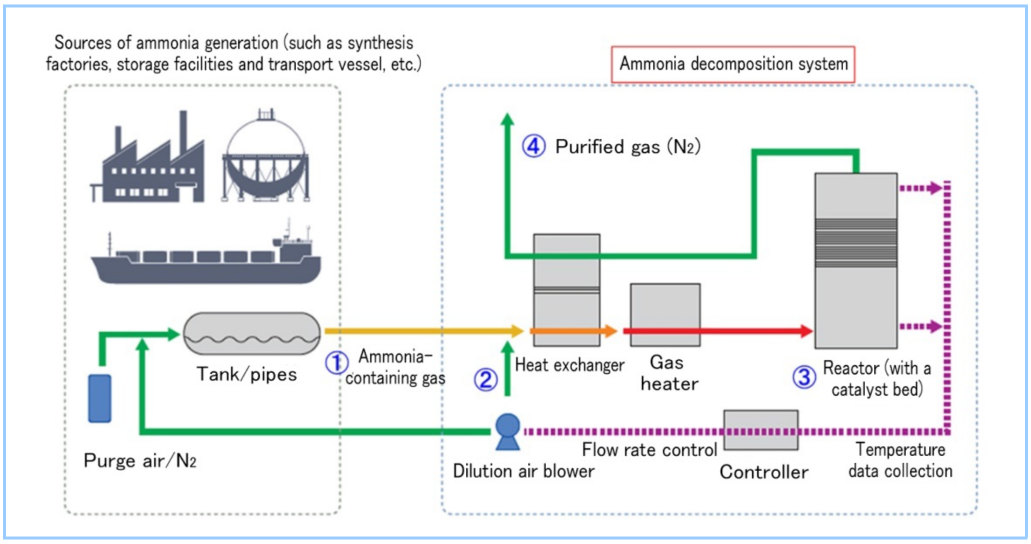

Figure 4 Ammonia decomposition system configuration and process flow

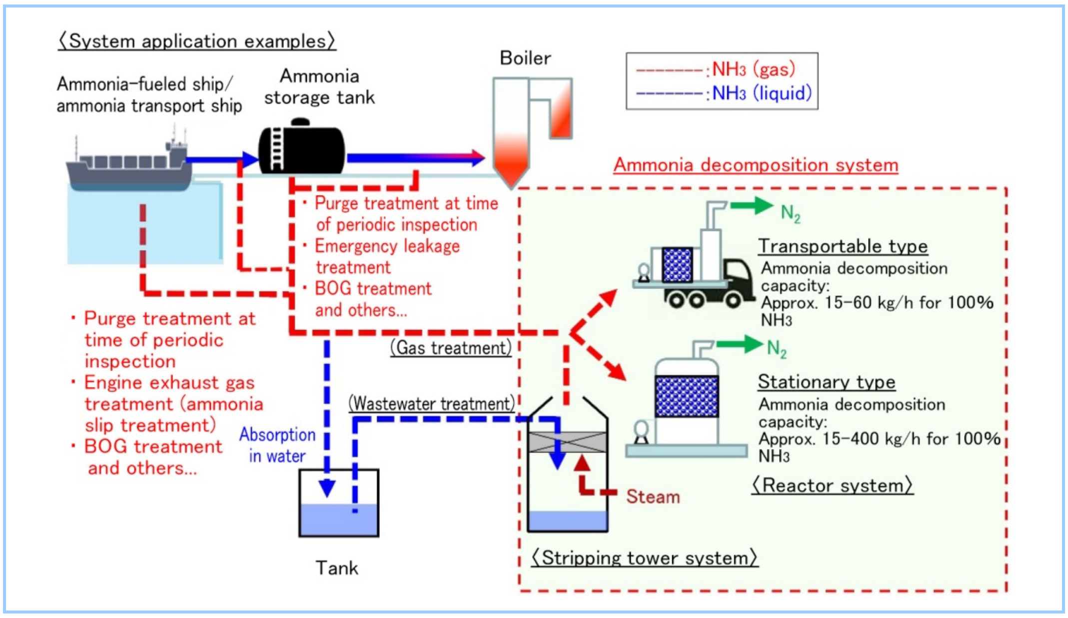

Figure 5 Conceptual diagram of application to ammonia fuel plants

4. System specifications and features

At this point in 2023, the commencement of demonstration of ammonia co-firing in the field of thermal power generation and the development of ammonia-fueled engines in the field of marine vessels are in progress. The requirements for the ammonia abatement system to be installed as their decomposition additional equipment have, in large part, yet to be clarified.

In MHI, the development design of the system is advanced, assuming the specifications are the same as the current ones. We will flexibly modify the system as needed, when new laws and regulations are set up or the customer narrows down the required specifications. To give a rough idea, **Table 2** lists our (target) specifications.

Table 2 List of ammonia decomposition system basic specifications (for reference)

Item	Basic specifications	Note
Ammonia decomposition capacity	15-60 kg/h (100% ammonia, transportable) 15-400 kg/h (100% ammonia, stationary)	
(Stripping tower inlet) Ammonia concentration in wastewater	30,000 mg/L	
(Stripping tower outlet) Ammonia concentration in the treated water	<125 mg/L as $N\text{-}NH_4$	Effluent standards by MLIT (in the case of discharging into the sewage treatment plants)(3)
(Reactor inlet) Ammonia concentration in gas	30,000 ppm	
(Reactor outlet) Ammonia concentration in gas	<25 ppm	ABS and NK guidelines(4)(5)
(Reactor outlet) NOx concentration in gas	<10 ppm	

Our plan is to provide two options of transportable or stationary, depending on the ammonia decomposition capacity. Specifically, the capacity ranges will be about 15-60 kg/h (100% ammonia) for the transportable type and about 15-400 kg/h (100% ammonia) for the stationary type, respectively. As for the transportable type, we plan to transport it as a single unit by truck, etc.

Economic evaluation of the system has been performed. With regard to the industrial waste treatment of ammonia-containing wastewater, we compared the costs of initial investment, operation and maintenance, when our system was introduced. Although the evaluation results vary depending on the scale of the system and the amount of wastewater, the investment can be recovered roughly in less than three years. As the amount of wastewater increases, a shorter period for investment recovery can be expected. We omit the detailed calculations, because otherwise it involves disclosing the customer’s system information. However, please feel free to contact us for inquiries as we can provide estimates according to the customer’s situation.

5. System delivery records

Lastly, our delivery records are presented. A total of 26 units have been delivered, including for ammonia denitrification tanks to be purged for periodic inspection, semiconductor factories and wastewater treatment facilities. Of these, two are shown below.

5.1 Delivery record (1): Power plant in Japan

- Transportable-type system intended for purging of gas in the ammonia denitrification tank at a power plant
- Gas treatment capacity: 670 Nm^3/h (equivalent to 20 Nm^3/h for 100% ammonia)
- Gas treatment results: <5 ppm for ammonia and <10 ppm for NOx

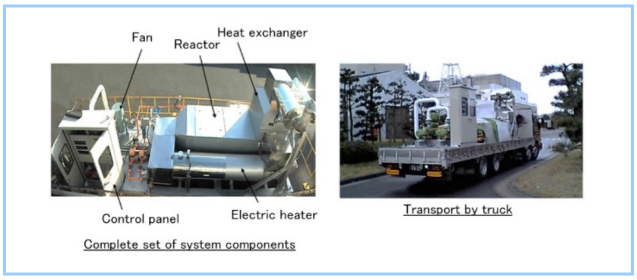

Figure 6 Delivery record (1)

5.2 Delivery record (2): Sludge wastewater treatment compost center

- Stationary-type system equipped with both stripping tower and reactor sub-systems for wastewater treatment
- Gas treatment capacity: 850 Nm^3/h (equivalent to 4 Nm^3/h for 100% ammonia)
- Having a proven record of 5,000 Nm^3/h or more gas treatment at a semiconductor factory as well.

Figure 7 Delivery record (2)

6. Conclusion

In order to achieve carbon neutrality, the demand for use of ammonia as a fuel is growing. Our proposal under such circumstances is MHI's ammonia decomposition system. In this report, we pointed out the three key factors for the system and described how our system handles each of them. With regard to safety, while the characteristics of our catalyst enable low-concentration gas to be decomposed, the concentration in the system is kept below a certain level to make sure that it is below the explosion limit. For economic efficiency, as there is almost no need to use power for anything other than the air fan during normal operation, our system's superiority in economic efficiency has been confirmed when compared with other methods such as industrial waste treatment and biological treatment. When it comes to environmentally conservative properties, our developed catalyst enables the formation of harmful by-products to be practically zero.

Although the market environment is expected to change considerably in years to come, we will continue to contribute to providing a solution to global issues such as energy and the environment.

References

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