

Improvement on Hybrid SNCR-SCR Process for NO Control: a Bench Scale Experiment

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Abstract

The reducing agent [ammonia (NH_3)] injection procedure was improved for the hybrid process of selective non-catalytic reduction followed by selective catalytic reduction (hybrid SNCR-SCR) to remove nitric oxide (NO) through a bench-scale experiment. Instead of injecting all of the NH_3 from the SNCR inlet, part of it was injected from the SNCR inlet and part from the SCR inlet, to react with NO in the flue gas. The experiment resulted in the significant reduction of NO. The effects of the operational conditions such as the SNCR reaction temperature, the SCR reaction temperature, and the initial concentration ratio of NH_3 to NO were also investigated. Under the initial NO concentration of 300 ppm (dry, 6% O_2), the space velocities of SNCR 5100-6300 hr^{-1} , the space velocities of SCR 7100-10000 hr^{-1} , and with the initial concentration ratios of NH_3 to NO 1.0-1.5, the best operational temperatures were discovered to be SNCR reaction of 850°C and SCR reaction of 350°C for the improved hybrid SNCR-SCR process. In addition, a correlation equation has been developed of the maximum NO reduction under the above best-operational temperatures for the hybrid SNCR-SCR process, and closely fits with the experiment results.

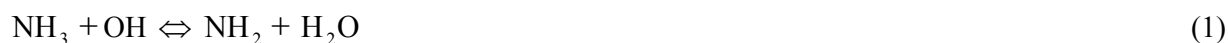
Keywords: hybrid SNCR-SCR, NO reduction, ammonia injection, ammonia slip

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INTRODUCTION

Selective non-catalytic reduction (SNCR) and selective catalytic reduction (SCR) are two major nitric oxide (NO) reduction technologies for post-combustion treatment of flue gas from industrial or utility boilers. The SNCR technology using ammonia (NH_3) as reducing agent to react with NO selectively to yield N_2 and H_2O in flue gas, is named the Thermal De- NO_x Process (Lyon, 1975). The optimal reaction temperature range for Thermal De- NO_x is around 900-950 °C (Muzio et al., 1977). Furthermore, to avoid ammonia slip in the exit flue gas, it was recommended that the reaction temperature higher than 930 °C and the resident time of reaction more than 0.25 s should be controlled (Pohl *et al.*, 1993). Miller and Bowman (1989) present a SNCR reaction mechanism, composed from several chain reactions, with the help of a self-generated active radical (OH, NH_2) to reduce NO. Two important reactions were identified:



Because of possible toxicity and safety problems while handling NH_3 , alternative SNCR processes were developed. These processes use agents, including urea (Arand *et al.*, 1980) and cyanuric acid (Perry and Siebers, 1986). These alternative agents decompose to form NH_3 and HNCO under high temperatures and reduce NO to N_2 or N_2O . The primary equations for HNCO to react with NO to form N_2O are:



N_2O is an environmentally harmful gas. It contributes to ozone layer destruction and increased global warming. When the SNCR processes were applied to stationary industrial pollution sites, the NO reduction range was around 30-60% (Himes *et al.*, 1995).

Selective catalytic reduction (SCR) is a process that also uses NH_3 as an agent, but with the help of a catalyst to reduce NO to N_2 in the lower temperature range. A SCR catalyst is commonly fabricated into a monolith with the shape of honeycomb or flat-plate, when applied to an industrial site. It is usually made by V_2O_5 active sites impregnated into porous TiO_2 carriers ($\text{V}_2\text{O}_5/\text{TiO}_2$), and then coated with the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst on the monolithic surface. The application of SCR in industrial or utility boilers can reach a higher NO reduction rate than the SNCR process. In applying the SCR process, European studies indicated that the lower the space velocity in catalyst bed the higher the NO reduction. The space velocity decreased from 3,400 hr^{-1} to 1,000 hr^{-1} , causing the resident time of the flue gas to increase

from 1.1 s to 3.6 s, and facilitating increased NO reduction from 70% to 90% (Cichanowicz, 1987). When the flue gas contained residual oxygen, the overall chemical reaction of SCR has the stoichiometry:



Equation (5) shows that NH_3 and NO, with the same chemical stoichiometry, cooperate with the higher NO reduction of SCR. It shows why the NH_3 slip of SCR is lower than that of SNCR.

A hybrid technology combining SNCR with SCR (hybrid SNCR-SCR) was developed in order to achieve higher NO reduction or to reduce costs. Gullett *et al.* (1994), and Groff and Gullett (1997) used urea as reducing agent, injecting it through the SNCR inlet, partially reducing NO and forming NH_3 from the decomposition of excessive urea. The process was then transferred to SCR for further NO reduction. This resulted in a space velocity of $10,000 \text{ hr}^{-1}$ for SCR and a total 85% NO reduction for a 590 kw package boiler. Under the stoichiometric ratio of nitrogen from urea, initial NO was controlled by 2:1. Wendt *et al.* (2002) studied a pilot-scale SNCR-SCR hybrid process using NH_3 as agent, where the total agent was also injected into the SNCR inlet. These results were used to develop a combined SNCR-SCR model, which was extended to operational coal-fired utility boilers to explore the economic benefits of the combined SNCR-SCR process under certain conditions.

While some high-efficiency SCR technologies are under development, minus SNCR, to achieve the same NO reduction (Zhu *et al.*, 1999; Hsu and Teng, 2001), this study attempted to improve the NH_3 injection technique of a hybrid SNCR-SCR process. Through a bench-scale hybrid process, NH_3 was injected separately, a part from the SNCR inlet and a part from the SCR inlet, to react with NO in the flue gas. NO reduction and NH_3 slip of the different agent injection procedures were measured and compared. Moreover, the effects of operational conditions to the hybrid SNCR-SCR process such as the SNCR reaction temperature, the SCR reaction temperature, and the initial concentration ratio of NH_3 to NO were also investigated. The optimal operational conditions to reach higher NO reduction and lower NH_3 slip were also revealed by the experiment's results.

EXPERIMENT

APPARATUS

Figure 1 is a schematic diagram of the experimental apparatus. The apparatus is composed of high-pressure gases, flow rate controllers, SNCR furnace, SCR furnace, and the NO, NH_3 measuring instruments. Dry flue gas composed of 81% N_2 , 6% O_2 , 13% CO_2 was simulated by controlling the flow rates of the high-pressure gases. Furthermore, the initial concentrations of NO and NH_3 in the flue gas

were controlled by adjusting the flow rates of the mixed gases of NO/N₂ and NH₃/N₂. The main feature of this experiment was that NH₃ was designed to be added into the simulated flue gas separately, part from the inlet of SNCR and a part from the inlet of SCR. The calibration data of all the flow meters were supplied by the manufacturer. The scale of the flow meter was tuned accordingly, with the flow rate of each flow meter calculated by volume balances of the gases contained in the flue gas. A hollow quartz tube with a 1.5 cm inner diameter and 23 cm long was put in the SNCR furnace. Another quartz tube the same diameter and length, but with a catalyst bed, was added to the SCR furnace. The V₂O₅/TiO₂ monolithic catalyst 1.0 cm in diameter supplied by a domestic SCR company, as shown in Fig. 2, was lined in SCR quartz tube with a total length of 11.5 cm. A total flue-gas flow rate was fixed at 1,500 ml/min (1atm, 300 K). Based on the fixed gas flow rate and the operation temperatures of SNCR and SCR, the space velocities of SNCR were calculated to be 5,100-6,300 hr⁻¹ (for SNCR temperature of 700-850 °C) and the space velocities of SCR were calculated to be 7,100-10,000 hr⁻¹ (for SCR temperature 200-450 °C).

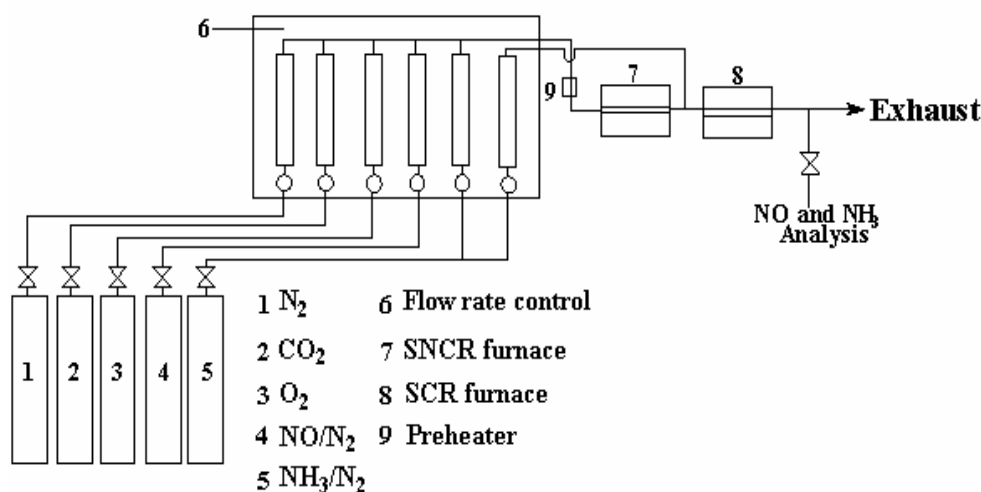


Figure 1. Schematic diagram of the experimental apparatus.

MEASUREMENT OF NO AND NH₃

The measuring point for NO and NH₃ was located at the SCR exhaust (Fig. 1). A Bacharach NONOXOR portable NO_x analyzer with the NO_x display range of 0-1,999 ppm, a resolution of 1 ppm, and the accuracy of ± 3 ppm was adopted for the NO measurement. The effects of NH₃ contamination in the simulated flue gas on the NO measured by the NO_x analyzer are shown in Fig. 3. It shows that the existence of NH₃ will not interfere with the NO measurement.

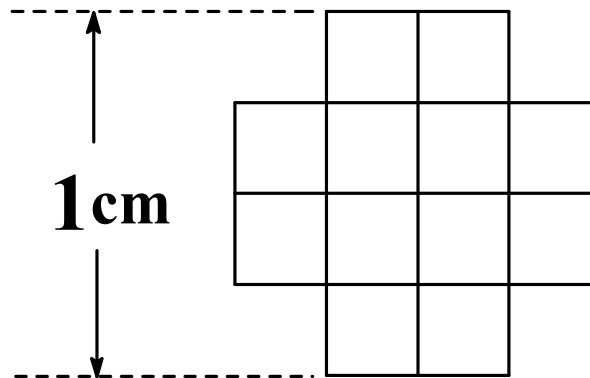


Figure 2. Cross section diagram of the SCR catalyst.

To measure the NH_3 in the flue gas, an electrical conductivity method was used. A sampling pump was employed to extract a fixed amount of flue gas (0.7 l/min), which was bubbling out and in contact with a fixed volume of distilled water (120 ml) in a sampling bottle for 10 min. After sampling, the water solution was taken from the sampling bottle and conductivity was measured. The concentration of NH_3 was then calculated by the following calibration equation:

$$C_{\text{NH}_3} = 4.20 \times (E_{\text{NH}_3} - E_{\text{H}_2\text{O}}) - 78.9 \quad (6)$$

$$C_{\text{NH}_3} = \text{NH}_3 \text{ concentration in the flue gas (ppm)}$$

$$E_{\text{NH}_3} - E_{\text{H}_2\text{O}} : \text{the solution electric conductivity differences after sampling and before sampling } (\mu\text{s/cm})$$

This equation was prepared by sampling flue gas with a known NH_3 concentration, following the same steps to measure the conductivity difference of the solution after and before sampling. The calibration diagram is shown in Fig. 4. It is suggested that the suitable application range of the NH_3 measurement is 0-400 ppm.

EXPERIMENTAL SCOPE

During the hybrid SNCR-SCR experiment, some of the reducing agent NH_3 was injected through the inlet for SNCR and some through the inlet for SCR. The NH_3 ratio was defined as the ratio of the percentages of ammonia injected from the inlet of SNCR to that injected from the inlet of SCR. The ratio values were controlled at 100:0, 66.6:33.4, or 50:50 for each set of experimental conditions. During the experiment, the initial NO concentration (*i.e.*, NO_i) was fixed at a value of 300 ppm in the simulated dry flue gas with 6% O_2 content, which is similar to the NO emissions of an industrial heavy oil-fired or

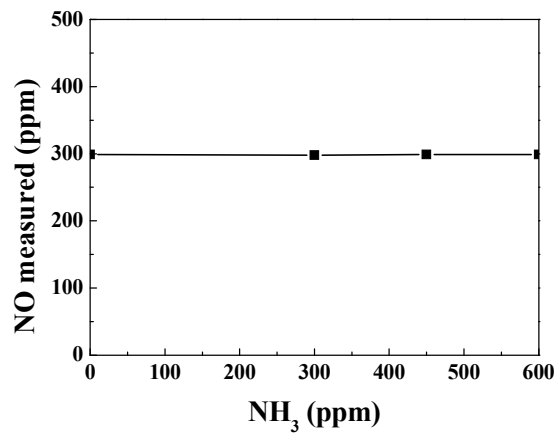


Figure 3. Effects of NH₃ contaminations in the simulated flue gas on NO measured value.

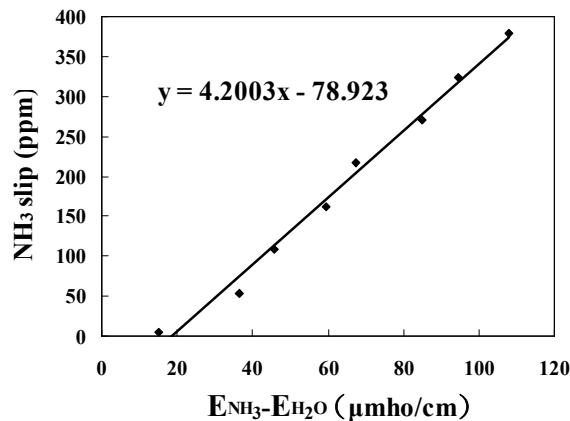


Figure 4. Calibrated relation between electric conductivity difference and NH₃ slip.

coal-fired boiler. Also, the total flow rate of the dry flue gas (*i.e.*, Q) was fixed at 1,500 ml/min (1 atm, 300K) and was preheated to 500°C before input into the SNCR furnace. Other experimental conditions include reaction temperature of SNCR (*i.e.*, SNCR temperature), reaction temperature of SCR (*i.e.*, SCR temperature), and stoichiometry ratio of initial total NH₃ to NO_x (*i.e.*, NH₃:NO). The ranges of all experimental conditions are summarized in Table 1.

RESULTS AND DISCUSSION

SCR REACTION ALONE

An SNCR reaction does not occur when set at a low temperature of 550°C. Figure 5 shows the effects of SCR temperature and a NH₃:NO ratio on NO reduction (*i.e.*, the percentage of NO reduced from NO_x)

of SCR reaction alone. NO reduction is increased as SCR temperature increases until an optimal temperature of 350°C is reached. Above 350°C, some NH₃ will decompose and cause the NO reduction to be lessened. In addition, optimal NO reduction occurs when NH₃:NO is at a 1:1 ratio. Furthermore, reduction improved from 77.5% at 1:1 to 85% 1.5:1. However, increasing NH₃:NO increases the unreacted NH₃ contained in the ventilated flue gas (*i.e.*, NH₃ slip) (Fig. 6). NH₃ slip increases from 11 ppm to 67 ppm when NH₃:NO increases from 1:1 to 1.5:1.

Table 1. The ranges of all experimental conditions.

Experimental Condition	Range
NO _i	300ppm (dry, 6% O ₂)
Q	1500 ml/min
NH ₃ Ratio	100:0, 66.6:33.4, or 50:50%
SNCR Temperature	550-900°C
SCR Temperature	200-450°C
NH ₃ : NO	1:1, 1.5:1, or 2:1

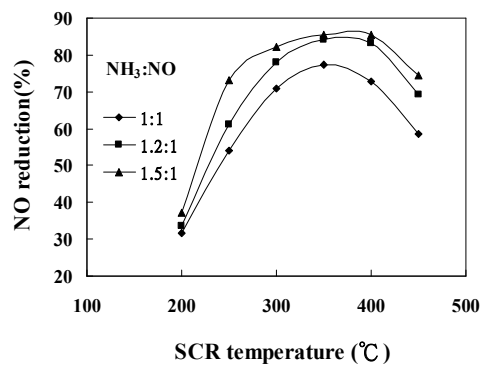


Figure 5. Effects of SCR temperature and NH₃:NO on NO reduction, SCR reaction alone.

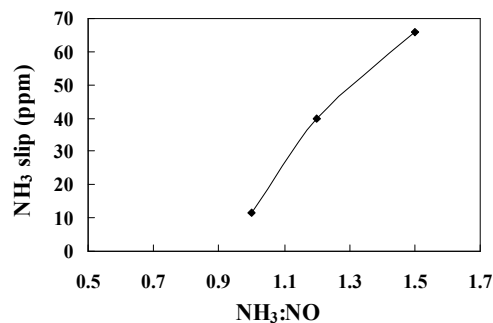


Figure 6. Effect of NH₃:NO on NH₃ slip, SCR reaction alone.

EFFECT OF SCR TEMPERATURE ON HYBRID SNCR-SCR

The effects of SCR temperature and NH_3 ratio on the hybrid SNCR-SCR process, at the SNCR temperature of 850°C and $\text{NH}_3:\text{NO}$ of 1:1 is shown in Fig. 7. This figure depicts the optimal operating temperature (with the maximum NO reduction) of SCR in the hybrid SNCR-SCR is the same as the SCR reaction alone; *i.e.*, 350°C . Figure 7 also shows that by reducing the NH_3 ratio (within range of NH_3 ratio shown in Table 1), part of the agent will input directly to SCR, avoiding the over consumption of NH_3 in SNCR, thus maximizing NO reduction. Comparing Fig. 7 with Fig. 5, the maximum NO reductions at the optimal SCR temperature of 350°C increases from 77.5% of the SCR reaction alone to 87% of the hybrid SNCR-SCR when the NH_3 ratio is 50:50. In addition, NH_3 slip is 11 ppm of SCR reaction alone comparing to 0 ppm of the hybrid SNCR-SCR, as indicated in Fig. 6 and Table 2.

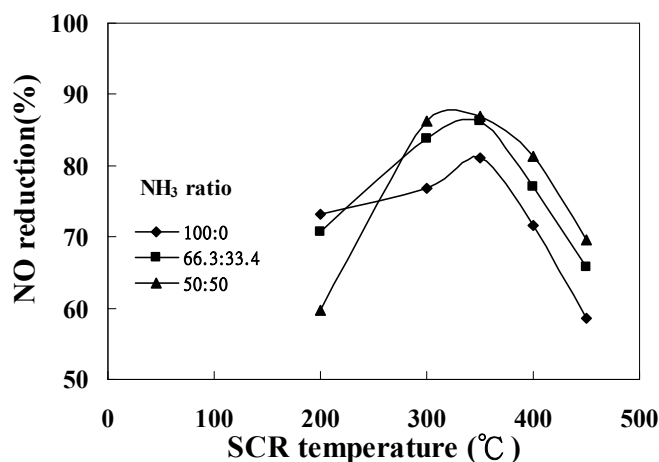


Figure 7. Effects of SCR temperature and NH_3 ratio on NO reduction: hybrid SNCR-SCR, $\text{NH}_3:\text{NO}=1:1$, SNCR = 850°C .

Table 2. The maximum NO reduction and NH_3 slip for the optimal SNCR temperature 850°C and SCR temperature 350°C .

Maximum NO Reduction (%) And NH_3 Slip (ppm)	Hybrid SNCR-SCR (NH_3 Ratio, %)			SCR Reaction Alone
	100:0	66.6:33.4	50:50	
$\text{NH}_3 : \text{NO}=1:1$	81% 0ppm	85% 0ppm	87% 0ppm	77.5% 11ppm
$\text{NH}_3 : \text{NO}=1.5:1$	88% 0ppm	89.5% 5ppm	91.5% 27ppm	85% 67ppm

EFFECT OF SNCR TEMPERATURE ON HYBRID SNCR-SCR

Figures 8-9 show the effects of SNCR temperature on NO reduction and NH₃ slip of hybrid SNCR-SCR process at the optimal SCR temperature 350 °C and NH₃:NO = 1.5:1.0. NO reduction begins to rise from the SNCR temperature of 750 °C to the maximum value when the SNCR temperature reaches 850 °C (Fig. 8). When the SNCR temperature is higher than 850 °C, the over consumption of NH₃ in the SNCR will happen. Without enough NH₃ in SCR the NO reduction decreases. The harmful effect of over consumption of NH₃ in SNCR on NO reduction can be improved by adjusting the NH₃ ratio. When the experimental range of NH₃ ratio is within 100:0 to 50:50, the maximum NO reduction increases from 88 to 92% when the NH₃ ratio reduces from 100:0 to 50:50 (Fig. 8). It is believed that an optimal NH₃ ratio exists for the hybrid SNCR-SCR, because when reducing NH₃ ratio to 0:100, the NO reductions of the hybrid SNCR-SCR will be the same as SCR reaction alone. The SNCR is unnecessary in such a condition. Figure 9 shows the effect of SNCR temperature on NH₃ slip of the hybrid SNCR-SCR. At a SCR temperature of 350 °C, NH₃:NO = 1.5:1.0, and SNCR temperature above 850 °C, NH₃ slip of hybrid SNCR-SCR is obviously lower than the SCR reaction alone (see Fig. 6).

EFFECT OF NH₃:NO ON HYBRID SNCR-SCR

The optimal SNCR temperature of 850 °C and SCR temperature of 350 °C, the effects of NH₃:NO on NO reduction, and NH₃ slip of the hybrid SNCR-SCR process are shown in Figs. 10-11. Figure 10 shows that NO reduction increases as the stoichiometry ratio NH₃:NO increases. This figure also demonstrates that when the ratio of NH₃:NO is higher than 1.5, the effect on NO reduction is insignificant. In Fig. 11 it can be seen that the NH₃ slip becomes serious when NH₃:NO is higher than 1.5. Therefore, it is not recommended to operate NH₃:NO any higher than 1.5 for the improved hybrid SNCR-SCR process.

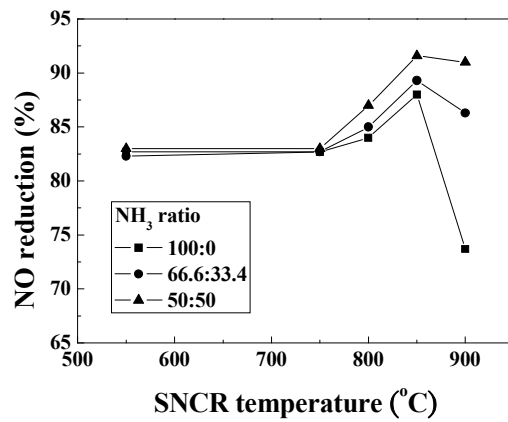


Figure 8. Effects of SNCR temperature and NH₃ ratio on NO reduction: hybrid SNCR-SCR, NH₃ : NO = 1.5:1, SCR = 350 °C.

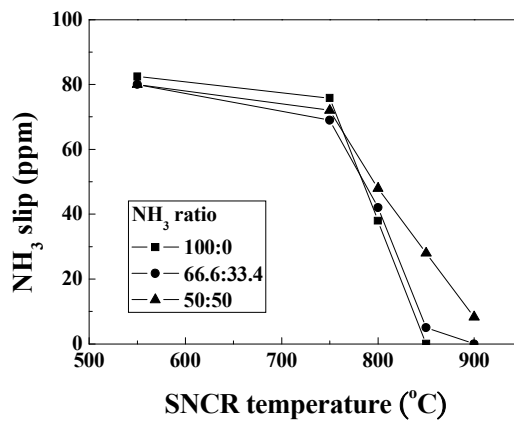


Figure 9. Effects of SNCR temperature and NH₃ ratio on NH₃ slip: hybrid SNCR-SCR, NH₃ : NO = 1.5:1, SCR = 350 °C.

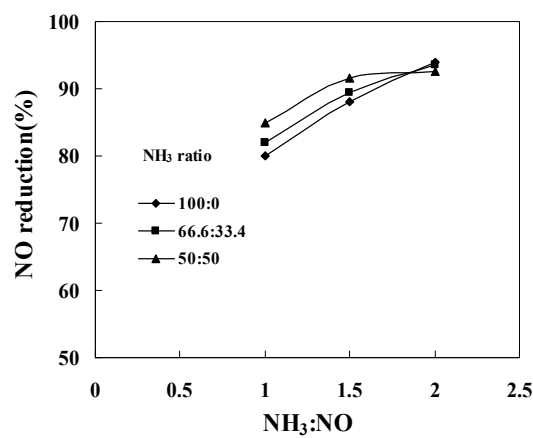


Figure 10. Effects of NH₃:NO and NH₃ ratio on NO reduction: hybrid SNCR-SCR, SNCR = 850 °C, SCR = 350 °C.

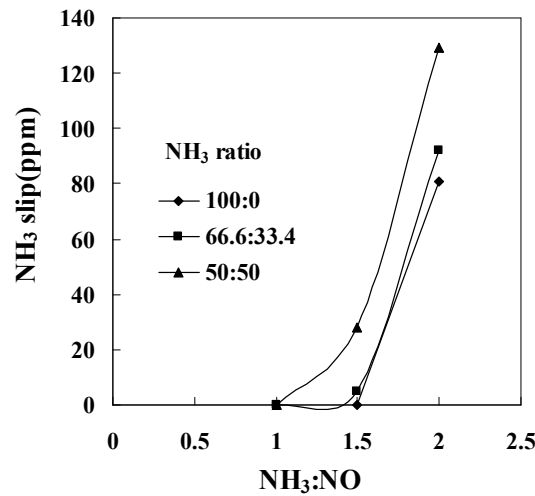


Figure 11. Effects of NH₃:NO and NH₃ ratio on NH₃ slip: hybrid SNCR-SCR, SNCR = 850 °C, SCR = 350 °C.

COMPARING NO REDUCTION AND NH₃ SLIP UNDER OPTIMAL TEMPERATURES

Maximum NO reductions are reached under the optimal SNCR and SCR temperatures with NH₃ slips for comparing the performance of hybrid SNCR-SCR and SCR reaction alone. Table 2 shows that the performance of hybrid SNCR-SCR is superior to that of the SCR reaction alone and NO reduction can be further improved for hybrid SNCR-SCR if NH₃ is injected partly from the inlet of SNCR and partly from the inlet of SCR.

A correlation equation of maximum NO reduction for hybrid SNCR-SCR from the experimental results of Table 2 is shown as:

$$R_{NO} = 81.5(R_{NH_3:NO})^{0.182}(R_{SNCR})^{-0.085} \quad (7)$$

where R_{NO} is maximum NO reduction (%), $R_{NH_3:NO}$ is NH₃:NO and R_{SNCR} is the ratio of NH₃ injected from the inlet of SNCR to the total NH₃ added to the hybrid SNCR-SCR. The comparison of the calculated R_{NO} from equation (7) and the measured R_{NO} from Table 2 for hybrid SNCR-SCR process is shown in Fig. 12. Figure 12 indicates that the calculated values from the correlation equation are qualitatively confirmed with the experimental results. The correlation equation identifies the conditions of SNCR temperature (850 °C), SCR temperature (350 °C), NH₃:NO = 1:1-1.5:1, and R_{SNCR} = 0.5-1.0. It is suggested to apply equation (7) within the identified conditions to avoid the misguided error for R_{NO} calculations.

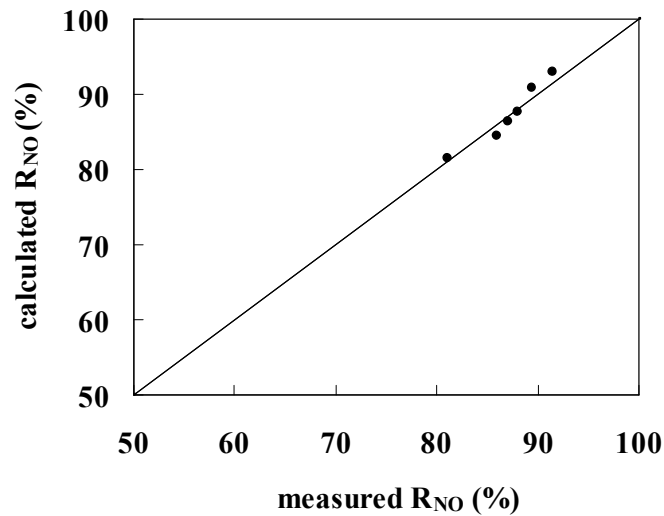


Figure 12. Comparison of the calculated and the measured maximum NO reductions for hybrid SNCR-SCR, SNCR = 850°C, SCR = 350°C.

CONCLUSIONS

The performance of the hybrid SNCR-SCR process has been improved by adding a controlled-parameter NH₃ ratio; *i.e.*, instead of injecting the total NH₃ through the SNCR inlet, NH₃ was injected partly during SNCR and partly during SCR. The experiment on the improved hybrid SNCR-SCR process was carried out using a bench-scale apparatus. The experimental results indicate that in order to reach the maximum NO reduction the optimal temperatures for SNCR is 850°C and for SCR it is 350°C. It is recommended that the values of NH₃:NO in the range of 1-1.5 for the improved hybrid process to avoid any serious NH₃ slip. The performances of the maximum NO reduction increase with reducing the NH₃ ratio, and the NH₃ slip is still superior to SCR reaction alone, as shown in Table 2. Also, the correlation equation of the maximum NO reduction for the hybrid SNCR-SCR process is developed and well-fitted with the experiment results.

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