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Research article

Investigation on the reduction in unburned ammonia and nitrogen oxide emissions from ammonia direct injection SI engine by using SCR after-treatment system

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ABSTRACT

Currently generated nitrogen oxides (NO_x) and unburned ammonia (NH_3) can be converted into nitrogen and moisture that are harmless to the human body and environment using selective catalytic reduction (SCR). The concentrations of NO_x and unburned NH_3 emitted from the ammonia combustion engines are significantly higher than those emitted by engines using existing hydrocarbon fuels. In this study, ammonia, a representative carbon-free fuel, was used in spark ignition engines for existing passenger vehicles to identify the trends in exhaust gases emitted from engines and conduct experiments on after-treatment strategies to reduce NO_x and unburned NH_3. The addition of oxygen significantly maximized the conversion efficiency of the SCR after-treatment system by changing the concentration of both NO_x and NH_3 in the exhaust gas.

1. Introduction

In response to the ‘2050 carbon neutral vision’ and to reduce greenhouse gases such as carbon dioxide, research on power sources is actively underway in the fields of power generation and transportation. These power sources use either carbon-free fuels such as ammonia, or fuels with low carbon numbers, such as natural gas [1]. Ammonia has the following advantages: highest hydrogen storage density per unit volume, easily liquefiable, and has been used for producing fertilizers for a long time. Owing to these characteristics, the production process and transportation infrastructure have been secured [2]. In addition, ammonia can be burned and used directly, and therefore it is viewed as a very advantageous hydrogen transport medium in many aspects. Although ammonia is a flammable gas, it has a high lower flammable limit, narrow range, and a minimum ignition energy of 680 mJ, which is significantly higher than that of methane (0.28 mJ) [3]. Whether ammonia will become a precursor technology to accelerate the realization of a hydrogen society and be used directly and consistently in an equal structure with hydrogen must be considered along with its economic feasibility, reliability and efficiency of the ammonia combustion system.

However, research on infrastructure construction and use plans for ammonia is insufficient compared to those of natural gas, which has successfully replaced existing liquid fuels in the automobile and ship fields. In addition, during the combustion of hydrocarbon-

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based fuels, nitrogen oxides (NO_x) are generated only in the high-temperature post-combustion area, whereas in the case of ammonia containing nitrogen, it is generally known that NO_x is additionally generated during the combustion process itself [4,5]. Therefore, measures for reducing additional NO_x is vital at this point to successfully reduce the greenhouse gases and other harmful exhaust gases that are byproducts during the application of ammonia.

At present, although the technology to reduce NO_x is vital, the technological development to reduce unburned ammonia (NH_3) is inevitable in order to reduce environmental problems in future fuel use. In particular, NH_3 itself causes toxicity and must be handled in an environmentally sensitive manner [4]. NH_3 causes bad odor even at a lower concentration of 5 ppm, which pose the need for its removal even at very low concentrations. Several technologies such as absorption, adsorption, condensation, biological filtration, and catalytic combustion are known to remove gaseous ammonia contained in the exhaust gas, but it is difficult to provide a universal solution owing to technical/economic limitations [6,7].

NO_x is a fine dust-causing substance that has been designated as a class 1 carcinogen among the air pollutants by the International Agency for Research on Cancer under the World Health Organization [8]. In addition, regulations are being strengthened worldwide as it is a major cause of ozone layer destruction, acid rain, and respiratory diseases. According to a new standard from the U.S. Environmental Protection Agency, all engines that are produced from 2027, must be certified for maintaining the amount of NO_x to be 0.035 g/bhp-h during normal operation and 0.050 g/bhp-h during low load. This is an 82.5 % reduction and reinforcement from the current 0.2 g/bhp-h during normal operation [9]. In the case of ammonia, there is a need to discuss not only safety standards, but also emissions regulations related to the environment. The draft interim guidelines for the safety of ammonia-fueled ships were submitted by Japan and Norway, and are being discussed with the participation of member countries based on the document submitted by Japan. The European Union is promoting zero pollution for a toxic-free environment by changing major environmental regulations and has added ammonia as a new regulated ingredient concerning exhaust gas components of passenger cars [10].

At present, there exists a mechanism to convert the generated NO_x and unburned NH_3 into nitrogen and moisture that are harmless to the human body and environment via selective catalytic reduction (SCR), which is an efficient technology that has been currently commercialized. In the case of after-treatment methods using catalysts, various materials are used depending on the catalyst material and reducing agent, but the most widely used NO_x reduction method currently is the SCR technology. The reduction reaction of NO_x is the main reaction of SCR reaction, and the reaction in which NO and NH_3 proceed 1:1 is called the "standard SCR", which proceeds relatively quickly [11]. The catalyst for proceeding the abovementioned reaction is V_2O_5-WO_3 (or MoO_3)/TiO_2 [12,13]. The denitrification reaction exhibits excellent performance at approximately 300–400 °C, and the performance decreases for lower temperatures owing to the decrease in heat energy, owing to the characteristics of the heated catalyst. At higher temperatures, a side reaction occurs: direct oxidation of NH_3, where a reducing agent, and NO_x is formed. Moreover, the catalytic performance is reduced at high temperatures due to the agglomeration of active metals, and therefore, research on thermal stability is in progress [6,7].

Various research is underway on catalysts for the selective oxidation reaction of NH_3, including noble metals, metal oxides, and zeolites [14,15]. Research on noble metal-based catalysts is being conducted to achieve high reactivity at low temperatures. However, the stronger the oxidizing power, the more important it is to evaluate selectivity because it converts NH_3 into NO_x or nitrous oxide (N_2O). In the oxidation reaction of a catalyst, the type of product is determined by the reaction mechanism. The oxidation reaction of NH_3 begins with the activation of gaseous oxygen (O_2) [16]. Activated O_2 reacts with NH_3, and the reaction path changes as various intermediate species are formed [17,18]. As suggested in many existing literature, it is important to design the catalyst to follow a reaction mechanism that ultimately proceeds to nitrogen (N_2) [19].

To change the catalyst method, the concentration of NO_x and unburned NH_3 contained in the exhaust gas emitted from the engine must be considered [20]. Previous researches have confirmed that the concentrations of NO_x and unburned NH_3 emitted from ammonia combustion engines are significantly higher than those emitted by engines that use existing hydrocarbon fuels. Accordingly, in this study, ammonia, a representative carbon-free fuel, was used in spark ignition engines for existing passenger vehicles to identify the trends in exhaust gases emitted from these engines and conduct experiments on after-treatment strategies to reduce NO_x and unburned NH_3. The exhaust gas compositions at the up- and down-stream were measured and analyzed using the SCR catalytic post-treatment system. Because the selective oxidation reaction of NH_3 was affected by the concentration and ratio of NO_x, additional oxygen was supplied to the engine's intake manifold to change the concentration of NO_x and unburned NH_3 in the exhaust gas, thereby changing the oxygen concentration in the intake manifold to reduce NO_x and the reduction rate of unburned NH_3 was confirmed. To determine the adequacy of the catalyst capacity for NO_x and unburned NH_3 emitted at relatively high concentrations, the reduction performance was observed by varying the engine speed and load operating conditions.

Table 1
Specifications of test engine.

Item	Specification
Displacement volume [cc]	2,497
Number of cylinders [−]	4
Compression ratio [−]	10.5
Bore X Stroke [mm]	88.5 × 101.5
Max. Torque [Nm]	26.0 @ 3,800 rpm (w/LPG)
Max. Power [kW]	101 @ 3,800 rpm (w/LPG)

2. Experimental setup and method

2.1. Experimental apparatus

Table 1 lists the specifications of the passenger liquified petroleum gas (LPG) engine that was used to examine the effect of variations in the concentration of NO_x and unburned NH_3 in the exhaust gas on the performance of the SCR catalyst after-treatment system in an NH_3 combustion engine using a direct injection fuel supply system. This 2.5 L supercharged LPG engine uses a direct injection fuel injector capable of responding to a fuel injection pressure of 15 MPa. However, to supply the liquid ammonia fuel with high injection pressure, it is equipped with an injector with changed materials of the O-ring (ethylene-propylene diene monomer) and orifice (stainless steel) applied to the fuel injector. Because ammonia is highly corrosive to copper, brass, and zinc alloys including aluminum brass, it forms cracks or green ammonia-corrosive compounds on the surface of the material. In the case of NBR material called nitrile rubber, its resistance to ammonia is low and deformed, which implies that the rubber of appropriate material should be used. Although it is based on the existing LPG engine, a piston with a relatively high compression ratio was applied, and various devices for high-pressure ammonia supply and control were added based on the engine. For example, to secure the flow rate of liquid ammonia, a low-pressure pump (G10X, Hydra-cell) was used to prevent the evaporation due to a decrease in the supply pressure upstream of the high-pressure pump. Afterward, the high-pressure fuel pump for the LPG installed in the engine was pressurized to a level of 15 MPa and supplied.

In the case of pure ammonia, the ammonia discharged from the liquid low-pressure gas container must be supplied in a liquid state so that it can be sufficiently pressurized by the high-pressure fuel pump attached to the engine and supplied to the fuel injector. The supply of O_2 for mixing O_2 in the intake air is stored by an O_2 gas tank at a pressure of 12 MPa. O_2 was introduced in the laboratory through an O_2 line connected to the engine laboratory, depressurized by a regulator, and supplied through the engine's intake manifold at a supply pressure of 0.8 MPa. The flow rate of supplied O_2 was controlled by a thermal mass flow controller (M3400V, Linetech), and the flow rate was measured using a Coriolis-type mass flowmeter (CMFS010M, Micro-Motion). A schematic diagram of the engine and experimental equipment used is depicted in Fig. 1.

Because the supplied ammonia fuel is controlled by the fuel injection period, which in turn is controlled by the engine control unit, the air-fuel ratio was controlled to enable the operation in a steady state, and a Coriolis-type mass flowmeter (CMFS010P, Micro-

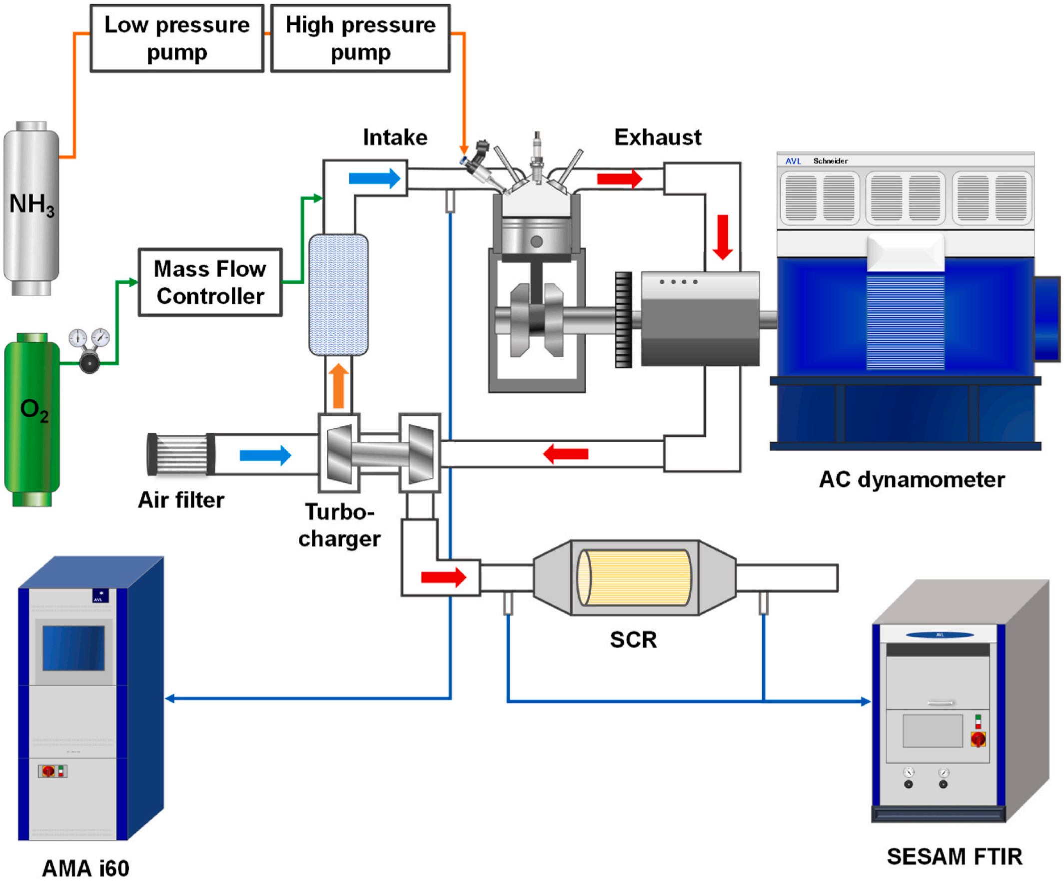

Fig. 1. Schematic of the experimental setup.

Motion) was used to measure the flow rate. By monitoring the engine control state, data such as the fuel injection duration and ignition timing, which are combustion control variables that directly affect engine performance, were acquired. The engine speed and load were controlled using an AC dynamometer (INDY S33-2/0700-1BS-1). Combustion performance was identified by measuring combustion pressure data through a spark plug-type pressure sensor (6115CF, Kistler) and combustion analyzer (DEWE211, DEWETRON co.). In addition, temperature and pressure sensors were installed to measure the temperature and pressure of the key parts of the engine. The airflow rate was measured using a flow meter (FSA 100, AVL). Emissions of NO_x, N_2O, and unburned NH_3, which are emitted without combustion among gases emitted from the engine, were measured using an exhaust gas analyzer (SESAM FTIR, AVL). The SCR after-treatment system used in this study is a prototype developed for an ammonia engine and is a Cu-Zeolite-based catalyst with specifications of closed-coupled SCR of 400/3, 1.5 L and under-floor SCR of 400/4, 6.03 L.

The conversion efficiency is the quantification of the amount of NO_x and NH_3 reduced in the SCR system and is expressed as a percentage using the concentration before and after treated by the SCR system, which is expressed as follows:

$$conversion\ efficiency = 100\left(\frac{x_{in} - x_{out}}{x_{in}}\right)$$

where x_{in} and x_{out} are the NO_x or unburned NH_3 concentrations before and after treated by the SCR system, respectively.

2.2. Experimental procedure

From previous research results [21,22], we confirmed areas, where driving with ammonia alone is possible under various engine speeds and load conditions. Under an engine speed condition of 1500 rpm, stable operation was possible with ammonia alone without the addition of other fuels such as hydrogen, except under low load conditions. In this study, changes in exhaust gas from an ammonia combustion engine were confirmed under low and high load operation conditions of 1000 rpm and 1500 rpm. Gas hourly space velocity (GHSV) values, exhaust gas/intake air temperatures, ammonia fuel and air flow rates, and excess air ratios for each operating condition are summarized in Table 2. The conversion efficiency of the SCR after-treatment system, which is a reduction device according to changes in the O_2 concentration, was experimentally confirmed by additionally supplying pure O_2 to the intake manifold.

Under high-load operating conditions, changes in the concentration of unburned NH_3 and NO_x and conversion efficiency of the after-treatment system were observed by increasing the exhaust gas flow rate without adding hydrogen. Under low-load operating conditions, the operation was possible only with the addition of O_2 owing to the slow-burning rate of NH_3. By supplying O_2, operability was confirmed and the performance of the after-treatment system was compared. For operations using O_2 with different loads under an engine speed condition of 1500 rpm, the O_2 concentration was increased by changing it in 1 % increments, and the maximum conversion efficiency conditions of the after-treatment system were confirmed according to the change in the concentration of unburned NH_3 and NO_x in the exhaust gas. The concentration of O_2 was measured using an exhaust gas analysis device (i60R1, AVL) by sampling the intake air mixed with O_2 from the intake manifold. Ignition timing optimization was performed in each operating condition to operate under the minimum advance for the best torque ignition timing condition. Because it is difficult to secure combustion stability even when the engine operating conditions are constant and the engine coolant and engine oil temperatures are low, the experiment was conducted in a sufficiently warmed-up state (90 ± 2.5 °C).

3. Experimental results and discussion

3.1. After-treatment system performance under operating conditions

First, to check the concentration of NO_x and unburned NH_3 in the exhaust gas of an ammonia combustion engine according to engine speed and load conditions, and the conversion efficiency of the SCR after-treatment system, the concentration of each exhaust gas at the engine outlet and down-stream of the SCR after-treatment device was examined under operating conditions of engine speeds of 1000 rpm and 1500 rpm, and break mean effective pressure (BMEP) of 0.4 and 1.2 MPa of the engine load. From Fig. 2, it is evident that the NO_x emitted from the engine through combustion was high under conditions of low rotational speed and high load with high thermal efficiency. After passing through the SCR after-treatment device, NO_x emissions were significantly reduced through

Table 2
GHSV values, exhaust gas/intake air temperatures, fuel and air flow rate, and excess air ratio under each operating condition.

Item	GHSV [h-1]	Exhaust gas temperature [° C]	NH_3 fuel flow rate [kg/h]	Intake air flow rate [kg/h]	Excess air ratio [−]	Intake air temperature [° C]
1000 rpm BMEP 0.4 MPa	3935	321	5.0	32.7	1.1	23.5
1000 rpm BMEP 1.2 MPa	5207	373	12.2	79.8	1.1	31.1
1500 rpm BMEP 0.4 MPa	5509	369	9.1	60.0	1.1	24.2
1500 rpm BMEP 1.2 MPa	8111	432	17.5	114.7	1.1	35.2

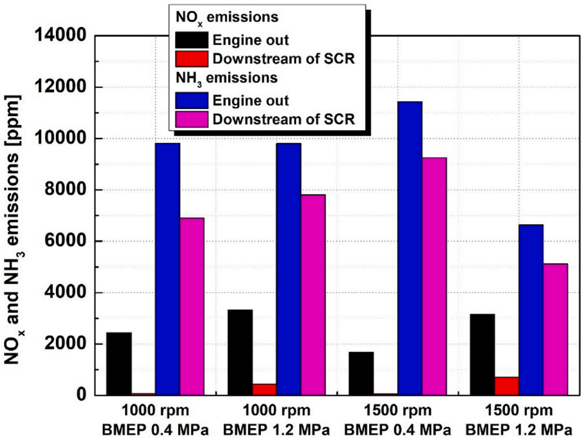

Fig. 2. NO$_x$ and unburned NH$_3$ in the exhaust gas of an engine-out and downstream of the SCR after-treatment system according to various engine speeds and load conditions of the ammonia direct injection engine.

denitrification reaction, reducing to a level where NO$_x$ emissions were almost nonexistent under low-load operating conditions, regardless of the engine speed. Under high-load operating conditions, the concentration of NO$_x$ emitted from the engine was high even after undergoing the denitrification reaction in the SCR after-treatment device, and several hundred ppm of NO$_x$ was emitted.

In the case of unburned NH$_3$ emitted via the combustion in the engine, the level was similar regardless of load under low engine speed conditions. At a relatively high rotation speed of 1500 rpm, the emission of unburned NH$_3$ increased under low-load conditions with low thermal efficiency and decreased under high-load conditions with high thermal efficiency. It increased as the load decreased, thereby resulting in high emissions under low-efficiency conditions, showing the opposite trend to NO$_x$ emissions. Due to the selective oxidation reaction in the SCR after-treatment system, the concentration of unburned NH$_3$ decreased at downstream of the after-treatment device, but the concentration of unburned NH$_3$ emitted from the engine was very high, so it was still at a high level.

Fig. 3 depicts the results of N$_2$O and O$_2$ concentrations in exhaust gas measured under the same operating conditions. The nitrogen component in fuel is an intermediate species in the process of NO$_x$ formation during ammonia combustion and also acts as a cause of N$_2$O generation. N$_2$O is known to have a global warming potential 265 times that of CO$_2$, so the need to reduce N$_2$O is recognized as important in power sources that use ammonia as a fuel [23]. Because N$_2$O is very stable in molecular structure, it is known that a decomposition catalyst to decompose it into N$_2$ and O$_2$ requires a temperature of approximately 300 °C or more [24–26]. Because huge amounts of heat energy is required to decompose N$_2$O independently, it is important to fundamentally reduce it by changing the control factor during ammonia combustion. As can be seen in Fig. 3, N$_2$O emissions are higher under low load conditions compared to high-load conditions. Under low-load conditions, the engine speed appears low at a low 1000 rpm, thereby indicating a tendency that is exactly opposite to NO$_x$ emissions.

The copper-based SCR post-treatment device used in this study has excellent redox characteristics and can be applied to the oxidation reaction of ammonia; however, it is known to generate N$_2$O with a strong oxidation tendency [19,27]. The results depicted in Fig. 3 also indicate that the concentration of N$_2$O increases downstream of the SCR after-treatment system, thereby exhibiting the same

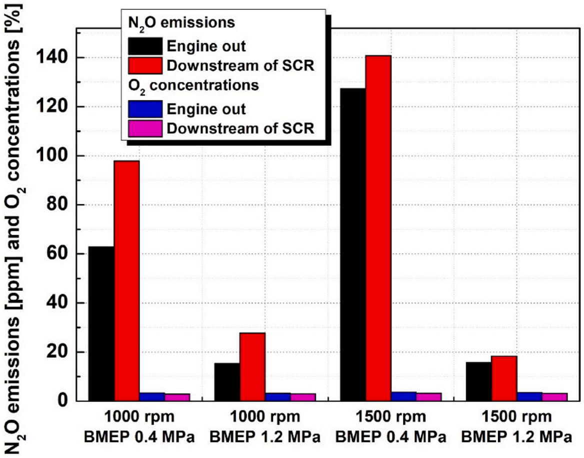

Fig. 3. N$_2$O and O$_2$ in the exhaust gas of an engine-out and downstream of the SCR after-treatment system according to various engine speeds and load conditions of the ammonia direct injection engine.

trend as the previous study. Because the oxidation reaction of NH_3 begins with the activation of O_2 in the gas phase in the after-treatment system, sufficient excess O_2 in the exhaust gas is required. Under each operating condition, the O_2 concentration in the exhaust gas is more than 3 %, which can be sufficiently utilized for an oxidation reaction. A decrease in the O_2 concentration of 0.3–0.5 % was observed at the rear of the SCR after-treatment system owing to the O_2 used in the selective oxidation reaction.

3.2. After-treatment system performance according to changes in oxygen concentrations

The main mechanism of the selective oxidation reaction that occurs in the catalyst of the SCR after-treatment system is as follows [28]: by considering that the ratio of NO_x and NH_3 is the same. SCR-related reactions can be divided into NO_x reduction reaction, NH_3 oxidation reaction, and additional reaction. The NOx reduction reaction is greatly affected by the concentration of reactants in the exhaust gas. On most SCR catalysts, the NH_3 oxidation reaction progresses more actively as the reaction temperature increases and competes with the main reaction, which is the NO_x reduction reaction. Because the exhaust gas temperature of the engine used in this study was sufficiently high, it was determined that the changes in NO_x and NH_3 emission concentrations could affect the improvement of the conversion efficiency of the SCR system.

Under the above operating conditions, the emission concentration of unburned NH_3 emitted from the engine through combustion of ammonia was relatively high, and as a result, NO_x was insufficient even under conditions with sufficient O_2; therefore, the reduction of unburned NH_3 emissions was not effective.

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$$

$$2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$

The SCR reaction proceeds by continuous adsorption and desorption of NO and NH_3 and the efficiency was determined by the transfer rate of substances to the active site, which directly affects the reaction and the reaction rate of each active site. Owing to these characteristics, there may be differences in the efficiency depending on the concentration of NO_x, which is a reactant [29], and under conditions where the concentration of unburned NH_3 is relatively high, the emission of NH_3 is not sufficiently reduced.

From previous research results [30], the authors confirmed that adding O_2 to the intake air increases the combustion rate of ammonia and consequently improves combustion stability and efficiency. The improvement in combustion speed by adding O_2 also affects the concentration of components in the exhaust gas, and as the O_2 concentration increases, NO_x increases while unburned NH_3 decreases. When considering the standard SCR mechanism [11], the trend of NO_x and NH_3 emissions is preferable for improving the SCR efficiency. Focusing on the possibility of changes in the concentration of NO_x and unburned NH_3 in the exhaust gas as described above, we attempted to confirm the operating conditions that can maximize the conversion efficiency in the SCR after-treatment system by changing the ratio of NO_x and unburned NH_3 through changes in the O_2 concentration.

Figs. 4 and 5 compare the change in concentration of NO_x and unburned NH_3 emitted from the engine and that in the concentration downstream of the SCR after-treatment system when the O_2 concentration increases thereby adding O_2 to the intake air, and exhibit the conversion efficiency for each. As the O_2 concentration in the intake air increases, the NO_x emitted from the engine increases linearly due to the increase in the combustion temperature owing to the increase in the combustion speed of ammonia. Although it reduced the downstream of the SCR after-treatment system due to the NO_x reduction reaction in the SCR after-treatment system, the conversion efficiency tends to decrease as the O_2 concentration increases.

In the case of unburned NH_3 emitted through the combustion of ammonia, unlike the trend of NO_x, it maintains an almost constant level despite the increase in the O_2 concentration in the intake air. As the O_2 concentration in the intake air increases, the concentration of unburned NH_3 discharged from the downstream of the SCR after-treatment system decreases. When the O_2 concentration exceeds 25.5 %, it decreases to less than 1000 ppm and no significant additional reduction was observed. Under conditions of relatively low O_2

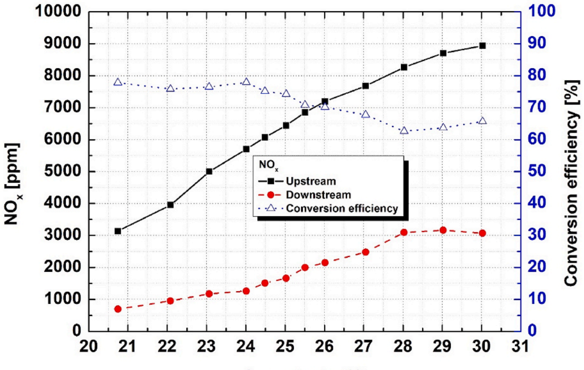

Fig. 4. Change in the concentration of NO_x emitted from the engine and concentration downstream of the SCR after-treatment system and conversion efficiency when the O_2 concentration increases at 1500 rpm and a BMEP of 1.2 MPa condition.

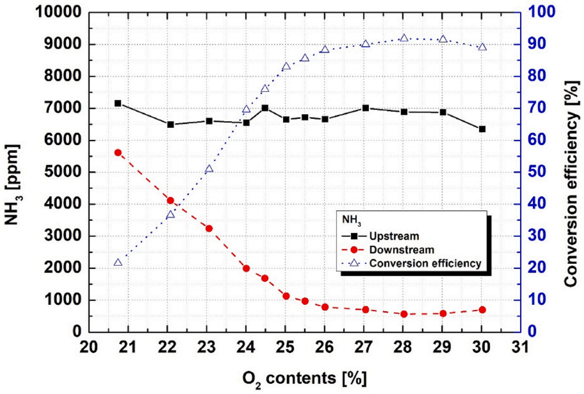

Fig. 5. Change in the concentration of unburned NH_3 emitted from the engine and concentration downstream of the SCR after-treatment system and conversion efficiency when the O_2 concentration increases at 1500 rpm and a BMEP of 1.2 MPa condition.

concentration, the conversion efficiency increases as the NO_x required for the reduction reaction of NH_3 increases. When the O_2 concentration reaches 25.5 %, the concentrations of NO_x and unburned NH_3 are reversed, and although most of the unburned NH_3 is reduced under conditions of higher O_2 concentration, it is believed that NO_x that was not used in the reduction reaction of NH_3 was discharged as is and had an effect on reducing the conversion efficiency of NO_x. Although the conversion efficiency of unburned NH_3 is lower than the NO_x conversion efficiency under conditions of relatively lower oxygen concentrations, the absolute concentration difference reduced through the SCR reaction was similar.

The NO_x conversion efficiency changes from 77.9 %, when no O_2 is added to the intake air, to 62.6 % at an O_2 concentration of 28 %. On the other hand, the conversion efficiency of unburned NH_3 varied from 21.6 % to 91.8 %, thereby showing differences by component. The changes in the efficiency of NO_x and unburned NH_3 according to changes in the O_2 concentration exhibit opposite trends, and when considering each exhaust gas component, the fact that a reduction effect close to 100 % cannot be achieved indicates that the SCR after-treatment system needs to be improved. Even under an O_2 concentration condition of 25.5 %, where the concentrations of NO_x and NH_3 were the most similar, the conversion efficiencies were 70.8 % and 85.6 %, respectively. It should be noted that under low-speed operation conditions where the GHSV value was not high, the conversion efficiency was lower than that of a general SCR after-treatment system owing to the high concentration of NO_x and unburned NH_3 emissions.

To confirm the change in GHSV due to the increase in O_2 concentration and its influence, the total flow rate of intake air and O_2 added under the same operating conditions satisfy with the excess air ratio measured from the exhaust pipe depicted in Fig. 6. Under operating conditions with a constant engine load, the amount of intake air required decreased as O_2 was added to the intake air and the total flow rate of O_2 and fresh air slightly increased as the O_2 concentration increased. However, it can be seen that the increase is at a level of 4.58 kg/h, which is similar to the GHSV under base conditions. In the case of excess air ratio, the excess air ratio was converted based on the oxygen sensor mounted on the exhaust pipe; therefore, it increased significantly to 1.9 for an O_2 concentration condition of 30 %. As the result is different from the tendency exhibited during the lean combustion in which excess air containing N_2 increases, an indicator to exhibit the effect of O_2 concentration is required in this case.

Fig. 7 depicts the variation in the N_2O concentration upstream and downstream of the SCR after-treatment system when the O_2

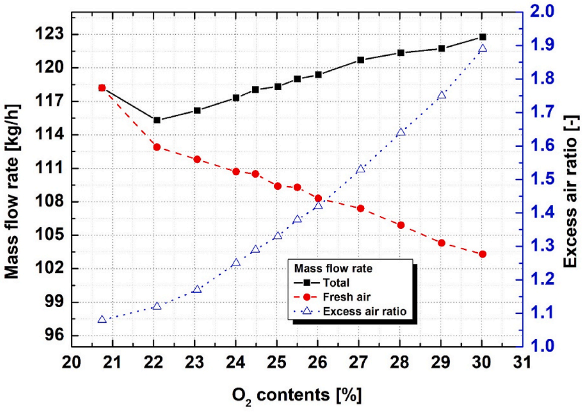

Fig. 6. Change in the total and fresh air mass flow rate and excess air ratio when the O_2 concentration increases at 1500 rpm and a BMEP of 1.2 MPa condition.

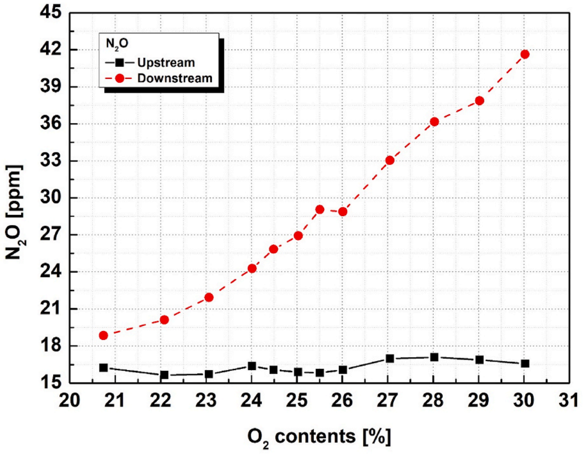

Fig. 7. Change in the concentration of N_2O emitted from the engine and concentration downstream of the SCR after-treatment system when the O_2 concentration increases at 1500 rpm and a BMEP of 1.2 MPa condition.

concentration in the intake air increases under the same operating conditions. Even as the O_2 concentration increases, N_2O emissions from the engine through ammonia combustion remain at a low level of 18 ppm or less, thereby showing a similar trend to that exhibited by unburned NH_3. However, unlike the tendency of NO_x and unburned NH_3 in which conversion efficiency increases or decreases with an increase in O_2 concentration, N_2O emissions increased linearly downstream of the SCR after-treatment system. This is believed to be the result of the effect of the high O_2 concentration in the exhaust gas on the oxidation of nitrogen components. Because N_2O is very stable in its molecular structure, a catalyst to decompose it requires a lot of heat energy, and moisture and oxygen present in the exhaust gas are known to reduce the decomposition ability of N_2O [31]. Therefore, the development of an after-treatment system using other metal compounds to fundamentally suppress the N_2O generated in the SCR after-treatment system is realistically promising.

The SCR system is a technology that can remove more than 90 % of NO_x and is commercialized as the optimal reduction technology in terms of price competitiveness and stability of catalytic activity [32]. However, considering the relatively high concentrations of NO_x and NH_3 emitted and the need to meet strengthened emission regulations, it is expected that a conversion efficiency of more than 95 % will be required. We attempted to maximize the conversion efficiency of the SCR after-treatment system by changing the concentration ratio of NO_x and NH_3 in the exhaust gas by changing the O_2 concentration in the intake air. However, a low conversion efficiency of less than 85 % was confirmed for both components at 1500 rpm and a BMEP of 1.2 MPa operating conditions. To confirm that this was a problem due to the capacity of the after-treatment system, the same experiment was conducted under low-load operation conditions with low GHSV, and the results were compared.

From Figs. 8 and 9, it is evident that when the O_2 concentration increases with the addition of O_2 to the intake air under the operating conditions of 1500 rpm and BMEP of 0.4 MPa, the graph also shows the conversion efficiency for each by comparing the concentration changes of NO_x and unburned NH_3 emitted from the engine and the concentration changes downstream of the SCR after-treatment system. When the O_2 concentration in the intake air is 22.0 %, although the NO_x concentration emitted from the engine is more than 4000 ppm due to increased combustion speed, it was mostly reduced downstream of the SCR after-treatment system. In the

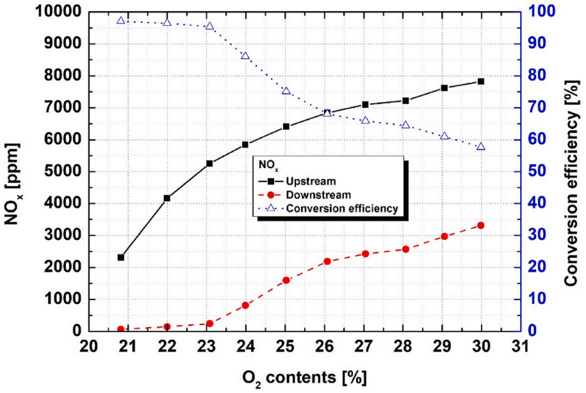

Fig. 8. Change in the concentration of NO_x emitted from the engine and concentration downstream of the SCR after-treatment system and conversion efficiency when the O_2 concentration increases at 1500 rpm and a BMEP of 0.4 MPa condition.

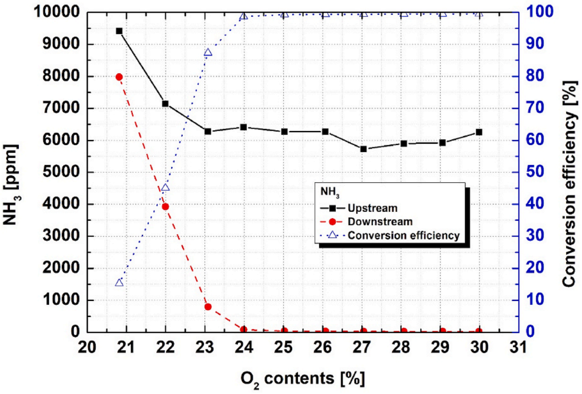

Fig. 9. Change in the concentration of unburned NH_3 emitted from the engine and concentration downstream of the SCR after-treatment system and conversion efficiency when the O_2 concentration increases at 1500 rpm and a BMEP of 0.4 MPa condition.

case of unburned NH_3, most of it was reduced to less than 100 ppm downstream of the SCR after-treatment system under conditions where the O_2 concentration in the intake air was 24.0 % or more. As in high load conditions, under conditions where the O_2 concentration is relatively low, the NO_x required for the reduction reaction of NH_3 was not sufficient, so the conversion efficiency of unburned NH_3 was low. Conversely, under conditions where the O_2 concentration was relatively high, the conversion efficiency of NO_x was low because NH_3 was insufficient compared to NO_x.

Because it was a relatively low load condition with low GHSV, the maximum conversion efficiency of NO_x and unburned NH_3 was high at 97.1 % and 99.5 %, respectively. While the O_2 concentration condition that can maximize the simultaneous reduction of NO_x and unburned NH_3 is 25.5 % under the relatively high load condition of 1500 rpm and BMEP of 1.2 MPa, it is 23 % based on NO_x and 24 % based on unburned NH_3, which shows that the optimal O_2 concentration required when operating the engine considers the after-treatment system and varies depending on the operating conditions under low load conditions. Under low GHSV conditions, the maximum conversion efficiency of NO_x and unburned NH_3 increases, but it can be seen that under maximum conversion efficiency conditions, the emission levels are 67.3 ppm and 25.3 ppm, respectively, which are higher than the emission levels required for general commercial engines. Table 3 lists the O_2 concentration in the intake air that can maximize the simultaneous reduction efficiency of the SCR after-treatment system under the operating conditions of engine speeds of 1000 rpm and 1500 rpm, and BMEP of 0.4 and 1.2 MPa, and the conversion efficiencies of NO_x and unburned NH_3.

4. Conclusions

In this study, we examined the concentrations of NO_x and unburned NH_3 in exhaust gas according to changes in operating conditions in a 2.5 L-class ammonia engine and the reduction rate through an SCR after-treatment system. When O_2 was added to the intake air, the ratio of NO_x to unburned NH_3 and the effect of exhaust flow rate on the conversion efficiency of the SCR after-treatment system were experimentally compared and analyzed for each operating condition. The summary of the results is as follows.

1. NO_x appeared high under conditions of low rotation speed and high load, which is highly efficient and was reduced significantly after going through the SCR after-processing system. Although the concentration of unburned NH_3 decreased downstream of the after-treatment system due to the selective oxidation reaction, it was still high because the concentration of unburned NH_3 discharged from the engine was significantly high.
2. N_2O emissions were higher under low load conditions compared to high load conditions. In low load conditions, the engine speed appeared low at low conditions, which was the opposite case for NO_x emissions, and the concentration of N_2O increased downstream of the copper-based SCR after-treatment system.
3. As the O_2 concentration in the intake air increased, NO_x emissions increased significantly. This reduced the downstream of the SCR after-treatment system owing to the NO_x reduction reaction, but the conversion efficiency decreased with an increase in the O_2 concentration.
4. In the case of unburned NH_3, even if the O_2 concentration in the intake air increases, it remains at an almost constant level, and the concentration of unburned NH_3 discharged downstream of the SCR after-treatment system decreases.
5. Under high GHSV conditions, the conversion efficiency of NO_x and unburned NH_3 was low, and the O_2 concentration in the intake air that can maximize the simultaneous reduction efficiency of the SCR after-treatment system was 25.5 % under high load conditions, whereas under low load conditions, it was 23 % based on NO_x and 24 % based on the unburned NH_3, which varied depending on the operating conditions.

Table 3
O_2 concentration of intake air that can maximize the simultaneous reduction efficiency of the SCR after-treatment system and the conversion efficiency of NO_x and unburned NH_3.

Item	O_2 concentration [%]	Conversion efficiency of NO_x [%]	Conversion efficiency of NH_3 [%]
1000 rpm BMEP 0.4 MPa	24.4	96.0	97.1
1000 rpm BMEP 1.2 MPa	26.2	83.5	75.6
1500 rpm BMEP 0.4 MPa	24.0	86.1	98.7
1500 rpm BMEP 1.2 MPa	25.0	74.2	83.0

5. Limitation of the present study

As the oxygen concentration increases, the conversion efficiency of NO_x decreases, whereas the conversion efficiency of unburned NH_3 increases; therefore, it was impossible to obtain results that simultaneously reduce NO_x and unburned NH_3 to near-zero levels.

6. Future works

By applying an improved SCR after-treatment system that can sufficiently reduce NO_x and unburned NH_3 emitted at a high level in the future, experiments on the strategy to confirm low concentration in the tail-pipe for commercialization of ammonia engines and maximize reduction under conditions without adding oxygen to the intake air should be conducted.

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CRediT authorship contribution statement

Cheolwoong Park: Writing – original draft, Supervision. **Yonghyun Choi:** Formal analysis. **Gyeongtae Park:** Validation. **Ilpum Jang:** Data curation. **Minki Kim:** Resources. **Yongrae Kim:** Methodology. **Young Choi:** Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Nomenclature

BTDC	Before top dead center
BMEP	Brake mean effective pressure
CAD	Crank angle degree
COV_{IMEP}	Coefficient of variation for indicated mean effective pressure
LPG	Liquid petroleum gas

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