SNCR-SCR 하이브리드 시스템의 질소산화물 제거 특성

차진선 · 박성훈* · 전종기** · 박영권†

서울시립대학교 환경공학부, *순천대학교 환경공학과, **공주대학교 화학공학부
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Nitrogen Oxides Removal Characteristics of SNCR-SCR Hybrid System

Jin Sun Cha, Sung Hoon Park*, Jong-Ki Jeon**, and Young-Kwon Park†

School of Environmental Engineering, University of Seoul, Seoul 130-743, Korea
*Department of Environmental Engineering, Sunchon National University, Suncheon 540-742, Korea
**Department of Chemical Engineering, Kongju National University, Cheonan 331-717, Korea
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SNCR-SCR hybrid system은 SNCR에서 NOx를 제거한 뒤, SCR로 NOx를 추가 제거하는 시스템으로 NOx 제거 효율을 향상시키는 경제적인 시스템이다. 본 연구에서는 SNCR-SCR hybrid system에서 운전 변수가 질소산화물 저감 효율에 미치는 영향을 고찰하였다. SNCR을 optimum temperature (900∼950 ℃)보다 낮은 온도에서 운전할 경우, 추가적인 암모니아 주입 없이도 NH_3 slip을 이용한 NO의 추가적인 제거의 효과가 있었으나 NH_3 slip이 높은 것으로 나타났다. 그러나 그 이상의 온도에서는 고온에 의한 암모니아의 분해로 SCR에 의한 추가 제거의 효과를 얻지 못했다. 따라서 SNCR 공정을 optimum temperature에서 운전하는 것이 NO 제거 효율과 NH_3 slip 농도를 고찰하였을 때 가장 적절하였으며, SR_{RES}가 적정 수준으로 유지되도록 NSR을 조절하는 것이 중요한 운전 변수인 것으로 나타났다.

The SNCR-SCR (selective non-catalytic reduction-selective catalytic reduction) hybrid system is an economical NOx removal system. In this study, the effect of the operating parameters of the SNCR-SCR hybrid system on NOx removal efficiency was investigated. When the SNCR reactor was operated at a temperature lower than the optimum temperature (900∼950 ℃), an additional NO removal is obtained basesd on the utilization of NH_3 slip. On the other hand, the SNCR reactor operated above the temperature resulted in no additional NO removal of SCR due to decomposition of NH_3. Therefore, the SNCR process should be operated at optimum temperature to obtain high NO removal efficiency and low NH_3 slip. Thus, it is important to adjust NSR (normalized stoichiometric ratio) so that SR_{RES} can be maintained at an appropriate level.

Keywords: hybrid system, NOx removal, SNCR, SCR

1. Introduction

Nitrogen oxide (NOx) in the atmosphere deteriorates immune system of humans and animals to respiratory diseases by destructing respiratory cells. It also obstructs oxygen transport by combining with hemoglobins in blood to form methemoglobins. As one of the representative air pollutants, it causes acid rain, ozone formation, and photochemical smog. In addition, under the presence of hydrocarbons, it induces formation of photochemical oxidants such as PANs (peroxyacetyl nitrates) and aldehydes[1,2].

Among the various methods to reduce NOx emission, selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) have most widely been used[3]. While SNCR requires minimal process modification, low start-up cost, and simple process constitution because it needs only a single process for treatment, storage and injection of reducing agent, its NOx removal efficiency is relatively low (30∼60%)[4]. SCR exhibits higher NOx removal efficiency than SNCR at the expense of high catalyst cost and inactivation and corrosion of catalysts[5]. The SNCR-SCR hybrid system, in which an SNCR process is followed by an SCR process, was proposed to accomplish effective treatment of unreacted ammonia of SNCR and additional NOx removal. In this system, the catalyst bed of the SCR installed next to the SNCR is smaller than that of stand-alone SCR processes, resulting in lower cost for catalyst and for retrofit of catalyst reactor, ducts and fans[6]. Therefore, the SNCR-SCR hybrid system is expected to bring about enhanced NOx removal efficiency, extended lifetime of catalysts, and reduced operation cost[7,8].

In this study, the effects of operation parameters of the SNCR-SCR hybrid system on the NOx removal efficiency and NH_3 slip were investigated.

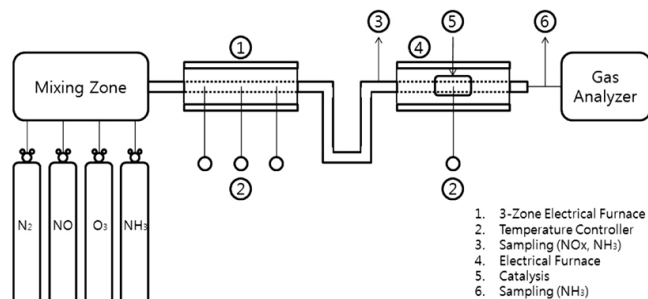† 교신저자 (e-mail: catalica@uos.ac.kr)

Figure 1. Flow diagram of experimental SNCR/SCR hybrid system.

1. 3-Zone Electrical Furnace
2. Temperature Controller
3. Sampling (NOx, NH₃)
4. Electrical Furnace
5. Catalysis
6. Sampling (NH₃)

2. Experimental Method

2.1. Apparatus

The experimental apparatus including an SNCR/SCR hybrid system used in this study is shown in Figure 1. Reactants were allowed to enter the SNCR reactor after being mixed in a mixing zone. An SNCR reactor and an SCR reactor were installed in series. The SNCR and SCR reactors were made of stainless steel that is inert and resistant to high temperature. Both reactors were in cylindrical shape with an inner diameter of 8 mm. The reactor length was 550 and 300 mm for SNCR and for SCR, respectively. Since the SNCR process is sensitive to temperature, temperature controllers were installed at three locations inside the reactor to maintain the temperature at constant. The residence time was controlled to be 0.3 s to ensure sufficient time for reaction.

2.2. Catalyst Synthesis

The catalysts used in this study were synthesized by impregnating TiO_2 and V_2O_5 on honeycomb-shaped cordierite ($2MgO$-$2Al_2O_3$-$5SiO_2$) substrate purchased from J company. The substrate was cut with an appropriate length and dried at 100 ℃ for 24 h. TiO_2 sol was coated on the dry substrate using vacuum impregnation method. The coated substrate was dried again for 24 h under constant temperature and humidity condition maintained at 60 ℃ and 60% and then was heat-treated at 500 ℃ for 1 h. Mixture of 99% ammonium vanadate (NH_4VO_3) and oxalic acid ($C_2HO_4 \cdot H_2O$) with the mass ratio of 1 : 2 was impregnated on the substrate using the same method as was used for impregnation of TiO_2 to synthesize the V_2O_5/TiO_2 catalyst.

2.3. Experimental Method

The reactants consisted of NO, O_2, NH_3 and N_2. 99.99% N_2, 99.995% O_2, and 99.99% NH_3 gases were used for experiments. The concentration of NO was 500 ppm. The flow rate of each reactant was controlled by a flow controller.

SNCR experiments were performed at different temperatures by rising the reactor temperature by 50 ℃ within the range of 500~1100 ℃. The NO removal was measured by allowing 500 ppm NO to react with NH_3. The NH_3 injection was controlled to adjust the normalized stoichiometric ratio (NSR) at 1.0, 1.5 and 2.0. The NO and NH_3 concentrations were measured before and after reaction.

The NO removal efficiency of the SCR reactor was measured at different reactor temperatures within the range of 300~420 ℃. The NH_3
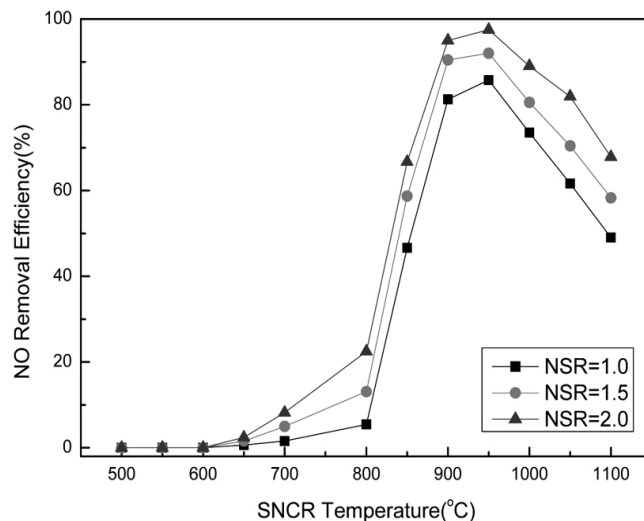

Figure 2. Effect of reaction temperature and NSR on NO removal efficiencies in SNCR system (NO : 500 ppm, O_2 : 4%, retention time = 3 s).

injection was controlled to adjust the NSR at 1.0, 1.5 and 2.0. Two space velocities (SVs) were used : 6500 and 13000 h^{-1}. The NO and NH_3 concentrations were measured after reaction.

For the SNCR-SCR hybrid system, the effluent of the SNCR reactor entered the SCR reactor. The NSR at the SNCR inlet was controlled at 1.0, 1.5 and 2.0. The NO and NH_3 concentrations at the SNCR outlet and at the SCR outlet were measured to evaluate the SCR efficiency as a function of SR_{RES}, additional removal efficiency of unreacted ammonia, and the NO and NH_3 removal efficiencies of the SNCR/SCR hybrid system. The concentrations of O_2, NO and NO_2 were measured by a gas analyzer, while the ammonia concentration was analyzed manually using the indo-phenol method.

3. Results and Discussion

3.1. SNCR System

One of the most important operation parameters that affect the NO removal in an SNCR process is the temperature distribution within the reactor. In advance to NO removal experiments, the temperature distribution within the reactor was measured with an interval of 5 cm by increasing the set reactor temperature by 50 ℃ within the range of 500 ~1100 ℃. The temperature was shown to be controlled within ± 4% from the set temperature for more than 80% of total reactor length.

Figure 2 shows the NO removal efficiency of the SNCR reactor as a function of reactor temperature obtained under the condition of 500 ppm NO and 4% O_2 with the balance gas of N_2. It is shown that the NO removal efficiency began to increase significantly at around 700 ℃ having the maximum efficiency at 950 ℃. This result agrees with the optimum temperature of 900~950 ℃ for SNCR reported by previous studies[9]. In the mean time, the NO removal efficiency of the SNCR process increased with NSR. The maximum NO removal efficiency at 950 ℃ with NSR of 1.0, 1.5 and 2.0 was 85.7, 92.0 and 97.5%, respectively.
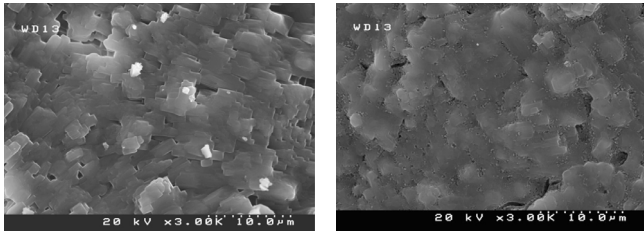
(a) before coating   (b) after coating

Figure 3. Scanning electron microscopy of (a) cordierite substrate (× 3000) and (b) V₂O₅/TiO₂ Catalyst (× 3000).

Table 1. Comparison of Specific Surface Area before/after V_2O_5-TiO_2 Impregnation

	Specific surface area (m^2/g)
Substrate (cordierite)	0.48
V_2O_5-TiO_2/Cordierite	0.68
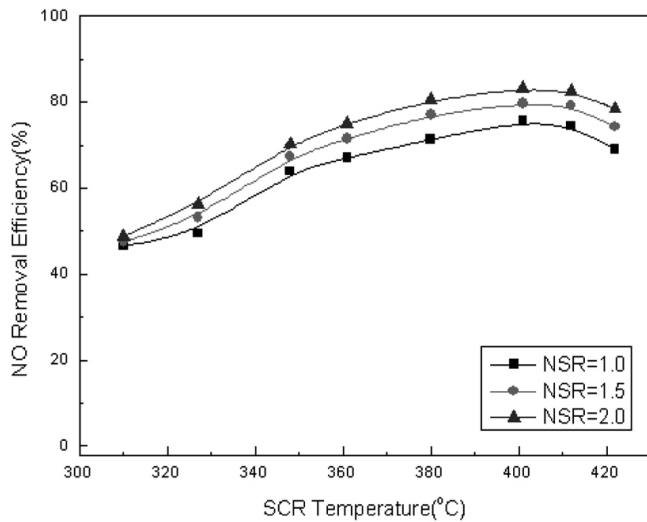
Figure 4. Effect of reaction temperature and NSR on NO removal efficiencies of SCR process (NO : 500 ppm, O₂ : 4%, Space Velocity : 6500 h⁻¹).

Figure 5. Effect of space velocity on NO removal efficiencies of SCR process at NSR = 1.0 (NO : 500 ppm, O₂ : 4%).

Figure 6. Effect of space velocity on NO removal efficiencies of SCR process at NSR = 1.5 (NO : 500 ppm, O₂ : 4%).

3.2. SCR System

NO removal experiments were carried out with the SCR system within the temperature range of 300~420 ℃ with NSR of 1.0, 1.5 and 2.0. The inlet NO and O₂ concentrations were 500 ppm and 4% and N₂ was used as the balance gas.

Figure 3 compares the scanning electron microscopy images taken before (a) and after (b) the impregnation of cordierite substrate with V₂O₅/TiO₂. Table 1 shows the change in the specific surface area due to the impregnation. The specific surface area was shown to increase due to the impregnation of cordierite substrate with TiO₂ and V₂O₅.

Figure 4 shows the NO removal efficiency obtained with different NSR values as a function of SCR reactor temperature. The NO removal efficiency was highest at 400 ℃ for all NSR values tested. As in the SNCR case, the NO removal efficiency increased with NSR. The maximum efficiency at 400 ℃ with NSR of 1.0, 1.5 and 2.0 was 75.6,
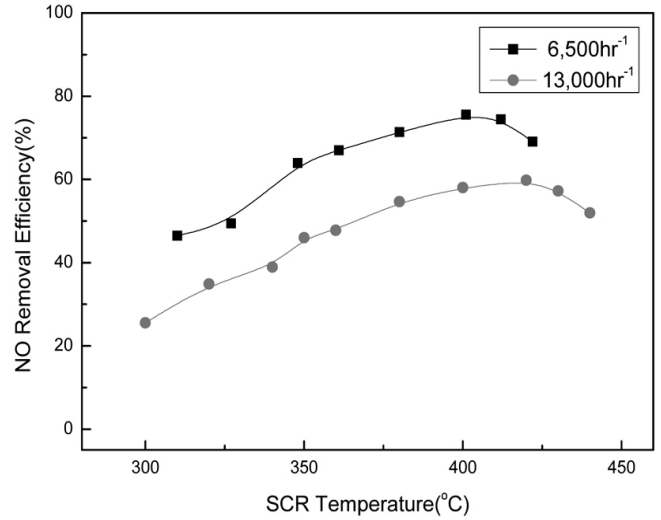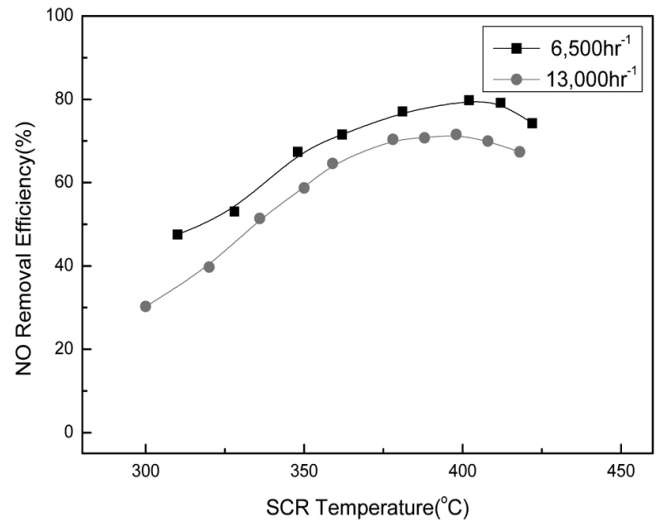
79.8 and 83.2%, respectively.

To examine the effect of SV on NO removal efficiency, experiments were performed with different SVs under the following condition : 500 ppm NO, 4% O₂, and the balance gas of N₂. Figure 5 shows the results obtained using two different SV of 13000 h⁻¹ and 6500 h⁻¹ with NSR = 1, while Figure 6 shows the results obtained with NSR = 1.5. Both figures show that the NO removal efficiency of the SCR system decreases with increasing SV, while the difference was smaller with higher NSR.

Figure 7 shows the ammonia concentration measured at the outlet of SNCR. At low temperatures (700 and 800 ℃), the NH₃ slip was high and increased with NSR. On the other hand, at high temperature (850 ℃ and higher), the NH₃ slip was low and was not dependent on NSR very much. The NH₃ slip decreased with increasing temperature throughout the temperature range tested in this study. The decrease of
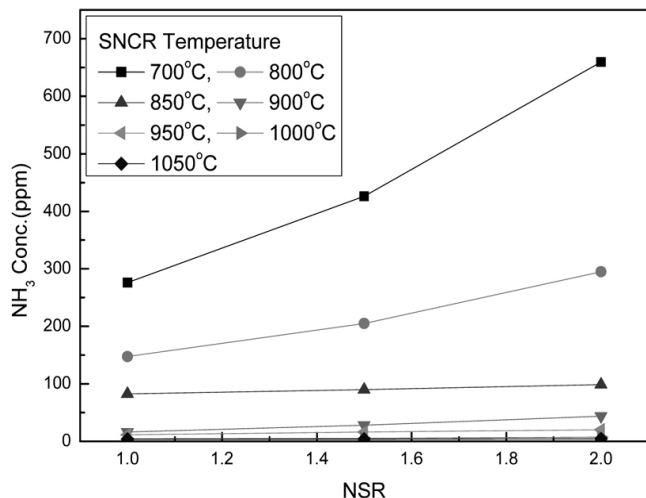
Figure 7. Effect of SNCR temperature and NSR on NH₃ slip of SCR process (NO : 500 ppm, O₂ : 4%).

Figure 9. Effect of SNCR temperature and NSR on NO removal efficiencies of SNCR-SCR hybrid system (NO : 500 ppm, O₂ : 4%, SCR Temp. = 400 ℃).

Figure 8. Effect of SNCR temperature and NSR on SR$_{RES}$ (NO : 500 ppm, O₂ : 4%).

NH₃ slip with increasing temperature under 950 ℃ is attributed to increasing reaction rate between NO and NH₃. On the other hand, the decrease of NH₃ slip with increasing temperature above 950 ℃, which is accompanied by decrease in NO removal efficiency, is attributed to decomposition of NH₃ due to high temperature. The ratio of NO and NH₃ concentrations, SR$_{RES}$, measured at the outlet of SNCR system is shown in Figure 8.

3.3. SNCR-SCR Hybrid System

The NO removal experiments were carried out using the SNCR-SCR hybrid system. The temperature of SNCR reactor was set within the range of 700~1050 ℃, while the SCR reactor temperature was set at 400 ℃ at which the maximum NO removal efficiency was obtained from the SCR system. No additional NH₃ was injected to SCR. Figure 9 shows the NO removal efficiency obtained with different SNCR reactor temperature. The temperature dependency of the NO removal effi-

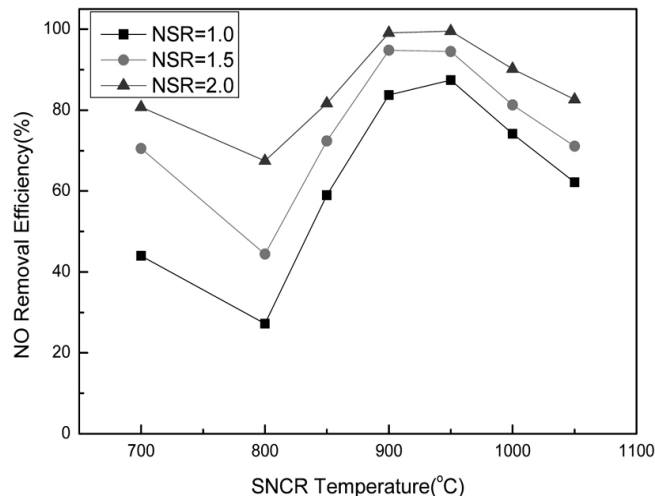ciency of the SNCR-SCR hybrid system was similar to that of the SNCR system shown in Figure 2 in that the maximum efficiency was obtained at 950 ℃. An apparent difference observed between Figures 2 and 9 is that the NO removal efficiency of the SNCR-SCR hybrid system was higher at 700 ℃ than at 800 ℃ in spite of the higher NO removal efficiency of SNCR reactor at 800 ℃. This result may be attributed to the higher SR$_{RES}$ of SNCR reaction obtained at 700 ℃ than that obtained at 800 ℃ (Figure 8), which resulted in a higher additional NO removal efficiency in SCR dominating over the lower efficiency in SNCR.

The NO removal efficiencies of the SNCR system and the SNCR-SCR hybrid system obtained as functions of SNCR reaction temperature with three different NSR are compared in Figures 10 through 12. It is shown in these figures that the additional SCR seldom enhanced the NO removal at temperature of 1000 ℃ and higher probably because of decomposition of NH₃ at high temperature resulting in very low NH₃ concentration at the SCR inlet.

Figure 13 shows the NH₃ slip measured at the outlet of the SNCR-SCR hybrid system. When the SNCR reactor temperature was 700 or 800 ℃, the NH₃ slip increased with NSR. At 850 ℃, the NH₃ slip decreased a little with increasing NSR, but the difference was small. At the SNCR temperature of 900 and 950 ℃, at which the NO removal efficiency was highest, the NH₃ slip was highest when NSR = 1.5 and was lowest when NSR = 2, implying that additional reaction in SCR consumed NH₃ when NSR = 2. At the SNCR temperature of 1000 ℃ and higher, the NH₃ slip did not change much. The result shown in Figure 13 suggests that the NH₃ slip after reaction in an SNCR-SCR hybrid system is affected by the SNCR reactor temperature as well as NSR and SR$_{RES}$. Although the additional NO removal effect of the hybrid system was high at the SNCR reactor temperature of 700~850 ℃, the NH₃ slip at the SCR outlet was high. The NH₃ emission standard as per the Atmospheric Environment Conservation Act of Korea valid from 1 Jan 2010 is 50 ppm. Therefore, to meet this emission standard, the SNCR process must be operated at 900 ℃ or a higher temperature.
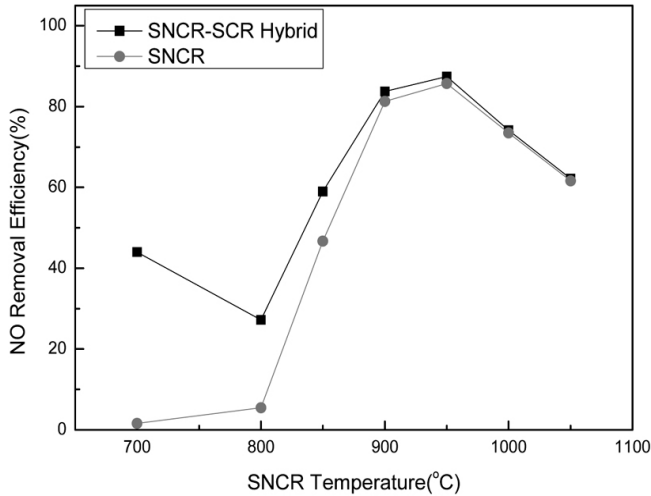
Figure 10. Comparison of NO removal efficiencies of SNCR and SNCR-SCR hybrid system at NSR = 1 (NO : 500 ppm, O₂ : 4%, SCR Temp. = 400 ℃).
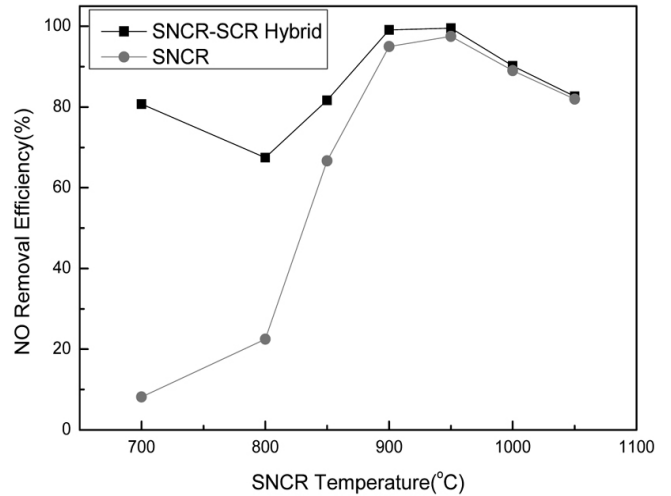

Figure 12. Comparison of NO removal efficiencies of SNCR and SNCR-SCR hybrid system at NSR = 2.0 (NO : 500 ppm, O₂ : 4%, SCR Temp. = 400 ℃).
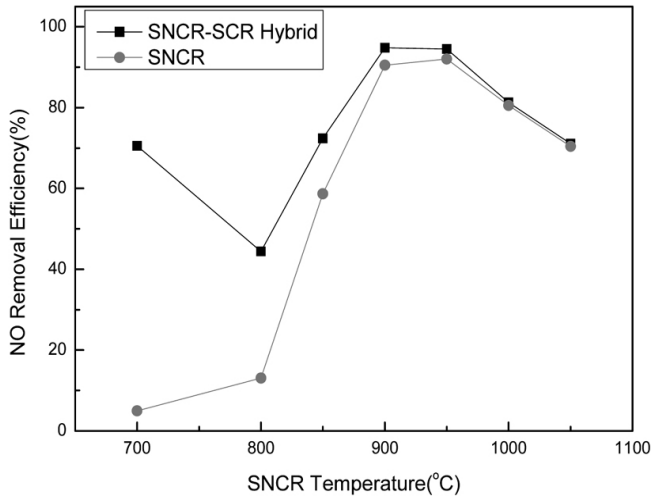

Figure 11. Comparison of NO removal efficiencies of SNCR and SNCR-SCR hybrid system at NSR = 1.5 (NO : 500 ppm, O₂ : 4%, SCR Temp. = 400 ℃).
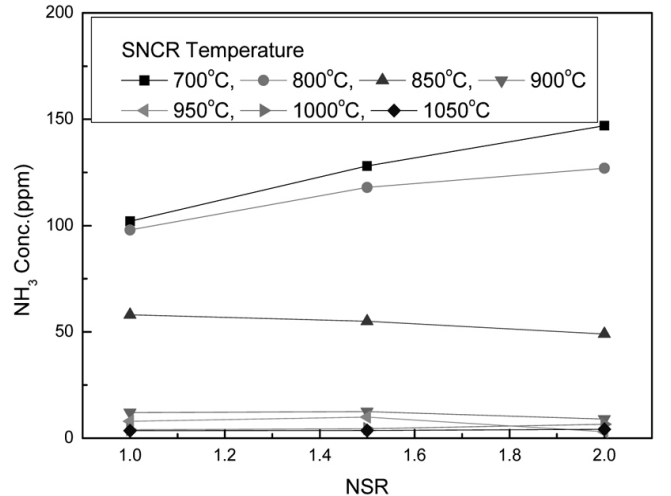

Figure 13. Effect of SNCR temperature and NSR on NH₃ slip of SNCR-SCR hybrid system (NO : 500 ppm, O₂ : 4%, SCR Temp. = 400 ℃).

4. Conclusions

The following conclusions were deduced from the NO removal experiments using an SNCR-SCR hybrid system in this study :

1) When the SNCR reactor of the SNCR-SCR hybrid system was operated at a lower temperature than the optimum temperature range (900∼950 ℃), significant additional NO removal effect was observed stemming from utilization of NH₃ slip without additional injection of ammonia, while the final ammonia outlet concentration exceeded the emission standard of 50 ppm. When the SNCR reactor temperature was higher than the optimum temperature range, no additional NO removal effect of SCR was observed because of decomposition of ammonia due to high temperature. Therefore, it is recommended to operate SNCR within the optimum temperature range.

2) Considering both NO removal efficiency and NH₃ slip, an important operating parameter to control is NSR of SNCR; it should be controlled so that SR$_{RES}$ can be maintained at an appropriate level. Therefore, the three most important operating parameters of the SNCR-SCR hybrid system to acquire additional NO removal effect were shown to be SNCR temperature, NSR and SR$_{RES}$.

3) Optimization of the SNCR-SCR hybrid system can be attained through the balance between the NO removal efficiency and the NH₃ slip by maximizing the NO removal efficiency of the SNCR process while minimizing the NH₃ slip at the SCR outlet.

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