

NO_x REDUCTION BY SNCR AND ITS REACTION MECHANISM UNDER OXIDIZING DIESEL FLUE GAS CONDITIONS

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Abstract : Direct injections of NH₃/urea into a simulated cylinder were performed for oxidizing diesel NO_x reduction where a diesel fuelled combustion-driven flow reactor was designed with the aim of simulating diesel engine geometry, aerodynamics and combustion products. NO_x reduction tests were carried out over a wide range of air/fuel ratios (A/F = 20~40) using an initial NO_x level of 530 ppm and for molar ratios (β = NH₃/NO_x) or normalized stoichiometric ratios (NSR = NH₃/NO_x for urea) of 0.5~2.0.

The results show that effective NO_x reduction with NH₃/urea occurred over an injection temperature range of 1,100~1,400 K in which the temperature window of urea was wider and shifted upward. NO_x reduction increased with increasing molar ratios, and about a 15~40% reduction of NO_x was achieved at optimum conditions. The effects of engine and exhaust parts on NO_x reduction potential are discussed following temperature profiles, and together with comparisons of urea with NH₃ DeNO_x characteristics. Through sensitivity and rate-of-production analyses, a reduced reaction mechanism for N/H/O species is suggested as a basic model of the SNCR process. Thus, key and detailed reaction paths are analyzed, understood for NO_x reduction and NH₃ oxidation. Validity and reliability of this model are further discussed.

Key Words : diesel NO_x, NO_x reduction, reaction mechanism, SNCR

INTRODUCTION

NO_x emissions from mobile and stationary sources such as transport vehicles, ferries, industrial boilers, and power plants have been a growing concern for several decades because of environmentally harmful impacts on global system. Particularly, in case of lean-burn and diesel engines, the reduction of diesel NO_x emissions has become a top priority of environmental research and engineering societies, since typical noble metal three-way catalysts show little

activity towards NO_x reduction under such oxidizing exhaust gas conditions.¹⁾ Over the last decade, the majority of diesel NO_x reduction studies have focused on the selective catalytic reduction (SCR) process by NH₃/urea and hydrocarbons agents (i.e. on the search for new catalysts with higher activity), together with recent plasma-catalytic processes, but some practical problems have still emerged.²⁻⁴⁾

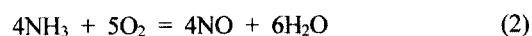
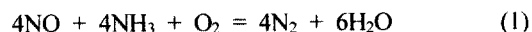
Alternatively, the gas-phase selective noncatalytic reduction (SNCR) technologies (thermal DeNO_x and NO_xOUT processes) using NH₃/urea are considered for the present diesel NO_x reduction. The SNCR process has been known as a widespread NO_x control technology mostly for stationary power plants, incinerators and

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industrial boilers.⁵⁻⁷⁾ Lyon⁵⁾ originally found that NO can be selectively reduced by the injection of N-containing compounds in the presence of oxygen without a catalyst over the high temperature range from 1,100~1,400 K. Despite the complex chain reactions involved, the reaction characteristics of this process can be explained by two overall reactions as follows;



Within the above temperature window, NO reduction occurs, mainly following the reaction of NO with NH₃ under excess oxygen conditions through reaction (1). But beyond ~1,400K, NH₃ oxidation to produce NO rather becomes dominant by reaction (2). Main drawback of this process is a narrow temperature window where many reaction parameters such as temperature, molar ratio (NH₃/NO_x), residence time, oxygen level and initial NO_x are simultaneously involved to affect the NO_x reduction potential, proved by extensive experimental observations and kinetic calculations.⁷⁻¹⁰⁾ However, only a few investigations^{11,14)} have been applied to diesel engines, based on this SNCR concept. Practically, diesel engine environments have high gas quenching rates ($dT/dt = 5,000\sim 8,000$ K/sec) from the cylinder to the exhaust pipe, relatively high CO/unreacted hydrocarbons (UHC) and a wide range of oxygen levels and short residence times, which are all different from those in stationary sources (including reactor geometries). Even, finding the proper injection timing (crank angle; CA) of the reducing agents into the actual cylinder is absolutely required for proper reaction temperatures, which could be rather a difficult task, compared with large-scale power plants. These have been all practical limitations of SNCR applications to diesel engine conditions. Nevertheless, Nam and Gibbs^{13,14)} tried to investigate systematically the application of SNCR for DeNO_x of diesel engines through direct injections of NH₃/urea into a simulated

cylinder and also performed chemical kinetic calculations under practical nonisothermal conditions for comparisons of experimental phenomena. Presently, some of experimental results are further reported, and the understanding of complex nitrogen chemistry is discussed by composing the reduced reaction model. In addition, comparisons of NH₃ with urea DeNO_x characteristics are also provided under these conditions.

EXPERIMENTAL

To conduct diesel DeNO_x experiments, a diesel-fueled, combustion-driven flow reactor was designed with the aim of simulating as close as possible, gas compositions and temperatures, gas cooling rates (quenching rates), residence times and aerodynamics of a diesel engine cylinder and exhaust. The system design, previously described in detail by Nam and Gibbs,¹⁴⁾ was based on a Perkins 4.236 single cylinder diesel engine (966 cm³ capacity). The flow reactor consisted of a combustor, fired on diesel fuel and utilizing preheated combustion air, a water-cooled section, a stainless steel tube of 76 mm ID and 213 mm long, simulating the cylinder which is bolted onto an engine cylinder head/exhaust manifold (cut from a real engine) and finally an exhaust pipe of 2 m long tube (40 mm ID). The airflow was kept constant at 1,000 L/min, and fuel flow rates normally varied in the range of 0.0832~0.0368 L/min (69~30 (g/min)) that are equivalent to air/fuel ratios (AF) of 20~45 ($\phi = 0.72\sim 0.32$), close to actual diesel operating conditions. Very efficient and reproducible combustion of air/fuel mixtures was achieved in the combustion section under fuel-lean oxidizing conditions. Thus, the residence time inside the simulated cylinder reached about 20 msec at a typical air/fuel ratio of 27.5. Primary reductant (NH₃/urea) was directly injected into the simulated cylinder whilst secondary hydrocarbon additives could be injected into the exhaust pipe. Gas temperatures in the simulated cylinder were finely controlled according to the air/fuel ratios (flow #; A, B, 1-6, as in

Figure 2) and typically maintained in the range of 1,000–1,400 K with oxygen levels varying from 6.6–12.8%. DeNOx reactions proceed mainly in the simulated cylinder where large quenching rates (~7,880 K/sec) were achieved because of water and natural cooling. Additional NOx reduction can also take place in the cylinder head and exhaust pipe section, despite low temperature levels. In fuel-lean, diesel combustion conditions, the emission levels of CO and UHC were relatively low at the end of exhaust pipe, maintaining less than 150 and 10 ppm, respectively, except for low combustion temperature of flow #5, #6. NOx levels produced by the atmospheric pressure combustion were also < 120 ppm, so NH₃ doping of the combustion air was adopted to produce proper initial NOx levels (500–950 ppm) for experiments. For the concentration measurements of various exhaust gases (NOx, N₂O, CO/CO₂, O₂, and UHC), the on-line gas analyzing systems were directly connected into the combustion rig, and operated simultaneously. Detailed descriptions for the emission levels and other analyzing systems including NH₃ can be found in the previous paper, including the above experiments.¹⁴⁾

On the other hand, a possible diagram of the actual engine cylinder complete with a reductant injector can be described as in Figure 1. The

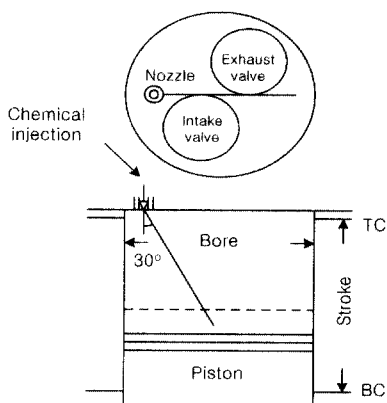


Figure 1. A possible schematic of injection direction of reductants at actual diesel engine cylinder; TC = top center, BC = bottom center).

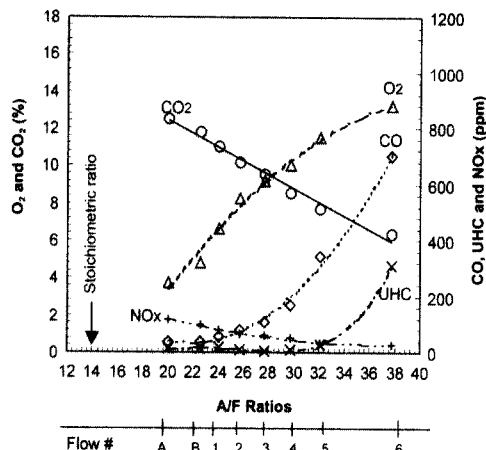


Figure 2. Combustion products emitted from the flow reactor over the range of air fuel/ ratios utilized in the SNCR tests.

main chamber should have an additional nozzle for reductant and also indicates its injection direction. In actual diesel engines, the key different parameters are temperature timing for injection of reductants and pressure ranges. The temperatures within actual engine cylinders at 40–50° CA ATDC (Crank angle, after top dead center) range from approximately 1,700–2,000 K, depending on the power outputs.¹⁵⁾ However, at around 70–90° CA ATDC, the temperatures are typically within 1,100–1,600 K at an equivalence ratio of 0.6, which would be close to the latter half of the expansion stroke, and satisfy the optimum temperature windows for diesel DeNOx reactions. Concerning the pressure effect conducted with an actual diesel engine (bore-stroke of 96 mm × 110 mm),¹¹⁾ the injection timing of about 90° CA ATDC was found to be an optimum range, where the pressure of several atmospheres would also be involved. Recent experimental and theoretical studies of pressure effects (1–10 bar) on the SNCR process indicated only minor variations of NOx reduction and temperature window under excess oxygen levels,¹⁶⁾ which provide the present experimental results with sufficient reliability and validity, compared with those obtained under actual engines.

RESULTS AND DISCUSSION

Temperature Window

In the SNCR process, temperature characteristic is the most important parameter, whether under isothermal or nonisothermal conditions. Figure 3 shows the effects of reaction temperature and molar ratio on NO_x reduction with an initial NO_x level of 530 ppm in which oxygen levels varied from 6.6 to 12.8% according to the air/fuel ratios. The curves show temperature windows based on injection temperatures, formed between 1,100~1,300 K, and about 15~40% NO_x reduction occurred as molar ratio was changed from 0.5 to 2.0 at the optimum condition flow #3 ($T_{in} = \sim 1,240$ K) and $\sim 9.2\%$ O₂. With $\beta = 1.5$, about 34% maximum reduction of NO_x was achieved at the same flow #3. NO_x reduction continues to develop up to the lowest temperature flow #6 (O₂ = 12.8%) by which NO_x reduction tends to decrease with decreasing injection temperatures, and is less dependent on the increase of molar ratio. However, increase beyond the optimum temperature causes NO_x reduction to be increasingly less effective. Nevertheless, the extent of NO_x reduction, as molar ratio increases at the higher temperatures, is much better than at the lower temperatures.

These experimental data are qualitatively in good agreement with those in the literature^{17,18)}

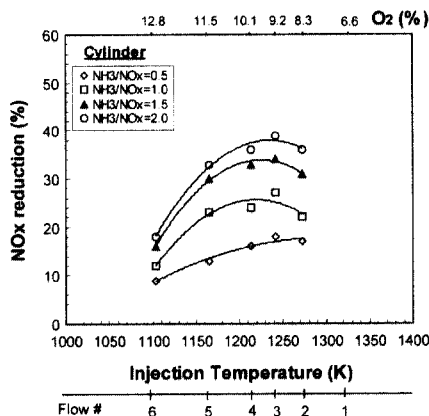


Figure 3. Temperature characteristics of NO_x reductions with varying molar ratios into the cylinder.

in the aspect of temperature window where optimum temperatures were usually centered at around 1,220 K (± 100 K). However, quantitatively about 70~95% NO_x reductions were easily reported with the similar range of molar ratios ($\beta = 1\sim 2.0$), which is compared with present low NO_x reductions (30~40%), and explained by the following different conditions. First of all, higher quenching rates of engine conditions ($-5,800 \sim -8,000$ K/sec) are surely detrimental for higher NO_x reduction, compared with $-200 \sim -290$ K/sec under boiler furnace conditions. Ostberg et al.¹⁹⁾ reported that when the axial temperature gradient was $-1,000$ K/sec in SNCR experiments in a plug flow reactor, it had a significant impact on the temperature window (i.e. shifting it upwards) and also on NO_x reduction (i.e. towards decreasing). Furthermore, higher CO/UHC levels (2,000/400 ppms) inside the simulated cylinder could also cause a decrease in NO_x reduction. In the SNCR process, injecting secondary additives (HC/NO_x = 50~100 ppm) such as CO and hydrocarbons can shift temperature window downwards by 100~150 K, but slightly affect NO_x reduction potential and emission levels in case of too much chemicals. Varying the oxygen concentration between 3 and 5%, known as an optimum range, has little influence on the NH₃ DeNO_x process, but a further increase over 10% transforms not only the shape of temperature windows wide, but slightly diminishes the degree of NO_x reduction. Consequently, diesel environments such as large temperature drops and higher CO/UHC levels throughout the combustion line could be the biggest challenge to the application of SNCR process, but a wide range of oxygen levels (6.0~13%) are less influential.

Role of Cylinder and Exhaust Pipe

Figure 4 shows the NO_x reduction and CO/UHC oxidation behaviors at a molar ratio of 1.5, as well as the temperature profile along the reactor positions (residence times) at optimum flow #3 ($T_{in} = 1,243$ K, O₂ = 9.2%). As expected,

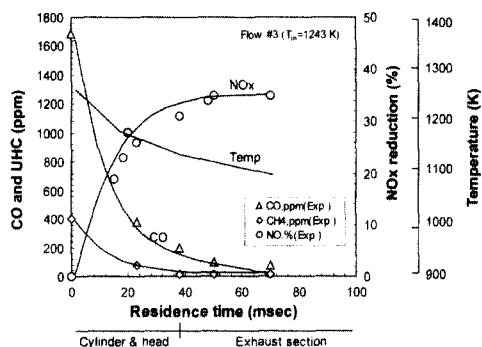


Figure 4. Effects of residence time and gas temperature on NOx reduction at the optimum flow #3; NOx = 530 ppm, NH₃/NOx = 1.5.

most of the NOx reduction occurs within the simulated cylinder and head section (residence time < 40 msec), and the rest of the NOx reduction takes place in the exhaust pipe (1/3 of total), reaching a maximum of around 34%. The temperature profile for flow #3 not only indicates good agreement with NOx reduction and CO/UHC oxidation profiles, but also shows that exhaust temperatures are too low for further NOx reduction. In other words, NOx reduction seems to be related to both temperature and CO/UHC oxidation profiles, since they simultaneously occur in the higher temperature cylinder section. One interesting feature is that the existence of CO/UHC species accelerates the rate of NOx reduction, but too higher concentrations decrease the selectivity for NH₃ with NOx, resulting in overall lower NOx reduction.¹⁴⁾ Nevertheless, accelerating the NOx reduction rate to within 40~60 msec has practically significant implications, since in previous experiment²⁰⁾ the NOx reduction time required was at least 200 msec to obtain enough NOx reduction in isothermal and CO/hydrocarbon-free conditions. Utility boilers usually provide sufficient space (residence time ≈ 1 sec) and locations (near superheater) for optimum temperature where the flue gas passes, so enough NOx reduction can be obtained. In gas turbines, however, very short residence time (~5 msec) and slightly higher gas temperatures > 1,400 K are

maintained, even with high-pressure environments, despite significant NOx emissions. Thus, the application of the SNCR process to gas turbine and engine systems might be achieved in some ways and could be another research field if the acceleration of the NOx reduction rate is possible up to < 40 msec.

Urea and NH₃ DeNOx Characteristics

Despite a different decomposition mechanism for NH₃ compared to urea, most of the NOx reduction features have been found to be similar as deduced from comparative tests carried out for cylinder injections. However, several differences were noticed. Figure 5 shows comparisons of NOx reduction efficiencies and N₂O emission levels between urea and NH₃ at the same NSR of 1.5. Three facts emerged as follows;

- With urea, the temperature window is wide and shifted upwards (50 K).
- At higher oxygen levels (10% or higher), urea produces a better performance.
- N₂O emission from urea injection is significant.

The temperature window for urea DeNOx was shifted upwards about 50 K and was much broader, compared with NH₃. The influence of oxygen levels (6.6~12.8%) for both reductants was also compared. It shows that urea achieved about 6% more NOx reduction than NH₃ at

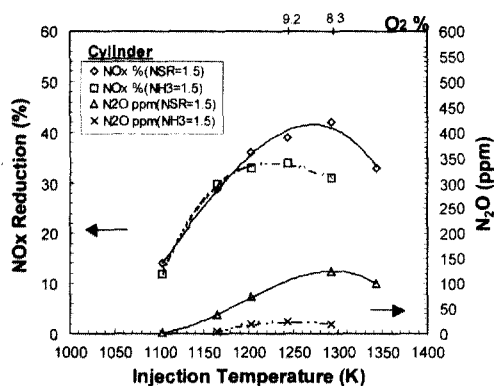


Figure 5. Comparisons of NOx reductions and N₂O emissions between urea and NH₃; 530 ppm NOx, NSR = 1.5.

Table 1. N₂O emissions from urea injection in SNCR process.

Urea NSR	NO _{x,i} (ppm)	ΔN ₂ O* (ppm)	N ₂ O _{urea} at 70 ppm NO _x (ppm)	$\frac{\Delta N_2O}{\Delta NO_{x, reduced}}$	$\frac{N_2O_{urea}}{N_2O_{total}}$
0	530	-	-	-	-
1.5	328	40	80	19%	67%
2	297	40	90	17%	69%
4	190	110	175	32%	61%
6	185	90	240	26%	73%
8	149	80	280	21%	78%
10	149	70	290	18%	81%

*ΔN₂O = [total N₂O-N₂O formed by urea itself]

NSR = 1.5 and optimum flows. This means that urea performance is not limited by high oxygen levels which can even enhance NO_x reduction by a small amount, while higher oxygen levels (usually > 7%) slightly become detrimental for NH₃ performance, as discussed above.

N₂O emissions from urea injection were substantial, and the location of N₂O formation curve virtually coincided with the temperature window for NO_x reduction.¹³⁾ The N₂O emission levels were about five times higher than for NH₃ (typically ~ 20 ppm) because there was insufficient N₂O decomposition in the exhaust due to low temperatures. Table 1 shows a more quantitative explanation of N₂O formation. Over NSR = 0.5~10, around 17~32% of the NO_x reduced was converted to N₂O, which are in good agreement with the previous values of 15~34%.^{17,18)} Increasing the amount of urea caused the N₂O level to increase up to a value of 360 ppm at NSR = 10 and 530 ppm initial NO_x. Even at 70 ppm initial NO_x, the N₂O level still reached 290 ppm for the same amount of urea injection, despite no NO_x reduction. Therefore, the ratio of N₂O generated from urea itself to the total N₂O reached 61~81%, and tends to increase with increasing NSR values. This means that urea itself significantly contributes to N₂O formation, especially for systems with high gas quenching rates.

SNCR Reaction Mechanism

Kinetic studies governing NO reduction in

NO/NH₃/O₂ combustion gas mixtures can be a significant aid in understanding and analyzing the experimental phenomena of the SNCR process. The detailed kinetic mechanisms^{8,9,21)} have been previously developed, but mostly for power plant conditions (1~5% O₂, negligible CO/UHC), among which Miller and Bowman (MB) model⁹⁾ provided fairly reasonable understanding for experimental features of SNCR process.

Under the present diesel combustion conditions, kinetic modeling work has been reported, based on the MB mechanism (73 N/H/O reactions + 161 C/H/O reactions = 234 reactions) where only two rate constants of NH₂ + NO = products channels (R22 and R23 below) were changed.¹⁴⁾ The calculations, conducted by gas-phase chemical kinetics codes, CHEMKIN and SENKIN,^{22,23)} well represented the experimental phenomena as regards temperature characteristics, residence time, molar ratio, NH₃ slip, and specified each reaction's role and CO/UHC effects.¹⁴⁾ On the other hand, the sensitivity analyses revealed that many reactions from the MB model's 73 N/H/O reactions still remained insensitive to NO reduction and the whole reaction scheme, so called "redundant reactions exist". Thus, the reduced reaction mechanism (Table 2) was derived from the MB mechanism through sensitivity and rate-of-production analyses, which were performed by the postprocessor, KINALC code.²⁴⁾ The concentration sensitivity analysis was proceeded by investigating the normalized sensitivity coefficients (S) below, within the temperature window centered to 1,263 K (±100) in the presence of water vapor and excess oxygen conditions and following similar temperature profiles as those in the present reactor.

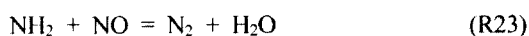
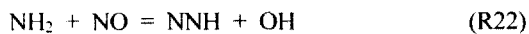
$$S = \frac{\ln C_k}{\ln k_i} \quad (3)$$

where C_k is the concentration of the kth species and k_i is the rate coefficient of the ith reaction. The rate-of-production analysis is based on the differences between the forward and

Table 2. A reduced mechanism for the SNCR process; rate constants in form $k_f = A \cdot T^{(n)} \cdot \exp(-E/RT)$. Units are $A = (\text{cm}^3/\text{mole} \cdot \text{sec})$, $T = \text{K}$, and $E = (\text{cal}/\text{mole})$.

Reaction	A	n	E
1. $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$	1.17E09	1.30	3,626
2. $\text{O} + \text{OH} = \text{O}_2 + \text{H}$	4.00E14	-0.50	0
3. $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$	3.61E17	-0.72	0
Enhanced third-body efficiencies(M): $\text{H}_2\text{O} = 10.0, \text{H}_2 = 2.9, \text{N}_2 = 1.3$			
4. $\text{H} + \text{HO}_2 = 2\text{OH}$	1.40E14	0.00	1,073
5. $\text{O} + \text{HO}_2 = \text{O}_2 + \text{OH}$	1.40E13	0.00	1,073
6. $2\text{OH} = \text{H}_2\text{O} + \text{O}$	6.00E08	1.30	0
7. $2\text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	2.00E12	0.00	0
8. $\text{H}_2\text{O}_2 + \text{M} = 2\text{OH} + \text{M}$	1.30E17	0.00	45,500
9. $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	1.00E13	0.00	1,800
10. $\text{NH} + \text{O}_2 = \text{HNO} + \text{O}$	1.00E13	0.00	12,000
11. $\text{NH} + \text{O}_2 = \text{NO} + \text{OH}$	7.60E10	0.00	1,530
12. $\text{NH} + \text{OH} = \text{HNO} + \text{H}$	2.00E13	0.00	0
13. $\text{NH} + \text{NO} = \text{N}_2\text{O} + \text{H}$	2.40E15	-0.80	0
14. $\text{N}_2\text{O} + \text{H} = \text{N}_2 + \text{OH}$	7.60E13	0.00	15,200
15. $\text{N}_2\text{O} + \text{M} = \text{N}_2 + \text{O} + \text{M}$	6.95E14	0.00	56,530
Enhanced third-body efficiencies: $\text{N}_2 = 1.5, \text{O}_2 = 1.5, \text{H}_2\text{O} = 5.0$			
16. $\text{N}_2\text{O} + \text{OH} = \text{N}_2 + \text{HO}_2$	2.00E12	0.00	10,000
17. $\text{NH}_2 + \text{H} = \text{NH} + \text{H}_2$	6.92E13	0.00	3,650
18. $\text{NH}_2 + \text{O} = \text{HNO} + \text{H}$	6.63E14	-0.50	0
19. $\text{NH}_2 + \text{O} = \text{NH} + \text{OH}$	1.99E13	0.00	993
20. $\text{NH}_2 + \text{OH} = \text{NH} + \text{H}_2\text{O}$	4.00E06	2.00	1,000
21. $\text{NH}_2 + \text{O}_2 = \text{HNO} + \text{OH}$	4.50E12	0.00	25,000
22. $\text{NH}_2 + \text{NO} = \text{NNH} + \text{OH}$	1.51E13	-0.48	0
23. $\text{NH}_2 + \text{NO} = \text{N}_2 + \text{H}_2\text{O}$	1.17E16	-1.24	0
24. $\text{NH}_3 + \text{OH} = \text{NH}_2 + \text{H}_2\text{O}$	1.76E12	0.00	1,710
25. $\text{NH}_3 + \text{O} = \text{NH}_2 + \text{OH}$	2.10E13	0.00	9,000
26. $\text{NH}_3 + \text{H} = \text{NH}_2 + \text{H}_2$	6.36E05	2.39	10,171
27. $\text{NNH} = \text{N}_2 + \text{H}$	1.00E04	0.00	0
28. $\text{NNH} + \text{NO} = \text{N}_2 + \text{HNO}$	1.20E06	2.00	-1,192
29. $\text{NNH} + \text{OH} = \text{N}_2 + \text{H}_2\text{O}$	5.00E13	0.00	0
30. $\text{NNH} + \text{NH}_2 = \text{N}_2 + \text{NH}_3$	9.20E05	1.90	-1,152
31. $\text{NNH} + \text{O} = \text{N}_2\text{O} + \text{H}$	1.00E14	0	0
32. $\text{HNO} + \text{M} = \text{H} + \text{NO} + \text{M}$	1.50E16	0.00	48,680
Enhanced third-body efficiencies: $\text{H}_2\text{O} = 10.0, \text{O}_2 = 2.0, \text{N}_2 = 2.0, \text{H}_2 = 2.0$			
33. $\text{HNO} + \text{OH} = \text{NO} + \text{H}_2\text{O}$	1.30E07	1.90	-953
34. $\text{HNO} + \text{NH}_2 = \text{NH}_3 + \text{NO}$	2.00E13	0.00	1,000
35. $\text{HNO} + \text{O} = \text{OH} + \text{NO}$	1.00E13	0	0
36. $\text{HO}_2 + \text{NO} = \text{NO}_2 + \text{OH}$	3.38E12	0.00	-198
37. $\text{NO}_2 + \text{H} = \text{NO} + \text{OH}$	3.50E14	0.00	1,500
38. $\text{HO}_2 + \text{NH}_3 = \text{NH}_2 + \text{H}_2\text{O}_2$	3.00E11	0	22,000
39. $\text{HNO} + \text{O}_2 = \text{HO}_2 + \text{NO}$	1.00E13	0.00	25,000
40. $\text{NO}_2 + \text{M} = \text{NO} + \text{O} + \text{M}$	7.00E14	0	53,000
Enhanced third-body efficiencies: $\text{N}_2 = 1.5, \text{H}_2\text{O} = 10.0$			
41. $\text{NO}_2 + \text{O} = \text{NO} + \text{O}_2$	1.00E13	0.00	596
42. $\text{NO} + \text{OH} (+ \text{M}) = \text{HONO} (+ \text{M})$	2.20E12	-0.1	-721
Enhanced third-body efficiencies: $\text{N}_2 = 1.0, \text{H}_2\text{O} = 5.0$			
43. $\text{HONO} + \text{H} = \text{NO}_2 + \text{H}_2$	1.20E13	0	7,350
44. $\text{HONO} + \text{O} = \text{NO}_2 + \text{OH}$	1.20E13	0	6,000
45. $\text{HONO} + \text{OH} = \text{NO}_2 + \text{H}_2\text{O}$	1.30E10	1.0	135

reverse rates of the reactions (i.e. $\Delta F_{ik} = \bar{F}^2 - \bar{F}$). The reduced mechanism obtained through these analyses consists of 45 elementary reactions with 18 species for N/H/O species. As a consequence, the first 35 reactions were based on the MB mechanism describing NO reductions and NH₃ oxidation, together with N₂O reactions for the N/H/O species. The reactions (R36 to R45) from Glarborg model,²¹⁾ which were sensitive under the low temperature and nonisothermal conditions, were especially added to represent NO₂-consuming and producing reactions. The important reactions (R25 and R26) were also included to reduce the degree of error and better account for excess NH₃ injection. In fuel-lean conditions, NH₃ is mostly initiated by NH₃+OH = NH₂+H₂O (R24), but the rate constant was changed from MB's one to a lower value, obtained from Silver and Kolb.²⁵⁾ The key reactions in the SNCR process are known as two product channels (R22 and R23) of NO+NH₂ reaction, a chain branching and a terminating respectively, as follows;



The chain branching ratio ($\alpha = k_{22}/(k_{22}+k_{23})$) and even its magnitude between two product channels tend to strongly affect NO reduction features such as reduction potential and temperature window. Considering the present gas quenching rates and a wide range of oxygen levels, two rate constants for the present calculations were replaced by the values from Glarborg model,²¹⁾ because of temperature dependence. Although many more recent rate constants²⁶⁾ are available, most rate constants remained unchanged from the original reaction mechanism, unless those are independent of temperature. The reaction scheme can be summarized by the above rate-of-production analysis as in Figure 6. This result provides information concerning the reaction paths. In the lower temperature range (1,100 ~1,250 K), NO effectively reacts with NH₂

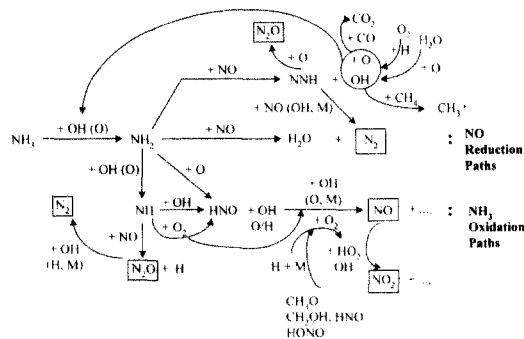


Figure 6. Reaction scheme for NO reduction and NH₃ oxidation paths presented in Table 2, with the effects of CO and hydrocarbons.

intermediate (amidogen) by reactions (R22, R23) and further chain reactions, leading to proper NO reduction paths. Meanwhile, over the high temperatures (> 1,250 K), NH₂ radicals rather react with active oxidants (O, OH) than NO to produce NH_i and HNO species, which further oxidize and decompose to produce NO, following so called NH₃ oxidation paths. So the competition and balance between NO reduction and NH₃ oxidation is maintained throughout as a function of temperature, forming the bell-shaped temperature windows as in experimental results.

Eventually, comparisons of the reduced (45 reactions) with the MB mechanism (73 reactions) show little difference in NO reduction features if the same rate constants of R22 and R23 are involved, which implies that the most important reactions for N/H/O species were effectively included in this reduced mechanism. Since diesel combustion products include various CO/UHC levels, this mechanism can be combined with C₁-, C₂-hydrocarbon reactions to account for their oxidation effects. Consequently, this reduced mechanism can be used as a useful and basic SNCR model with validity and reliability, particularly for nonisothermal combustion facilities.

CONCLUSIONS

Diesel NO_x reduction experiments were conducted using the SNCR process in a com-

bustion-driven stainless steel flow reactor, which closely simulated the actual cylinder and head, exhaust pipe and combustion products. About 15~40% NOx reduction was possible with the molar ratio from 0.5~2.0 at the optimum conditions where with a molar ratio of 1.5, about 34% reduction was achieved. The major parts for NOx reduction were the high temperature cylinder and head section, while exhaust temperatures were too low for further reduction. Urea DeNOx performance was better than that of NH₃ especially at higher oxygen levels, whereas a substantial amount of N₂O (> 110 ppm) was emitted with urea injection.

The reduced SNCR mechanism was effectively set up through sensitivity and rate-of-production analyses for N/H/O species, by which key reaction paths were easily analyzed and a better understanding achieved for the whole NOx reduction and NH₃ oxidation paths. Little difference in calculations between this reduced and MB model provide fairly reasonable validity and reliability. The SNCR application to diesel engine DeNOx has significant practical implications, and is worth comparing with other catalytic processes, and also applying to gas turbine system.

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