

Article

Study on Rates of NH₃ Adsorption and Desorption in SCR on Various Engine Operation Conditions

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Abstract: Aging diesel engines on the road require the development of an after-treatment system to meet current emission regulations, and a reduction in NO_x (Nitrogen Oxide) is significant. The SCR (Selective Catalytic Reduction) system is the after-treatment system for removing NO_x from exhaust gas in diesel engines using NH₃ (Ammonia) gas. However, the mixing and conversion process between NH₃ and NO_x in SCR has not been entirely clarified. That process produces NH₃ slip in the catalyst surface; the NH₃ slip will make the after-treatment performance worse. This study informs how the UWS (Urea Water Solution) injection controlling method can minimize the NH₃ slip in the after-treatment system. For this, the NH₃ adsorption and desorption rates are important factors for determining the quantity of UWS injection in the system. The NH₃ adsorption rate and desorption rate in the SCR are not significantly affected by engine speed, i.e., the exhaust gas flow rate. However, as the exhaust gas temperature increased, the adsorption rate and desorption rate of NH₃ in the SCR increased. Through this, the exhaust gas temperature dramatically affects the NH₃ adsorption rate and desorption rate in the SCR. Therefore, if the urea water is injected based on this knowledge that the NH₃ adsorption amount in the SCR decreases as the exhaust gas flow rate increases, NH₃ slip can be suppressed and a high NO_x reduction rate can be achieved. Therefore, if the SCR adsorption and desorption mechanisms are analyzed according to the exhaust temperature and the exhaust flow rate in this paper, it can be used as a reference for selecting an appropriate SCR when retrofitting an old diesel engine car.

Keywords: urea-SCR; diesel engine; NH₃ adsorption; NH₃ slip; nitrogen oxides (NO_x)



Citation: Jo, H.; Ko, A.; Jang, J.; Lim, O. Study on Rates of NH₃ Adsorption and Desorption in SCR on Various Engine Operation Conditions. *Sustainability* **2023**, *15*, 14468. <https://doi.org/10.3390/su151914468>

Academic Editors: Weixin Yang, Guanghui Yuan and Yunpeng Yang

Received: 16 June 2023

Revised: 29 September 2023

Accepted: 1 October 2023

Published: 4 October 2023



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1. Introduction

As environmental regulations on internal combustion engines are strengthened worldwide, technologies to reduce emissions are needed for the future of internal combustion engines. The main harmful exhaust gases of diesel engines are PM (Particle Matter) and NO_x. To reduce harmful emissions, various studies are being conducted, ranging in focus from the combustion process to the emission process. Among the methods of after-treatment systems for reducing harmful emissions in exhaust gas, there is the method of oxidizing carbon monoxide (CO) and hydrocarbons through the DOC (Diesel Oxidation Catalyst) and collecting PM through the DPF (Diesel Particle Filter). The DOC and DPF mainly comprise a Pt catalyst and a substrate of cordierite or SiC. However, there are some differences in catalyst composition or substrate characteristics depending on the automobile manufacturer or the after-treatment device. The catalyst oxidizes THC (Total Hydro Carbon) and CO (Carbon Oxide) emissions and regenerates the trapped PM in the DPF. Most of the composition of NO_x emitted from diesel engines is NO, but it is converted to NO₂ through DOC and DPF [1,2]. NO₂ would affect the regeneration process of PM in DPF and the performance of SCR [3,4]. To reduce NO_x efficiently, controlling

NO₂ conversion in the DOC and DPF is necessary. The LNT (Lean NO_x Trap) and SCR are the most representative after-treatment methods for reducing NO_x. The NH₃-SCR system is the most widely used in diesel engines due to its high efficiency and wide operating temperature range [5]. Hydrocarbons are alternatives for overcoming the disadvantages of the NH₃-SCR reaction [6,7]; by adding hydrocarbon, the oxygen concentration is increased in the NH₃-SCR system [8]. The chemical properties will assist NH₃ to decrease NO_x and increase the generation of H₂O (Water) and CO. In previous studies, the NH₃/NO_x ratio, NO₂/NO_x ratio, hydrocarbon concentration, NO_x conversion efficiency, and HSO (Hydrolysis + SCR + Oxidation catalyst) in the SCR with vanadium and zeolite material were analyzed to judge the possibility of the after-treatment. Experimental studies on the conversion efficiency were used to analyze the performance of NO_x reduction, depending on the gas hourly space velocity (GHSV) and the monolith volume for the oxidation catalysts and VHSO (oxidation + HSO catalysts) SCR systems [9–11]. The SCR effectively reduces NO_x in a steady-state engine; however, it still has a problem reducing NO_x and producing the NH₃ slip in transient-state engines such as vehicles [12–16]. Based on this, the methods for improving Urea-SCR system performance are introduced in this study, in which we control the amount of urea injection into the SCR to improve the performance of the NO_x reduction and reduce the NH₃ slip simultaneously via the adsorption and desorption of NH₃ in SCR [17]. When the amount of UWS in the SCR increases, the vapor pressure will decrease; the urea droplet temperature suddenly drops, and this phenomenon leads to low evaporation of urea droplets in the SCR [18]. The hydrolysis phenomenon with various physical models can validate the NH₃ slip quantity in the SCR based on the evaporation quality [19]. The NO and NO₂ ratio, the SCR temperature, and the engine speed conditions can affect the NH₃ slip quantity and the NO_x reduction rate [20]. The ratio of NO and NO₂ in the NO_x concentration when entering the SCR directly affects the performance of SCR; based on that condition, the commercial after-treatment adds the DOC and DPF in front of the SCR [21]. Since the SCR is greatly affected by the exhaust gas temperature, research was conducted to improve the NO_x reduction rate by analyzing the ratio of NO to NO₂ from a low temperature [22]. The temperature of SCR is the main factor of fast chemical reactions in the SCR system to reduce NO_x [23]. A study was conducted to develop an optimized injection control strategy where the DOC, DPF, and SCR were installed. To analyze the amount of NH₃ adsorption in SCR, the maximum adsorption amount of NH₃ in SCR for the NO_x reduction and the NH₃ slip were separately measured. As a result, the NH₃ slip occurred during the NH₃ adsorption in SCR. Therefore, it was not easy to remove the NH₃ slip altogether without an AOC (Ammonia Oxidation Catalyst) [24,25]. To achieve complete NH₃ slip removal according to various exhaust temperatures and exhaust flow rates, it is necessary to analyze the adsorption amount of NH₃ in the SCR and the adsorption rate and desorption rate.

In this study, we show the performance of the DOC, DPF, and SCR according to reducing harmful emissions such as PM and NO_x generated from an aging diesel engine under various engine operating conditions. To achieve this, as mentioned earlier, it is necessary to clarify how the amounts of NH₃ adsorption and desorption in SCR appear under various operating conditions of the engine. In addition, since the NH₃ slip cannot be prevented by any amount of NH₃ adsorption and desorption in SCR, this paper considered strategies to prevent the NH₃ slip by analyzing the adsorption rate and desorption rate of NH₃ in SCR according to engine operating conditions. The DOC and DPF are being developed as a natural regeneration DPF suitable for the retrofit market. The DOC and DPF catalysts used in this study were intermediate developments, consisting of Pt and a promoter with a BPT (Balance Point Temperature) of 285 °C. SCR is a primary material to remove NO_x using gaseous NH₃. Observing the NH₃ adsorption and desorption mechanisms is essential in controlling NH₃ slip and optimizing the NO_x reduction efficiency. The adsorption and desorption of the NH₃ mechanism in SCR were analyzed according to engine and catalyst conditions.

2. Experimental Setup

Experimental Apparatus

This study used Ssang-yong's in-line 5-cylinder 2696 cc diesel engine. Table 1 shows a detailed description of the engine's specifications. The valve type of the engine is a DOHC (Double OverHead Camshaft). The bore and stroke of each cylinder are 86.2 mm and 92.4 mm, respectively, and the compression ratio is 17.5. The maximum power of the engine is 191 PS at 4000 rpm, and the maximum torque is 410 N·m when the engine speed is at 3000 rpm. The fuel injection system is a common rail, and the environmental regulation that the engine meets is Euro 2. The engine used in the experiment was used only for experimental purposes, and the engine was managed using the manual and reference materials for a vehicle that has the same engine. The reason for using the old version of the engine is that the goal is to research an after-treatment system for the continued use of the old diesel engine. The experiment was carried out under various engine load ranges in which the engine speeds were 1500, 2000, 2500, and 3000 rpm and the exhaust gas temperatures were 250, 300, 350, and 400 °C, respectively. The reason for these conditions is to realize the range of daily driving conditions of a diesel engine.

Table 1. Diesel engine specifications.

No. of Cylinders	5
Valve type	DOHC 20 valve
Strokes	4
Type	Turbo diesel
Rated power P (PS)	186/4000 rpm
Rated torque M (Nm)	418/1600–3000
Experiment engine speed (rpm)	1500, 2000, 2500, 3000
Exhaust gas temperature (°C)	250, 300, 350, 400
Manufacture	2006
Emission standards	Euro 2

An overview of the overall experimental setup is shown in Figure 1. The engine is connected to a dynamometer to control the operating range, and the DOC, DPF, and SCR are installed in the after-treatment system. The specifications for each catalytic unit are given in Table 2. The substrate of the DOC and DPF is cordierite coated with Platinum. The BPT of DOC and DPF is 285 °C, and the cell density of each catalyst is 400 cpsi and 300 cpsi. The diameter is the same at 5.66 inches, and the length is 4 inches for the DOC and 10 inches for the DPF. The DOC and DPF were contained in the same case in this study. The substrate of SCR is cordierite, coated with a Vanadium base. The cell density of the SCR is 400 cpsi, and the diameter and length are 6.77 inches and 10 inches, respectively. The DOC, DPF, and SCR are all sequentially connected in series from the engine, and the experiment is conducted after sufficient time was given for the target exhaust gas temperature to be reached. In this study, AOC is not installed because it is necessary to analyze the amount of NH₃ slip according to the urea water injection strategy. The sampling line of exhaust gas is installed before and after each DOC, DPF, and SCR to analyze the exhaust gas, and a thermocouple is used to measure the temperature. Each tube is connected to HORIBA's MEXA 1400 QL-NX, an exhaust gas analyzer, and NO, NO₂, N₂O, and NH₃ were measured in real time using this equipment. When analyzing the exhaust gas, the sampling line was heated to 150 °C to prevent PM fouling and NH₃ deposition.

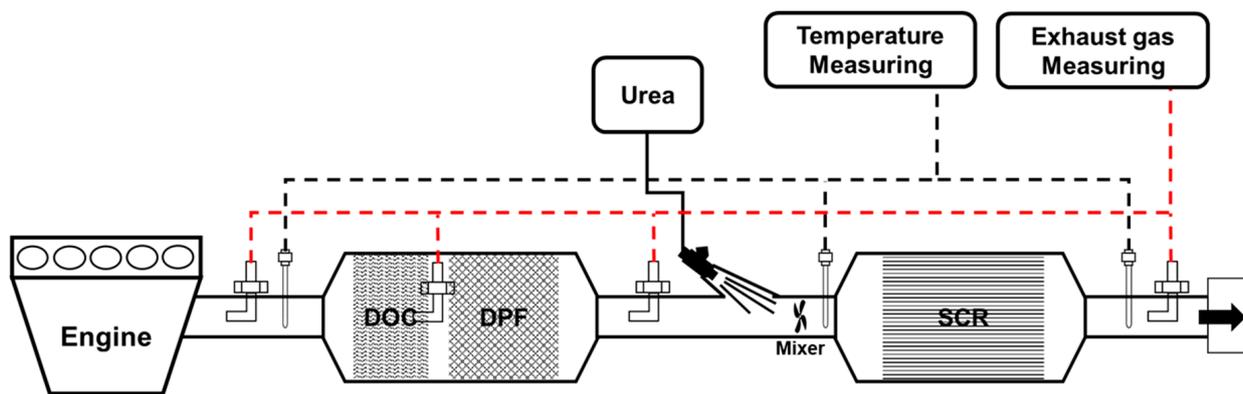


Figure 1. Schematic diagram of experimental equipment.

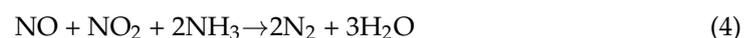
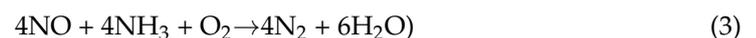
Table 2. SCR system specifications.

Category	DOC	DPF	SCR
Substrate	Cordierite		
Catalyst	Pt + Promoter/TiO ₂		V-W/TiO ₂
BPT	285 °C		-
Cell density	400 cpsi	300 cpsi	400 cpsi
Diameter	5.66 inch	5.66 inch	6.77 inch
Length	4 inch	10 inch	10 inch

The urea water is injected between the DOC/DPF and SCR. A mixer is installed at the inlet of the SCR so that the injected urea water is uniformly distributed in the SCR. The injection pressure of urea water is maintained at 5 bar and repeated at a rate of 3.3 Hz.

3. Methods and Analysis

The chemical reaction process of general urea-SCR is as follows. The urea water is first decomposed into NH₃ in two steps. As in Reaction (1), instead, HNCO and NH₃ are produced via the thermolysis of urea water, and NH₃ and CO₂ are produced by isocyanic acid hydrolysis of HNCO in Reaction (2). NH₃ made in this way reacts with nitrogen oxides inside SCR, and the representative responses are called Standard SCR (3), Fast SCR (4), and NO₂ SCR (5).



Based on this reaction process, the theoretical amount of urea required to reduce NO_x emitted was calculated assuming that the ratio of NH₃ to NO_x was 1:1. The ratio of NO and NH₃ in the standard SCR reaction and the percentage of NO_x and NH₃ in the Fast SCR reaction is 1:1. However, in the NO₂-SCR reaction, the reaction between NO₂ and NH₃ was not 1:1. In general, in NO_x emitted from diesel engines, the proportion of NO is higher than that of NO₂, and most of the NO₂ is reduced in the fast SCR reaction. If NO is

oxidized through the DOC and DPF, the ratio of NO₂ should be higher than that of NO, but this was not seen in the experimental results. In addition, it did not significantly affect the process of observing the adsorption and slip of NH₃ in the SCR, which is the focus of this study. Therefore, assuming that the reduction ratio of NH₃ and NO_x is 1:1, the injection amount of urea water was calculated as in Equation (6).

$$\dot{M} = (N_{in} \times \dot{m} / M_{exh}) / (d_{urea} / M_{urea} \times 2 \times 10^6) \quad (6)$$

As shown in Table 3, the experiment was conducted under 16 different engine operating conditions, respectively, in which the engine speed was 1500, 2000, 2500, and 3000 rpm and the exhaust gas temperature was 250, 300, 350, and 400 °C. After operating the engine and waiting until the fluctuation of emission gas is reduced, the urea-water solution is injected to measure the change in NO_x and NH₃ according to the evolution of time when the engine and catalyst conditions are different. The amount of urea-water solution with which NH₃ can react with NO_x and create 100 ppm of NH₃ slip was injected. The reason for injecting the excess urea is to check the total amount of NH₃ adsorbed to the SCR by intentionally causing a NH₃ slip and preventing the trend. So, to establish a urea-water-solution injection strategy, we investigated how the amount of NH₃ adsorbed in the SCR appears according to engine and catalyst conditions. Exhaust gas analysis with a single exhaust gas analyzer was performed by controlling valves on the sampling line at different locations. After injecting urea water, sufficient time is required for ammonia to be adsorbed and desorbed in the SCR. Therefore, preliminary experiments were conducted to determine how much time is required for a stable experiment to reduce uncertainty. In this study, a measurement experiment was conducted for 30 min before and after urea water injection to adsorb and desorb the NH₃ in SCR enough.

Table 3. Engine operating conditions under which the experiment was performed.

Category	Engine Operating Conditions
Engine speed [rpm]	1500, 2000, 2500, 3000
Exhaust gas temperature [°C]	250, 300, 350, 400

Figure 2 shows the results of measuring the exhaust gas when the engine speed is 1500 rpm and the exhaust gas temperature is 250 °C according to the above-mentioned method. In the graph, there are fluctuations in the measured value of each exhaust gas. NH₃ and NO fluctuated around 10 ppm and NO₂ fluctuated around 12 ppm. However, it was determined that this fluctuation was negligible and had an insignificant impact on the exhaust gas measurement results, so the error was eliminated by taking sufficient measurement time and analyzing the results by averaging the values. In Phase M₂, after injecting the amount of urea with an excess reduction, NO_x decreased and NH₃ slip increased. Phase M₃ shows a tendency of NH₃ slip to reduce and NO_x to increase again after the urea water injection stopped. Although the NO_x reduction efficiency differs depending on the space velocity and temperature of the exhaust gas depending on the engine conditions, NH₃ slip occurs after a certain period has passed since the NO_x reduction was performed in common. The amount of NH₃ adsorbed in the SCR until the NH₃ slip appears through the measured amount of NO_x and NH₃ change (M₁), the amount of NH₃ adsorbed after the NH₃ slip (M₂), and the amount of adsorption based on the reduced amount of NO_x (M₃) were calculated, respectively.

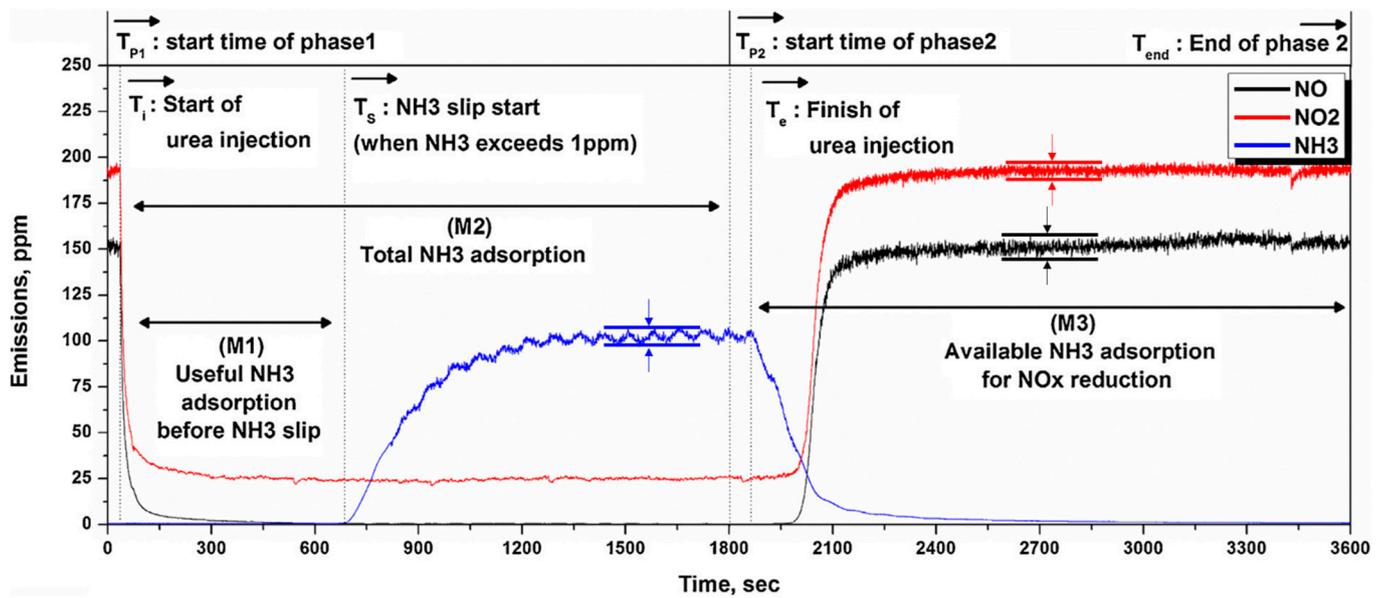


Figure 2. Adsorption and desorption of NH_3 in SCR experiment results and analysis methods (Engine speed: 1500 rpm, Exhaust gas temperature: 250 °C).

To investigate the range that can be controlled so that the NH_3 slip does not appear, the range for measuring the amount of NH_3 adsorbed in the SCR until the NH_3 slip occurs is M_1 . The adsorption amount of NH_3 in the period before the occurrence of NH_3 slip is equal to the amount of NH_3 slip during the period in which NH_3 slip appears stably. Therefore, the value obtained by accumulating the amount of NH_3 slip stabilized until the appearance of NH_3 slip for the M_1 period can be regarded as the amount of NH_3 adsorbed on the SCR. Further, assuming that the reaction ratio of NH_3 and NO_x is 1:1, NO_x appears in the NH_3 slip so it cannot be reduced. Therefore, it is necessary to consider NO_x emissions when the NH_3 slip stabilizes and NO_x emissions during the transient period. Based on this, the amount of adsorption until the NH_3 slip appears can be calculated by the following formula:

$$M_1 = \int_{t=T_i}^{t=T_s} \left[\{A_{mean} - A_t + (N_{mean} - N_t)\} \times \dot{V}_{exh} \times \rho_{\text{NH}_3} \right] \quad (7)$$

The standard moment at which the NH_3 slip started to appear was set when NH_3 exceeded 1 ppm—after the appearance of the NH_3 slip, a stabilization time of approximately 1500 to 1800 s passed. Adsorption of NH_3 in the SCR continues even when the NH_3 slip occurs, but the amount of NH_3 that can be adsorbed in the SCR is complete when the NH_3 slip stabilizes. This is because when NH_3 can no longer be adsorbed on the SCR, the further charged NH_3 is discharged as it is. Therefore, the total amount of NH_3 adsorbed in the SCR can be calculated by the following equation, and the calculation range is set to the time when the NH_3 slip stabilizes:

$$M_2 = \int_{t=T_i}^{t=T_{P2}} \left[\{A_{mean} - A_t + (N_{mean} - N_t)\} \times \dot{V}_{exh} \times \rho_{\text{NH}_3} \right] \quad (8)$$

As mentioned above, the change in NO_x emissions after the completion of urea water injection was measured in Phase M_3 . When the urea water injection is completed, NO_x emissions gradually increase even though ammonia is no longer input. It can be assumed that the conventionally adsorbed NH_3 reacted with NO_x if there was no further NH_3 charged in the SCR. Therefore, by integrating the amount of NO_x emitted during this period, it is possible to estimate the amount of NH_3 that was conventionally adsorbed on the SCR. However, since this method calculates the amount of NH_3 adsorbed based on

the NO_x reduction reaction if the existing NH₃ does not react to the reduction in NO_x, it may differ from the result of the amount of NH₃ adsorbed by the M_2 calculation method. Therefore, in the case of M_3 , the following equation can be used to estimate the percentage of how much NH₃ adsorbed in the SCR can be used to reduce NO_x emissions:

$$M_3 = \int_{t=T_e}^{t=T_{end}} \left\{ (N_{2_{mean}} - N_{2_t}) \cdot \frac{\rho_{NO_2}}{M_{NO_2}} \right\} \cdot \frac{\dot{V}_{exh}}{1000} \quad (9)$$

4. Results and Discussion

4.1. NH₃ Adsorption in SCR in Different Engine Conditions

Figure 3 shows NO and NO₂ measured after the engine, the DOC, and the DPF. As is generally known, in this experiment, most of the NO_x generated during diesel combustion took the form of NO, and the NO increased in proportion to the temperature of the exhaust gas from combustion. When the exhaust gas temperature was approximately 400 °C, the NO was measured to be low due to the activation of the EGR. The EGR was activated when the engine speed and load were medium, and EGR activity stopped when the exhaust gas temperature was above 450 °C to achieve a high engine output. As described above, since the diesel engine used in the experiment satisfies EURO 2, the EGR operating area is relatively narrow compared to the latest machine. After that, looking at the amount of NO and NO₂ through the DOC and DPF, the amount of NO₂ gradually increased due to NO oxidation as the DOC and DPF were activated.

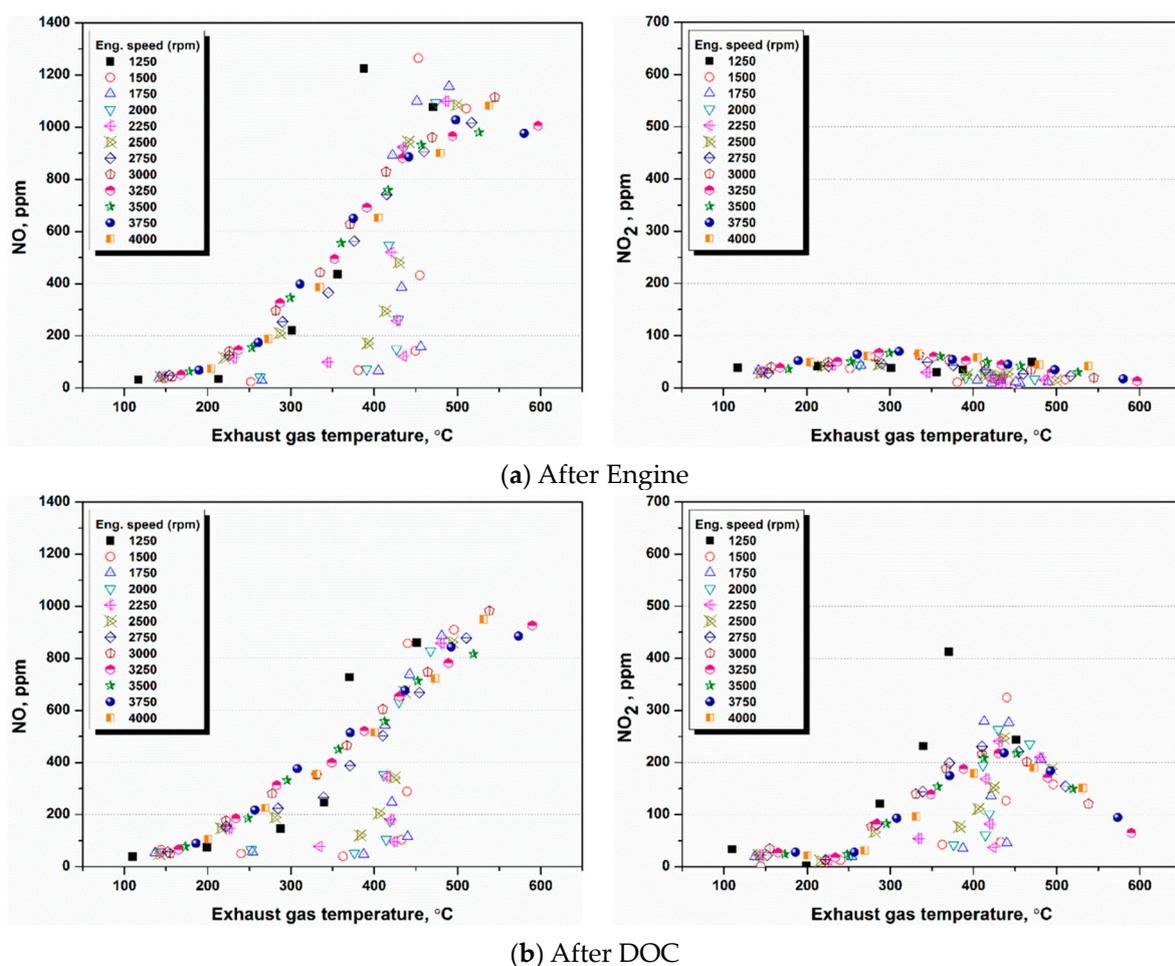


Figure 3. Cont.

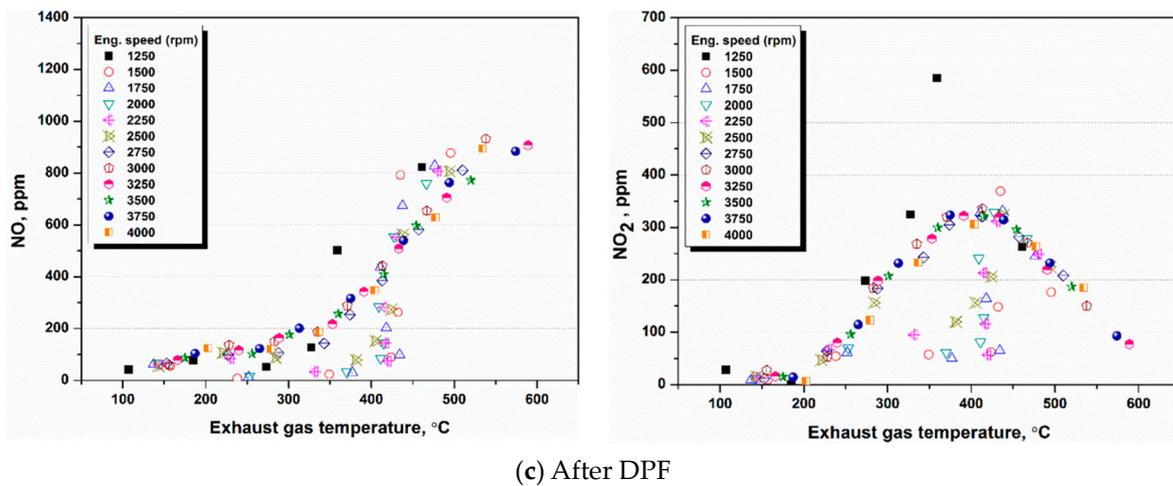


Figure 3. NO and NO₂ emission characteristics (a) after engine, (b) after DOC, and (c) after DPF.

Figure 4 shows the results of changes in the amount of NO and NO₂ through NO oxidation in the DOC and DPF. When the exhaust gas temperature was below 250 and 200 °C, respectively, NO was hardly oxidized due to the inactivation of the DOC and DPF. Still, as the catalyst started to be activated, NO began to be eroded to NO₂. When the exhaust gas temperature was 450 °C, the oxidation rate of NO was highest in the DOC, and the oxidation rate of NO was highest at 350 °C in the DPF. Through this, the central temperature range of this study was 250 °C to 400 °C, which indicates the temperature at which SCR was activated for the oxidation of NO reached the maximum.

First, the relationship between the reduction efficiency of SCR according to the ratio of NO and NO₂ in NO_x was investigated through the experimental results. Figure 5 shows the SCR reduction efficiency according to the NO and NO₂ ratio. Each color represents the engine speed, and the *x*-axis represents the exhaust gas temperature. The solid square results show the NO_x reduction ratio of SCR, and the empty square shows the percentage of NO and NO₂ inside the SCR exhaust gas. The right *y*-axis shows the proportion of NO and NO₂, and the left *y*-axis shows the NO_x reduction rate. The closer the ratio of NO to NO₂ is to 1:1, the closer to 1, and the larger the percentage of NO, the larger the value. The NO_x reduction ratio is more comparable to 1.0 the closer the NO_x reduction is to 100%. The solid square results show the NO_x reduction ratio of SCR, and the empty square shows the percentage of NO and NO₂ inside the SCR exhaust gas.

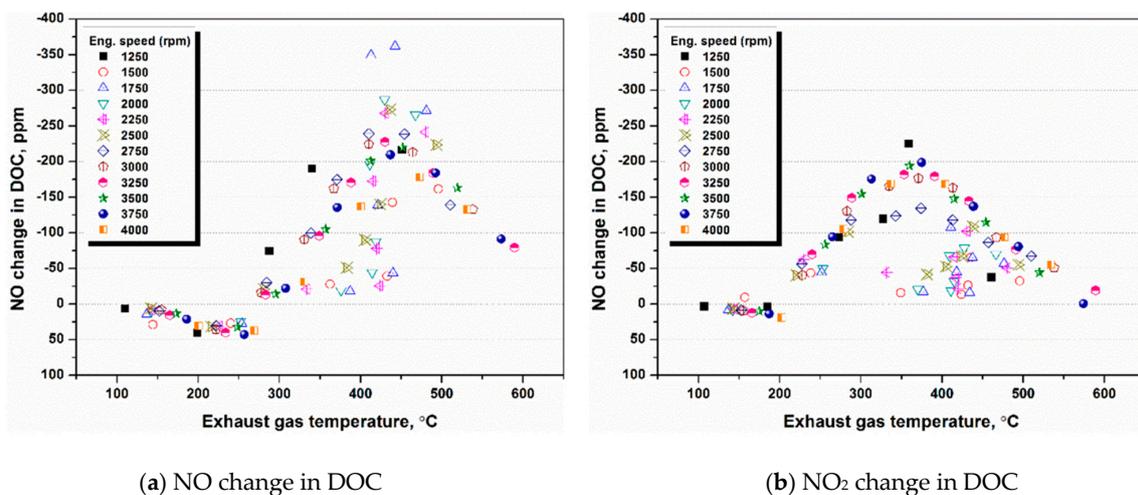


Figure 4. Cont.

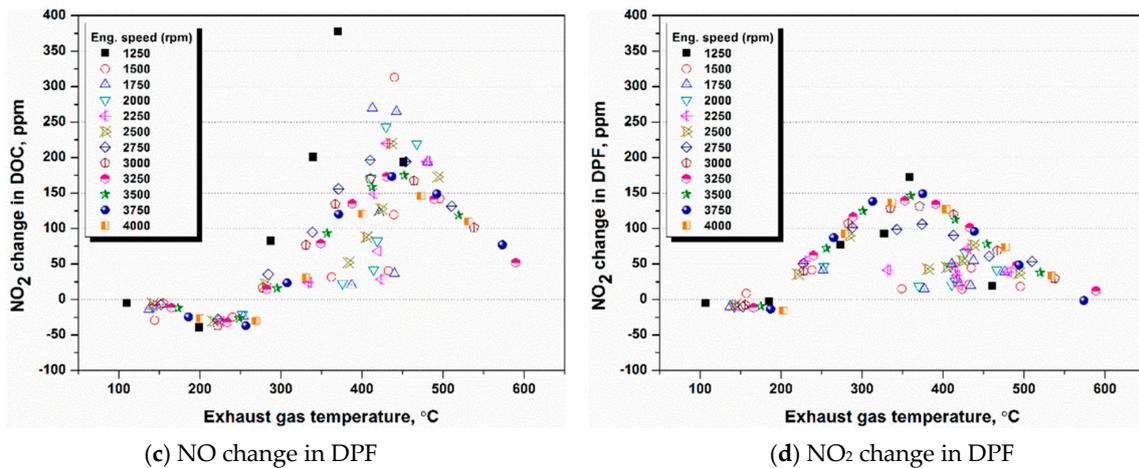


Figure 4. NO and NO₂ changes in DOC (a,b) and DPF (c,d).

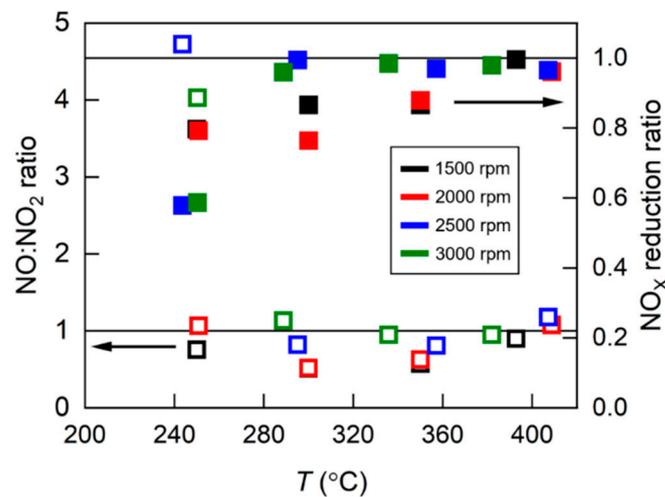


Figure 5. Ratio of NO and NO₂ according to the experimental conditions.

As a result, the ratio of NO and NO₂ in the exhaust gas that passes through the DOC differs depending on the exhaust gas temperature and the engine speed. When the engine cranking speeds were 1500 and 2000 rpm, it was found that NO₂ accounted for a more significant proportion than NO in the range of the exhaust gas temperature in the field of 300 to 350 °C, which lowered the NO_x reduction ratio inside the SCR. When the engine speed was 2500 and 3000 rpm, the exhaust gas temperature was slightly 250 °C or less. Still, at this time, the NO ratio was 300 °C or more, significantly higher than NO₂, and the NO to NO₂ ratio was almost 1:1. The NO_x reduction ratio inside the SCR was also the lowest when the exhaust gas temperature was approximately 250 °C. Still, the percentage of NO and NO₂ was 1:1, and the reduction efficiency was considerably high. As a result, the exhaust gas was partially oxidized to NO₂ via the shear activation DOC and DPF, and NO and NO₂ in a 1:1 ratio entered the SCR. The highest SCR efficiency was achieved then, and excessive conversion to NO₂ reduced the reduction efficiency. Based on the above NO_x reduction ratio, the amount of NH₃ that slipped was predicted from the amount of urea injected, and the NH₃ adsorbed on the SCR was calculated.

Figures 6–8 show the amount of SCR adsorbed on the SCR in different ways through Equations (7)–(9). The adsorption amount at each operating point is displayed, and the average value is displayed on the trend line. As in previous studies, the amount of NH₃ adsorbed on the SCR decreased as the exhaust gas temperature increased. Looking at Figure 6, which shows the amount of NH₃ adsorbed on the SCR until NH₃ slip occurs, the

amount of NH_3 adsorbed is approximately 1.25 to 0.25 g in the exhaust gas temperature range of 250 to 400 °C.

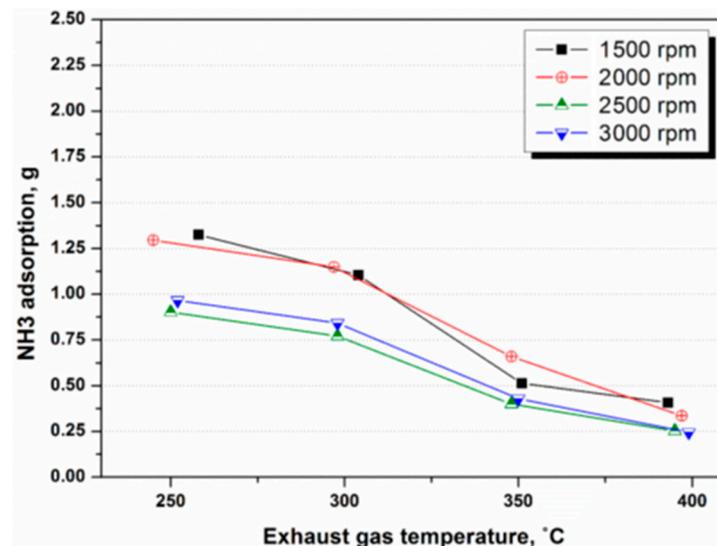


Figure 6. NH_3 storage amount calculated in Phase M_1 according to experimental conditions.

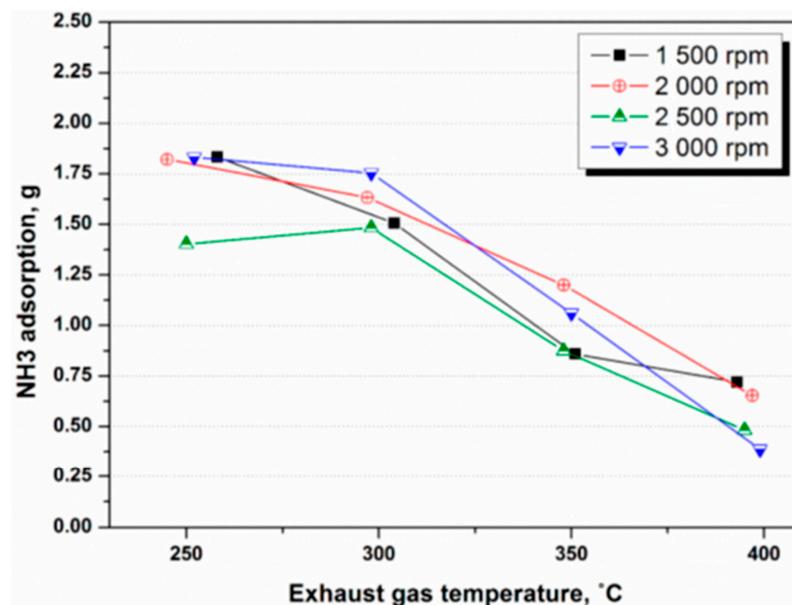


Figure 7. NH_3 storage amount calculated in Phase M_2 according to experimental conditions.

Figures 7 and 8 show the total amount of NH_3 adsorbed on the SCR after the appearance of the NH_3 slip and the total amount of NH_3 adsorbed on the SCR after stopping the urea water injection. From the above results, the total amount of NH_3 adsorbed on the SCR is 1.8 to 0.4 g. Here, the NH_3 adsorption amount substantially utilized for NO_x reduction is the result of reversely calculating the NO_x amount reduced while desorbing NH_3 adsorbed on the SCR. Therefore, the impact of M_3 can be estimated as the amount of NH_3 adsorbed that can be utilized for actual NO_x reduction. It was found that the NH_3 adsorption amount calculated by the M_2 method was slightly higher than the NH_3 adsorption amount calculated by the M_3 method. It can be presumed that this is because NH_3 is adsorbed on the region where the catalyst is not applied and the low-temperature portion, particularly on the outer wall of the SCR.

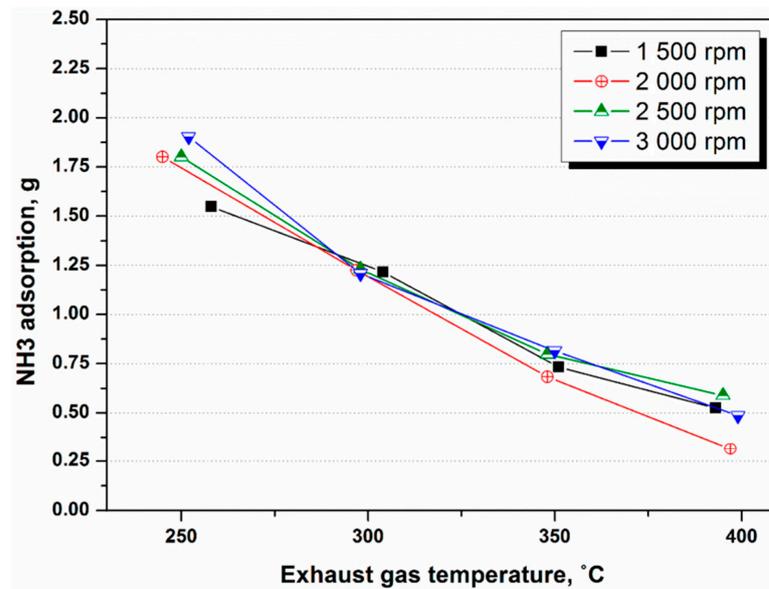


Figure 8. NH₃ storage amount calculated in Phase M_3 according to experimental conditions.

Based on this, the NH₃ adsorption amount used for NO_x reduction was regarded as the M_3 result value, and the useless NH₃ adsorption amount was calculated by subtracting the M_3 result value from the M_2 result value. The amount of useless NH₃ adsorption was 0.1 to 0.2 g over the entire temperature range. Figure 9 shows a graph of the proportion of NH₃ adsorption and total adsorption that is unnecessary for NO_x reduction. In general, the NH₃ slip reduced the amount of NH₃ adsorbed inside the SCR in the operating region where the exhaust gas temperature was high. In addition, the amount of unnecessary NH₃ adsorption also increased in the active area where the exhaust gas temperature was higher. As a result, the amount of NH₃ adsorbed unnecessarily under the experimental operating conditions was insignificant from 0.1 to 0.2 g. However, the proportion of total NH₃ adsorbed increased to 60% at the highest temperature. As a result, as the exhaust gas temperature increased, the amount of NH₃ adsorption decreased, and the buffer section was reduced, making it challenging to control NH₃ slip.

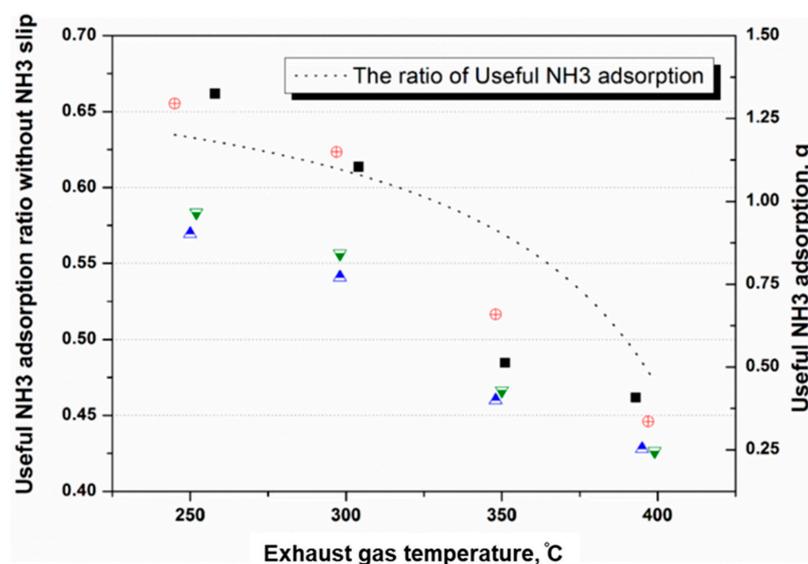


Figure 9. Useful NH₃ adsorption amount and ratio used for actual NO_x reduction according to exhaust gas temperature.

4.2. NH₃ Adsorption and Desorption Rate in SCR in Different Engine Conditions

The amount of NH₃ adsorbed in the SCR varies depending on the engine's operating conditions. Therefore, if not only the adsorption amount but also the adsorption rate and the desorption rate are not considered, an acceptable urea water injection strategy for controlling the NH₃ slip can be established. Figure 10 shows how the NH₃ adsorption and desorption rates were calculated.

$$\dot{m}_{\text{ammonia, adsorb}} = \partial m_{\text{NH}_3, \text{adsorb}} / \partial t \quad (10)$$

$$\dot{m}_{\text{ammonia, desorp}} = \partial m_{\text{NH}_3, \text{desorp}} / \partial t \quad (11)$$

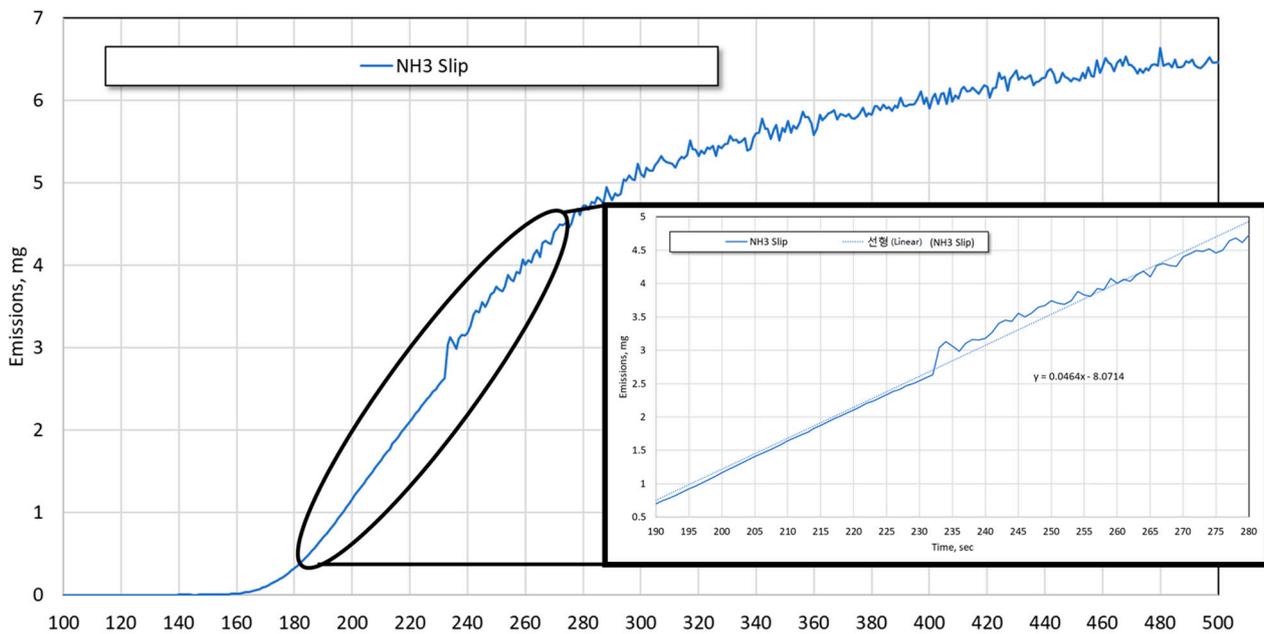


Figure 10. Calculation of the NH₃ adsorption rate and desorption rate (at 3000 rpm and 300 °C).

Figure 11 shows the results calculated according to Equations (9) and (10) for the NH₃ adsorption and desorption rates inside the SCR under experimental operating conditions. Graph (a) shows the NH₃ adsorption rate in the SCR depending on the operating conditions and graph (b) shows the NH₃ desorption rate in the SCR. Looking at the adsorption rate, the adsorption rate appeared relatively fast at an engine cranking speed of 2000 rpm and temperatures of 300 to 350 °C. The proportion of NO₂ in NO_x discharged in this range is high, the NO_x reduction efficiency is relatively low, and a large amount of NH₃ slip occurs, so the adsorption rate of SCR seems to appear rapidly. Therefore, this result alone does not clearly show the relationship between the NH₃ adsorption rate and the desorption rate depending on the operating conditions. The total amount of NH₃ adsorbed in the SCR changes depending on the operating conditions, and the NH₃ slip also changes. Therefore, the results of calculating and comparing the adsorption and desorption rates of NH₃ in consideration of the NH₃ storage amount are shown in Figure 12.

The results in Figure 12 show that the engine cranking speed does not significantly affect the adsorption and desorption rates of NH₃ in the SCR. However, it turned out to be substantially affected by the exhaust gas temperature. This supports the idea that the total occlusion of NH₃ decreases as the exhaust gas temperature rises so that the rate at which NH₃ is adsorbed inside the SCR and the desorption rate increase. In addition, as the temperature of the exhaust gas rises, it affects the internal temperature distribution of the entire SCR, and it can be expected that the degree of catalytic activation will also be affected. For this reason, in later studies, it is necessary to analyze the NH₃ adsorption

and desorption rates depending on the temperature distribution inside the SCR and the degree of activation. Based on these results, if a urea water injection strategy is established through experiments on the relationship between the temperature distribution inside the SCR and the engine's operating conditions, NH_3 slip can be reduced while maximizing the NO_x reduction efficiency.

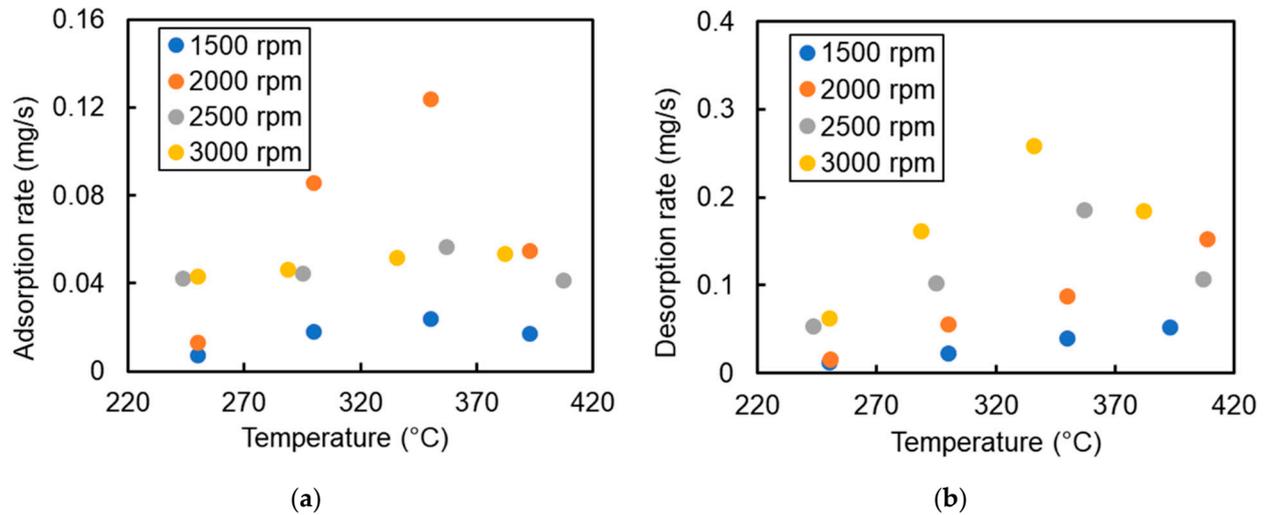


Figure 11. Adsorption (a) and desorption (b) rates of NH_3 in SCR in various conditions.

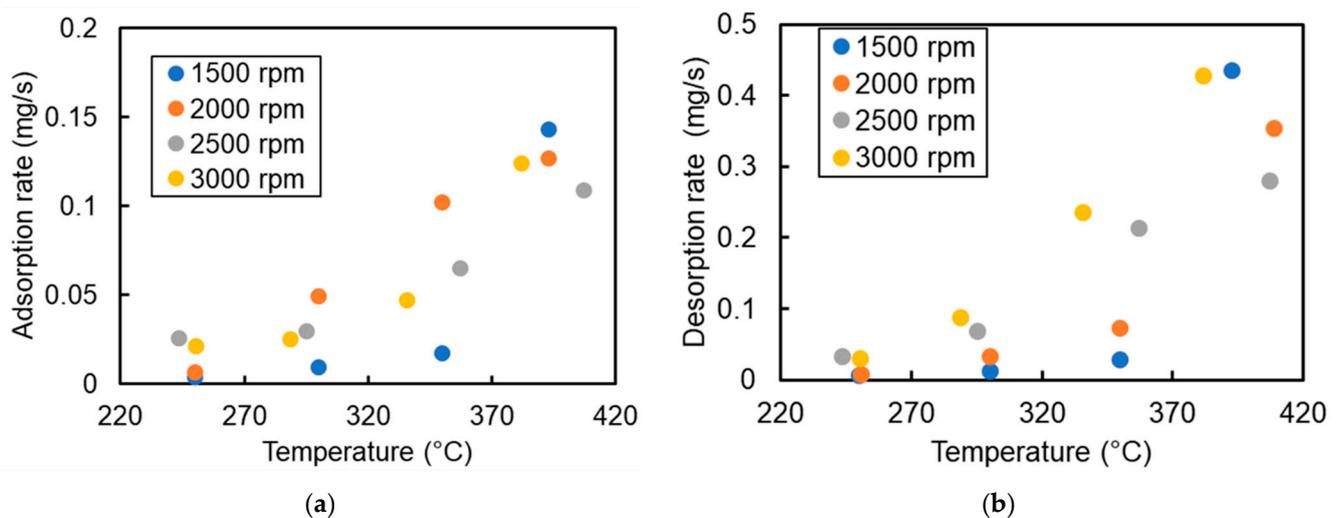


Figure 12. Relative values of adsorption (a) and desorption (b) rates of NH_3 in SCR in various conditions.

5. Conclusions

The adsorption and desorption mechanism of NH_3 in SCR is one of the key factors to prevent NH_3 slip while improving the NO_x reduction performance. In particular, the control strategy is more complicated in the real-time operation method, in which the temperature of the exhaust gas changes in real time. In this study, we considered improving the NO_x reduction efficiency and preventing the NH_3 slip by analyzing the adsorption rate and desorption rate of NH_3 in SCR under various engine operating conditions.

The amount of NH_3 adsorbed inside the SCR under the engine operating conditions of this experiment was 0.4 to 1.8 g. The amount of NH_3 adsorbed inside the SCR decreased as the exhaust gas temperature increased. Among the NH_3 adsorbed inside the SCR, the amount of NH_3 not utilized to reduce NO_x was approximately 0.1 g to 0.2 g. This ranged from 65% to 94% of the solubility, and similarly, the higher the exhaust gas temperature, the

lower the availability. Further, the range of the amount of NH_3 adsorbed until just before the appearance of NH_3 slip is 0.25 g to 1.25 g, and the availability calculated based on this is 47% to 63%.

In real-time operation conditions, analyzing the adsorption rate and desorption rate of NH_3 in SCR and the total adsorption amount of NH_3 in SCR is necessary. As a result, the adsorption rate and desorption rate of NH_3 in SCR were not significantly affected by the engine rotation speed. However, it was shown that the adsorption rate and desorption rate increase as the exhaust gas temperature rises. This is expected to increase the adsorption rate and desorption rate as the total amount of NH_3 adsorbed in the SCR decreases. In addition, although not analyzed in this study, it is necessary to examine the adsorption mechanism by comparing the temperature distribution inside the SCR with the exhaust gas temperature and the degree of activation. As a result, the decrease in the amount of NH_3 adsorbed inside the SCR at a high exhaust gas temperature suggests that NH_3 slip control is difficult when the engine is under high-load transient conditions. However, the urea water injection strategy is established by grasping the temperature of the exhaust gas and the temperature change inside the SCR according to the engine's operating conditions. In that case, the urea water consumption efficiency can be improved while reducing the NH_3 slip.

As exhaust emission regulations for diesel engines are becoming stricter worldwide, it is unavoidable that aging diesel engine vehicles be retrofitted with aftertreatment devices such as SCR. In this paper, the mechanism of ammonia adsorption in the SCR is dependent on the exhaust temperature and exhaust flow rate. Therefore, if the SCR adsorption and desorption mechanisms are analyzed according to the exhaust temperature and exhaust flow rate of each old diesel engine in this paper, it can be used as a reference for selecting an appropriate SCR when retrofitting an old diesel engine vehicle.

Author Contributions: Conceptualization, H.J.; methodology, H.J.; validation, H.J.; formal analysis, H.J.; investigation, H.J., J.J., A.K. and O.L.; resources, H.J., J.J., A.K. and O.L.; data curation, H.J., J.J., A.K. and O.L.; writing—original draft preparation, H.J.; writing—review and editing, O.L.; visualization, H.J., J.J., A.K. and O.L.; supervision, J.J., A.K. and O.L.; project administration, J.J., A.K. and O.L.; funding acquisition, J.J., A.K. and O.L. All authors have read and agreed to the published version of the manuscript.

Funding: This research is financially supported by the Global Top Environmental Technology Development Project of the Korea Environmental Industry and Technology Institute (RE202001110, Development and Demonstration of simultaneous PM and NO_x reduction system of military vehicles and RE2016001420002; Development of the PM- NO_x purifying system and the core technology; Shipbuilding and Offshore Industry Core Technology Development Business by the Ministry of Trade, Industry, and Energy (MOTIE, Republic of Korea) [Development of Low Print Point Alternative Fuel Injection System for Small and Medium Vessel Engines for Ships Hazardous Emission Reduce]. (20013146).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: This work was supported by a research program in the Department of Mechanical Engineering (Generation Fuel and Smart Power Train Laboratory), University of Ulsan, Republic of Korea. This research is financially supported by the Global Top Environmental Technology Development Project of the Korea Environmental Industry and Technology Institute (RE202001110, Development and Demonstration of simultaneous PM and NO_x reduction system of military vehicles and RE2016001420002; Development of the PM- NO_x purifying system and the core technology; Shipbuilding and Offshore Industry Core Technology Development Business by the Ministry of Trade, Industry, and Energy (MOTIE, Republic of Korea) [Development of Low Print Point Alternative Fuel Injection System for Small and Medium Vessel Engines for Ships Hazardous Emission Reduce]. (20013146). This research is financially supported by the individual basic research project by the National Research Foundation of Korea (NRF-2021R1F1A1048238, Reliability Improvement

of Ammonia- Diesel Dual-Fuel Combustion Model regarding Optimized Combustion Strategy for Improved Combustion Efficiency and Emission Characteristics). This results was supported by 'Regional Innovation Strategy (RIS)' through the National Research Foundation of Korea(NRF) funded by the Ministry of Education(MOE)(2021RIS-003).

Conflicts of Interest: The authors declare no conflict of interest.

Nomenclature

DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
UWS	Urea Water Solution
SCR	Selective Catalyst Reduction
NH ₃	Ammonia
H ₂ O	Water
NO _x	Nitrogen Oxide
N ₂	Nitrogen
O ₂	Oxygen
CO	Carbon Oxide
THC	Total Hydro Carbon
PM	Particle Matter
BPT	Balance Point Temperature
LNT	Lean NO _x Trap
DOHC	Double OverHead Camshaft
AOC	Ammonia Oxidation Catalyst

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