

ORIGINAL ARTICLE

Effect of Hydrocarbon Additives on SNCR DeNO_x Characteristics under Oxidizing Diesel Exhaust Gas Conditions

Changmo Nam*

Division of Health and Science, Yeungnam University College, Daegu 42415, Korea

Abstract

DeNO_x experiments for the effects of hydrocarbon additives on diesel SNCR process were conducted under oxidizing diesel exhaust conditions. A diesel-fueled combustion system was set up to simulate the actual cylinder and head, exhaust pipe and combustion products, where the reducing agent NH₃ and C₂H₆/diesel fuel additives were separately or simultaneously injected into the exhaust pipe, used as the SNCR flow reactor. A wide range of air/fuel ratios (A/F=20~40) were maintained, based on engine speeds where an initial NO_x level was 530 ppm and the molar ratios (β =NH₃/NO_x) ranged between 1.0~2.0, together with adjusting the amounts of hydrocarbon additives. Temperature windows were normally formed in the range of 1200~1350K, which were shifted downwards by 50~100K with injecting C₂H₆/diesel fuel additives. About 50~68% NO_x reduction was possible with the above molar ratios (β) at the optimum flow #1 (T_{in}=1260K). Injecting a small amount of C₂H₆ or diesel fuel (γ =hydrocarbon/NO_x) gave the promising results, particularly in the lower exhaust temperatures, by contributing to the sufficient production of active radicals (OH/O₂/HO₂/H) for NO_x reduction. Unfortunately, the addition of hydrocarbons increased the concentrations of byproducts such as CO, UHC, N₂O and NO₂, and their emission levels are discussed. Among them, Injecting diesel fuel together with the primary reductant seems to be more encouraging for practical reason and could be suggested as an alternative SNCR DeNO_x strategy under diesel exhaust systems, following further optimization of chemicals used for lower emission levels of byproducts.

Key words : Diesel SNCR, DeNO_x, NO_x Reduction, Hydrocarbon additive, Oxidizing exhaust gas

1. Introduction

Recently, more NO_x emissions from diesel engines made by a major commercial car company have been a great issue worldwide during all normal driving than in the laboratory or testing station. This violates not only each country's stringent emission standard, but also may cause a serious health concern and environmental problems (Palash et al., 2013, U.S. EPA, 2018). Although diesel engines have various advantages like fuel economy, high engine efficiency (~52%) and lower emissions of CO/CO₂ species, the

efforts to decrease diesel NO_x emissions have been little successful since the current state of the art three-way catalysts (noble metals) for gasoline engines hardly work particularly under oxygen-rich exhaust gas conditions (Nakatsuji et al., 2008; Toops, et al., 2010). Thus, many investigations into diesel NO_x reduction have been conducted first of all using the Selective Catalytic Reduction (SCR) process by NH₃/urea or by hydrocarbon agents in search of so called "lean NO_x catalysts." Especially, the fact that NO_x could be reduced by hydrocarbons over Cu loaded/metal oxide catalysts has brought much

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*Corresponding author: Changmo Nam, Division of Health and Science, Yeungnam University College, Daegu 42415, Korea
Tel: +82-53-650-9284
E-mail: cmmam@ync.ac.kr

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attention over the possibility of diesel NO_x reduction, but the technology is still far away from commercial production (Heimrich and Deviney, 1993; Anderson, et al., 1997; Yang, et al., 2011).

In the present work, the alternative Selective Non-Catalytic Reduction (SNCR) process was implemented for diesel NO_x reduction under oxidizing exhaust conditions, which has been well practiced as a proven NO_x control technology mostly in stationary power plants, incinerators and industrial boilers (Lyon, 1987, Jodal, et al., 1990, Capener, 2008). One major drawback of the SNCR process is the narrow temperature window (1100~1300 K), close to isothermal temperatures preferred, in which NO selectively reacts with reducing agents (NH₃ and urea) in the presence of oxygen among combustion products. Another challenge is that diesel engine environments for NO_x reduction are so severe, which could include high gas quenching rates ($dT/dt = -8000$ to -5000 K/sec) from the cylinder to the exhaust pipe, relatively high CO/unreacted hydrocarbons (<0.3% CO, <400 ppm UHC) and a wide range of oxygen levels (3~14%), short residence times and so on. These are all severely different from those in stationary sources like power plants (-200 to -300 K/sec) and waste incinerators (including reactor geometries), which may influence NO_x reduction characteristics. Despite practical limitations, several SNCR applications to mobile or stationary diesel engines have been previously reported for NO_x reduction. Miyamoto et al.(1995) however conducted to achieve diesel NO_x reduction by directly injecting NH₃/urea into the actual 4-stroke diesel engine cylinder (796 cm³). But unfortunately too much chemicals (NH₃/NO_x=16,6) were injected for about 50% NO_x reduction at 90° CA ATDC (Crank Angle After Top Dead Center), which dropped quickly to less than 10% beyond 100° CA ATDC (less than 1000 K). Nam and Gibbs(2002) have systematically investigated the application of SNCR for DeNO_x of

diesel engines through direct injections of NH₃/urea into a simulated cylinder (965 cm³ capacity) and exhaust pipe section. Recently, another SNCR experiments were performed under a stationary single cylinder diesel engine (bore~stroke of 87.5~110 mm²) by Vedharaj et al.(2014). Practically, they injected reducing agents into the low temperature exhaust manifold, where only 13.4% NO_x reduction was obtained because of lower exhaust temperatures. It is quite evident that NO_x reduction potential is absolutely dependent on injection temperatures and their profiles, although many other reaction parameters are simultaneously involved. To overcome such trends of lower NO_x reduction at lower exhaust temperatures is practically required, considering severe diesel engine environments. Numerous investigations (Duo, et al., 1990; Weijuan et al., 2009; Yao, et al., 2017) have shown that the addition of various additives such as H₂, H₂O₂, CO, various alkanes and alkenes (CH₄, C₂H₄, C₂H₆, C₃H₈), alcohols (CH₃OH, C₂H₅OH) and aldehydes with the primary reducing agents tends to shift the optimum temperature to lower temperatures by 100~200 K. But unfortunately, most SNCR experiments injecting hydrocarbon additives have been conducted under stationary power plant and laboratory conditions, which provide more amenable DeNO_x environments than those of diesel engines. Until now, few experiments have been conducted regarding the direct injection of hydrocarbon additives into exhaust pipe conditions for diesel NO_x reduction. This paper interestingly presents hydrocarbon-enhanced, DeNO_x experimental results by describing the effects of hydrocarbon additives on diesel SNCR process, following previous NO_x reduction characteristics obtained in the simulated cylinder and head section (Nam and Gibbs, 2012). The exhaust pipe having a longer residence time (~50 msec) than the cylinder and head section was used as the flow reactor for diesel NO_x reduction into which additives were

separately or simultaneously injected together with the reducing agent. The effects of hydrocarbon additives on temperature shifts and NOx reduction characteristics are discussed with the possibility of the exhaust pipe and practical implications, based on N/H/O species reactions. Other emission increases and trends of exhaust byproducts caused by hydrocarbon additives are further discussed throughout.

2. Experimental

To investigate the effects of hydrocarbon additives on the diesel SNCR process under oxidizing exhaust gas conditions, a diesel-fueled, combustion-driven flow reactor was set up to simulate as closely as possible gas compositions, temperature profiles (gas quenching rates), residence times and aerodynamics

of a diesel engine cylinder and exhaust pipe. The detailed experimental system was previously described by Nam and Gibbs(2012), based on a Perkins 4.236 single cylinder diesel engine (965 cm³ capacity), and a schematic diagram is illustrated in Fig. 1. The flow reactor consisted of a combustor, firing diesel fuel and the simulated cylinder (76 mm ID and 213 mm long, stainless steel tube) which was bolted onto an engine cylinder head/exhaust manifold (cut from a real engine) and finally an exhaust pipe of 2 m long tube (70 mm ID). The exhaust pipe insulated with kaowool fibre included 4 sampling ports, which allowed gas samplings at different residence times along the pipe. And the primary reducing agent (NH₃) was first directly injected into the inlet of the exhaust pipe (Injector 2), used as the SNCR flow reactor. Then, C₂H₆ or diesel fuel additive was further introduced simultaneously or

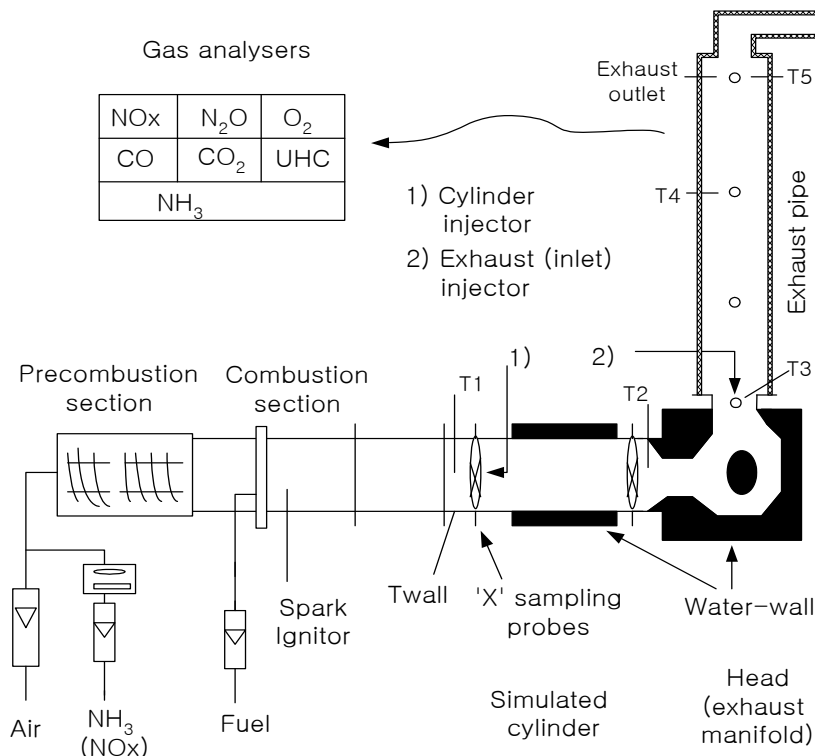


Fig. 1. A schematic diagram of a diesel-fueled, combustion-driven flow reactor for SNCR DeNOx experiments.

Table 1. Initial levels of combustion products at the inlet of the exhaust pipe section for all flows in SNCR DeNOx experiments

Flow #	NOx	CO	UHC	O ₂	CO ₂
A	530	558	200	3.7	11.31
B	530	490	185	4.8	10.67
1	530	482	180	6.6	9.56
2	530	552	100	8.3	8.56
3	530	602	150	9.2	8.01
4	530	838	250	10.1	7.47
5	530	1070	280	11.4	6.95
6	530	1250	365	12.8	6.37

separately together with NH₃ to investigate the effects of hydrocarbon additives on NOx reduction characteristics both in diesel combustion products and in low temperature exhaust conditions. Three different airflow rates were used such as 1000, 800 and 600 L/min, which corresponded to engine speeds of 3000 rpm, 2000 rpm and 1200 rpm, respectively, based on the above single cylinder (Perkins 4.236). 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 (AFR) of 20~45 ($\phi = 0.72 \sim 0.32$), close to actual diesel operating conditions. At a typical air/fuel ratio of 27.5, the residence time of the exhaust pipe section reached about 50 msec, while the simulated cylinder only provided ~20 msec, varying with air flow rate and temperature. The gas concentration measurements (NOx, N₂O, CO, CO₂, O₂ and UHC) were achieved using the on-line gas analyzing systems, directly connected into the exhaust pipe section. Meanwhile, NH₃ slip measurements were separately carried out by a wet chemical method, using a diluted acid solution. NOx concentrations were continuously measured by a chemiluminescent analyser (Rotork Model 440), while other instruments for emission concentrations were described in previous study (Nam and Gibbs, 2012). Typical initial levels of combustion products at the inlet of the exhaust pipe

for all 8 flows are presented in Table 1. The initial NOx concentrations for all flows were set to ~530 ppm. For instance, CO/UHC levels (flow #1) were maintained around <482/180 ppm, but these gases continuously oxidized to the end of exhaust pipe, eventually remaining very low, less than 30/4 ppm respectively, while those of flow #6 reached high about 1250/365 ppm due to the lower temperatures. As O₂ level increases from 3.7 to 12.8%, CO₂ concentration inversely decreases from 11.31 to 6.37% according to air/fuel ratios. Typical temperature profiles along the exhaust pipe section are shown in Fig. 2, where the initial gas temperatures for all flows covering a wide range of engine operating conditions were maintained in the range of 1000~1350 K for possible DeNOx experiments. Particularly, the gas quenching rates (temperature gradients) of -1430 to -3260 K/sec were developed along the exhaust pipe for all flows due to natural cooling. Gas temperatures were measured by shielded thermocouples (type K) and corrected for radiation losses (20~40 K).

3. Results and Discussion

3.1. DeNOx characteristics without additive

The selective noncatalytic reduction (SNCR) of NOx was investigated under diesel combustion conditions, by directly injecting NH₃ into the exhaust

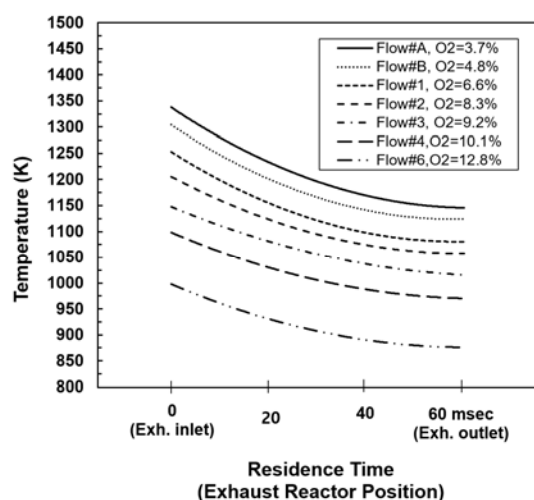


Fig. 2. Typical temperature profiles of all flows along the exhaust pipe (reactor) positions.

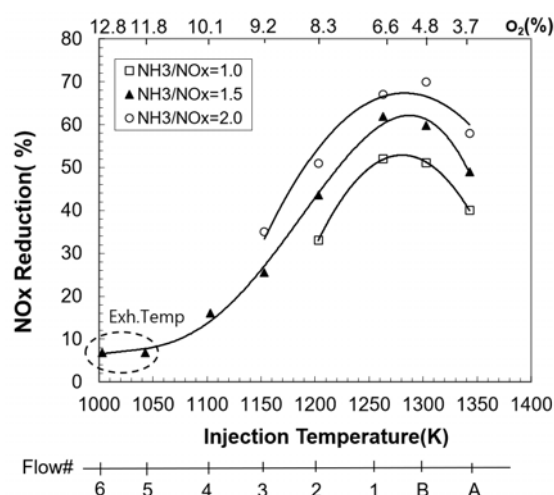


Fig. 3. Temperature characteristics of NO_x reductions through direct injection of NH₃ into the inlet of the exhaust pipe under various molar ratios ($\beta = 1.0\text{--}2.0$) without hydrocarbon additive.

pipe, used as the SNCR flow reactor. The initial NO_x level was set to ~ 530 ppm, changing the molar ratio ($\beta = \text{NH}_3/\text{NO}_x$) from 1.0 to 2.0, when air flow rate was normally maintained at 1000 L/min. The effect of temperature on NO_x reduction without additives is shown in Fig. 3 in which O₂ levels varied from 3.7 to 12.8% at each flow according to the air/fuel ratios. About 50–68% NO_x reduction occurred as the molar ratio was changed from 1.0 to 2.0 at the optimum flow #1 ($T_{\text{in}} \sim 1260$ K) and O₂ level of 6.6%. Temperature windows were formed in the range of 1200–1350 K, not much different from previous laboratory and power plant conditions (Stohr et al., 1997; Quang Dao et al., 2009). NO_x reduction tends to decrease with decreasing injection temperatures or with increasing above the optimum flow #1. As molar ratio increases, the extent of NO_x reduction at the higher temperatures turned out to be much better than those at the lower temperatures. When temperature further decreased, much closer to the typical exhaust temperature (~ 1000 K), only 8% NO_x reduction was obtained at a molar ratio of 1.5. First

of all, the SNCR process proved to be highly dependent on optimum injection temperature even in diesel conditions, particularly requiring uniform and isothermal conditions, which are not available, although many other parameters such as residence time, initial NO_x levels and various combustion products were simultaneously involved. On the other hand, the above sufficient diesel combustion products (CO/UHC levels and a wide range of O₂, as in Table 1) were not significantly affecting NO_x reduction potential in three major reaction components (NH₃/NO/O₂), implying that the key reaction factor should be still the temperature.

From kinetic calculations (Miller and Bowman, 1989; Nam and Gibbs, 2002; An et al., 2015), NH₃ is mostly initiated by active OH radical among many species (OH/O/H/HO₂) to produce NH₂ (amidogen) intermediate in oxidizing diesel exhaust conditions as follows;



Then, NH_2 species effectively reacts with NO by the key reactions (R2, R3) below among complex chain reactions, leading to proper NO reduction paths.



Meanwhile, over the higher temperatures (>1260 K), NH_2 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 NH_3 oxidation paths. So, the competition and balance between NO reduction and NH_3 oxidation is maintained throughout, depending on the injection temperature, as in experimental results.

Another big challenge is that the temperature gradients (-2240 K/sec at flow #1, Fig. 2) are also quite substantial both axially and radially along the exhaust pipe, which must be one of the main reasons for low NOx reductions. Ostberg and Dam-Johansen (1994) reported that when the axial temperature gradient was -1000 K/sec in SNCR experiments in a plug flow reactor, it had a significant impact on the temperature window shifting upwards and developed into a little lower NOx reduction. This implies that direct injection of NH_3 or other reducing agents into the exhaust pipe would not probably be a suitable DeNOx strategy in mobile or stationary diesel engines, because of the lower temperatures and even severe temperature gradients along the exhaust pipe. Therefore, an alternative strategy by adopting hydrocarbon additives was implemented to investigate possible increase of NOx reduction and further emission trends, particularly in the exhaust temperatures.

3.2. C_2H_6 additive

C_2H_6 was injected simultaneously with the primary

reducing agent (NH_3) into the inlet of the exhaust pipe, using a molar (mass) ratio ($\Upsilon = \text{C}_2\text{H}_6/\text{NO}_x$) of 0.2 to 0.5 and 1.0, when the value of $\beta = \text{NH}_3/\text{NO}_x$ was set to a constant value of 1.5.

The influence of C_2H_6 additive on NOx reduction is shown in Fig. 4. The first interesting thing is that the addition of C_2H_6 with the range of $\Upsilon = 0.2 \sim 1.0$ mostly shifted the temperature windows downwards. With the molar ratio of $\Upsilon = 0.2$, the temperature window was shifted downwards by about $50 \sim 100$ K with little change of shape where the optimum temperature was centered at around $1150 \sim 1200$ K from 1260 K. However, further increases of Υ from 0.2 to 0.5 and 1.0 caused further shifts of the temperature windows at higher temperatures ($1150 \sim 1300$ K), but had little effect at lower temperatures ($1000 \sim 1100$ K).

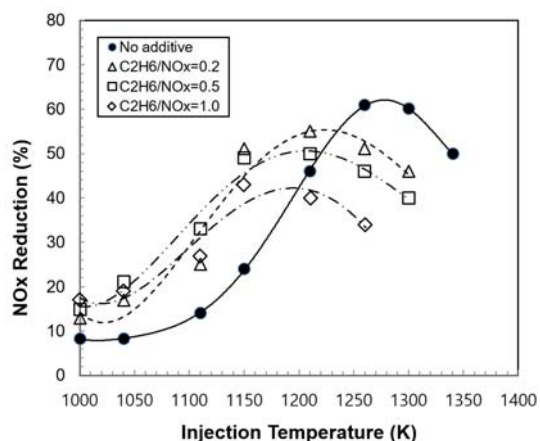
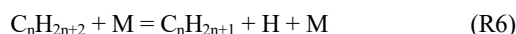
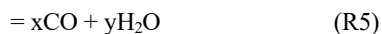
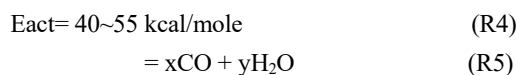
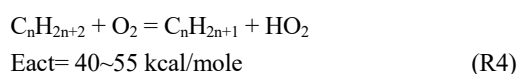


Fig. 4. C_2H_6 effects as additive on NOx reduction characteristics with the simultaneous NH_3 ($\beta = 1.5$) injection into the exhaust inlet; 530 ppm NOx.

The second, prominent feature is the change of NOx reduction potential caused by additive. At a molar ratio of $\Upsilon = 0.2$, the degree of NOx reduction is similarly maintained, showing about 60% NOx reduction, compared with those of NH_3 alone (no additive). Any further increase of Υ from 0.2 to

0.5~1.0 caused the NOx reduction to diminish significantly up to 40% at the higher temperatures. In the lower exhaust temperatures, more NOx reduction efficiencies (reaching about 15~25%) were surprisingly achieved by the injection of C₂H₆, which is compared with about 8% NOx reduction potential (NH₃ only). According to the previous results (Duo et al., 1990; Yao et al., 2017), C₂H₆ addition caused temperature windows to be shifted downwards by about 150~200 K, mostly under laboratory and oil fired boiler (1MJ/sec) conditions (negligible CO/UHC and <3% O₂). The present results show that the shift of temperature windows and the extent of NOx reduction were less effective, due to the severe temperature loss along the exhaust pipe and sufficient diesel combustion products (CO/UHC and O₂). Nevertheless, the most encouraging finding is that less amount of C₂H₆ (γ=0.2) gave better NOx reduction potential, reaching almost as good level as with no additive.

The hydrocarbons are ignited and broken into their fragments in the presence of excess O₂ than NH₃ because of their lower activation energies (40~55 kcal/mole), compared with 62 kcal/mole for the NH₃+O₂ reaction (Niu et al., 2010; Raj et al., 2011). The addition of hydrocarbons prompts more active radical production even at lower temperatures, hence shifting the temperature window downwards, based on the following general reactions (R4~R6).



In these reactions, alkyl radicals further decompose mainly via dissociation reactions or via reactions with molecular O₂. In case of C₂H₆, alkyl radicals such as C₂H₅, C₂H₃, and HCO are dissociated into highly reactive H and HO₂ radicals, which would

again lead to further formation of sufficient OH/H/O radicals. The existence of these radicals not only shifts the temperature window downwards, but also accelerates NO reaction with NH₃ in the presence of O₂ to increase NOx reduction potential, particularly in the lower exhaust temperatures.

3.3. Diesel fuel additive

The injection of diesel fuel as an additive for diesel SNCR process will be much more practical than any other hydrocarbons (CH₄, C₂H₆, C₃H₈ and CO) investigated, due to the ease of use and transport safety to actual diesel engines.

Therefore, diesel fuel was simultaneously added together with NH₃, based on the mass ratio (γ=diesel fuel/NOx) from 1.6 to 3.2~5.4. Fig. 5 shows the effects of diesel fuel on NOx reduction as a function of temperature under the same conditions as in Fig. 4. Relatively, at the smaller mass ratio (γ=1.6), the temperature window was first shifted downwards by about 100 K, where the optimum temperature was centered at around 1150~1200 K. As the mass ratio increased up to 5.4, the shape of the temperature curves turned out to become more flat, compared with no additive DeNOx characteristics. The degree of NOx reduction at a mass ratio of 1.6 was slightly diminished, achieving about 50% at the optimum temperature. With further increases in the amount of diesel fuel to γ=3.2 and 5.4, NOx reduction potentials were more decreased at the higher temperatures. However, diesel fuel proved to be much more effective than C₂H₆ additive, particularly in the lower exhaust temperatures (1000~1100 K). About 20~35% NOx reductions were achieved, recording about 3 times higher than that of no additive (8%). Mostly, the exhaust section having a longer residence time (~50 msec) depending on engine speeds (air flows) is of little use to achieve extra NOx reduction because of too lower temperatures, compared with those of the cylinder

and head section (~ 20 msec) and higher temperatures, In actual engine cylinders, proper temperatures (1100~1400 K) for NO_x reduction can be obtained from the latter half of expansion stroke, close to 70~90° CA ATDC, depending on the power outputs (Miyamoto et al., 1995). Usually, increasing engine speeds not only causes the optimum injection timing advanced (i.e. from 90° to 70° and 50° CA ATDC), but also decreases the residence time, which might be explained in a way for the present lower NO_x reduction potentials, compared with the required residence time for enough NO_x reduction reaching around 200 msec (Glarborg et al., 1994; Srivastava et al., 2005). Through previous direct injection of NH₃ ($\beta=1.5$) into the simulated cylinder (Nam and Gibbs, 2012), only 34% NO_x reduction was achieved since severe diesel engine environments existed such as large temperature drops (i.e. -7000 K/sec) and the above insufficient residence time. Among them, especially less than 1/3 of NO_x reduction potential (9%) was only obtained from the low temperature, exhaust pipe section (~ 1000 K). Therefore, the above finding suggests that further NO_x reduction could be developed by injecting a small amount of diesel fuel

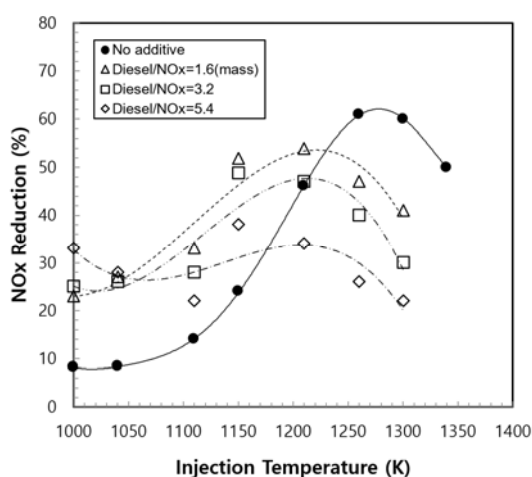


Fig. 5. Diesel fuel effects as additive on NO_x reduction characteristics with the simultaneous NH₃ ($\beta=1.5$) injection into the exhaust inlet; 530 ppm NO_x.

as an additive into the exhaust pipe. Diesel fuel would be much more useful than any other hydrocarbons due to the practical reason, where the smallest mass rate of diesel fuel ($\gamma=1.6$) promised the best performance for the present diesel NO_x reduction. This is encouraging for the potential application of the SNCR process to diesel engines, and further investigations may be needed, regarding the optimization of chemicals used and their emission trends.

3.4. Emission Levels of CO, N₂O and NO₂

Fig. 6(A, B) shows the emissions of CO and N₂O before and after injecting C₂H₆ and diesel fuel as additives for the whole flows (#A to #6). Simultaneous measurements were carried out for these emissions. UHC emission levels were negligible, almost a factor of 10 smaller than CO levels for all flows except #6 and not depicted due to complexity.

First, without additive (NH₃ only, $\beta=1.5$), maximum N₂O emission (~ 23 ppm) peaks around 1260 K (flow #1), which is consistent with maximum NO_x reduction flow. At higher temperatures (1300~1350 K), N₂O emissions tend to decrease slightly by decomposition, where less NO_x reduction was also achieved. At lower temperatures (1000~1100 K), N₂O production sharply decreased to ~ 8 ppm even at flow #2 (1210 K), despite substantial NO_x reduction occurred at the same flow.

When C₂H₆ was added together with NH₃ (Fig. 6A), N₂O emissions were almost doubled (45~50 ppm) with increasing C₂H₆ amounts ($\gamma=0.2\sim 1.0$) at and above the optimum temperature, despite the adverse effect on the NO_x reduction (Fig. 4). However, at the optimum temperature of 1210 K, N₂O emissions fall and continue to decrease as the temperature goes down further.

The temperature characteristics of N₂O emissions with diesel fuel (Fig. 6B) are quite different from

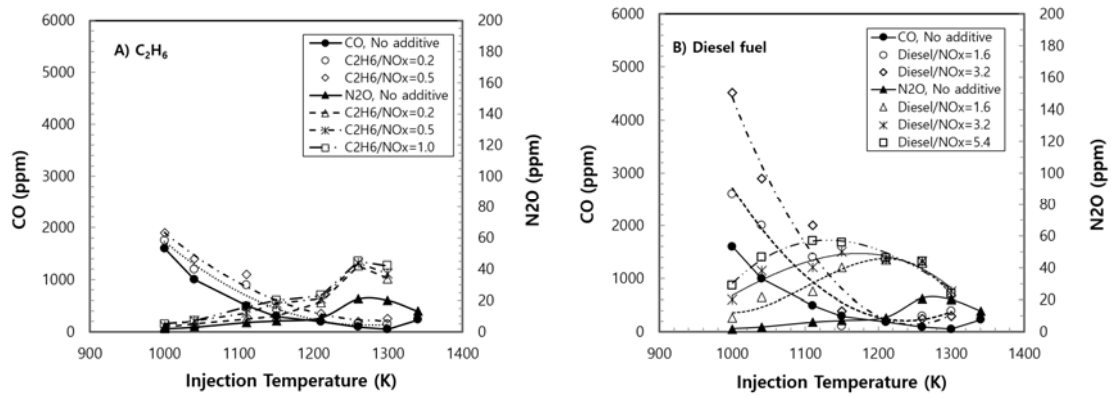


Fig. 6(A, B). Variations of CO and N₂O emissions by injecting C₂H₆ (A) and diesel fuel (B) as additives with the simultaneous NH₃ ($\beta=1.5$) injection into the exhaust inlet; 530 ppm NO_x.

those of C₂H₆. Injection of diesel fuel triggered temperatures a little high by about 20–40 °C, depending on the mass ratios (diesel/NO_x), so that less N₂O production occurred at the higher temperatures due to decomposition reaction. However, at lower temperatures, unlike C₂H₆, a substantial amount of N₂O (20–65 ppm at 1100K) was still produced, depending on the mass ratios of diesel fuel.

Secondly, the CO emissions with no additives at the higher temperatures (1200–1350 K) usually remained quite low at the end of exhaust pipe because of very efficient combustion (Fig. 6A). As temperatures go down, the CO emission levels become significant, and increased up to ~500 ppm at flow #4 (1100 K), and again rose up to about 1600 ppm due to the low combustion temperatures (1000 K). With C₂H₆ injection at the molar ratios ($\gamma = C_2H_6/NO_x$) of 0.2 and 0.5, CO emissions were

slightly increased by about 100–300 ppm at the lower temperature flows, but at the higher temperatures, the extent of increase was negligible. As diesel fuel was injected, two different aspects emerged according to the temperature (Fig. 6B). At higher temperatures, CO emissions were further decreased by additional combustion. However, at the lower temperatures (1000–1100 K of flow #6–#4), CO emission levels were substantially increased by almost two or three times those of no additive because of incomplete combustion and higher carbon content of diesel fuel, compared to C₂H₆.

Table 2 shows a comparison of “carbon content” between C₂H₆ and diesel fuel for the injected quantities. The carbon content of diesel fuel was 6–9 times higher than C₂H₆ according to the mass ratios. Therefore, more CO and N₂O emissions were observed with diesel fuel, although more NO_x reductions were achieved at the same conditions.

Table 2. Comparison of carbon content between C₂H₆ and diesel fuel additives injected

$\frac{\text{diesel fuel}}{NO_x}(\text{mass ratio})$	$\frac{C_2H_6}{NO_x}$	$\frac{\text{diesel fuel}}{C_2H_6}(\text{mass ratio})$	$\frac{C \text{ of diesel fuel}}{C \text{ of } C_2H_6}$
1.63	0.2	8.15	9.05
3.27	0.5	6.54	7.24
5.45	1.0	5.45	6.05

Fig. 7 shows NO_2 increase, resulting from the $\text{NO}/\text{NH}_3/\text{O}_2$ reactions with/without the injection of C_2H_6 and diesel fuel, as observed in Fig. 6. At higher temperatures (1150~1200 K), actually lower parts of temperature windows for NO_x reduction, the NO_2 emissions were less than 2% (<10 ppm), and not affected by either existing combustion products (CO/UHC) or by further injecting C_2H_6 /diesel fuel additives. However, as temperature was lowered to 1040~1000 K (flows #5 and #6), the NO_2 emissions sharply increased and reached ~50 ppm at 1000 K without additives. Injecting C_2H_6 or diesel fuel caused the NO_2 emissions to increase substantially from ~50 ppm to about 80~95 ppm at $T_{\text{in}}=1000$ K where for diesel fuel ($\gamma=3.2$), more NO_2 was produced due to its higher carbon content.

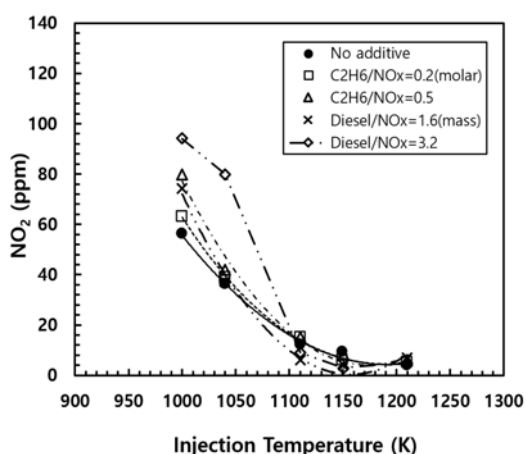


Fig. 7. NO_2 emission increase by injecting C_2H_6 and diesel fuel as additives with the simultaneous NH_3 ($\beta=1.5$) injection into the exhaust inlet; 530 ppm NO_x .

The oxidation of CO and $\text{N}_2\text{O}/\text{NO}_2$ formation in a SNCR process including diesel combustion products can be explained via the following reactions below (Glarborg et al., 1994; Yao et al., 2017);



And



And



The injection of NH_3 for NO reduction retards the main CO oxidation reaction rate (R7), resulting in the increase of CO concentration because many chain reactions compete for OH radicals, and particularly the reaction (R1) is very rapid, compared with reaction (R7). The major sensitive reactions for N_2O formation are (R8) and (R9), while the conversion of NO to NO_2 is mainly dominated by the reaction (R10) at the lower temperatures. Increasing C_2H_6 and diesel fuel additives would increase the concentrations of not only active radicals ($\text{OH}/\text{O}/\text{HO}_2/\text{H}$), leading to further NO_x reduction particularly at lower temperatures, but also of nitro-carbonaceous species (NCO , NH , HCN and CN) and hydrocarbon fragments (C_xH_y), which then eventually contribute to the increase of N_2O and NO_2 byproducts and CO emissions as well through complex chain reactions.

4. Conclusions

The effects of hydrocarbon additives for diesel NO_x reduction were investigated using the SNCR process under oxidizing diesel exhaust gas conditions. A diesel-fueled combustion system was set up to simulate the actual cylinder and head, exhaust pipe and combustion products, where the reducing agent NH_3 and C_2H_6 /diesel fuel additives were separately or simultaneously injected into the exhaust pipe, used as the SNCR flow reactor. With NH_3 alone, temperature windows were formed in the range of 1200~1350 K, where about 50~68% NO_x reduction was possible with the molar ratio (β) of 1.0~2.0 at the optimum flow #1 ($T_{\text{in}}=1260$ K). As temperature goes down to the typical exhaust

temperatures (~1000 K), only 8% NO_x reduction was obtained because of too lower temperatures. More encouragingly, together with additives of 0.2 (C₂H₆/NO_x) and 1.6(diesel/NO_x), temperature windows were shifted downwards by about 50~100K from the optimum temperatures with little change in NO_x reduction potential. Diesel fuel turned out to be much more effective than C₂H₆ especially at lower temperatures (Fig. 5) in which about 20~35% NO_x reductions were maintained, recording about 3 times higher than that of no additive (8%). However, the addition of hydrocarbons increased emission levels of byproducts such as CO, UHC, N₂O and NO₂. At and above the optimum temperature (1260~1300 K of flow #1~#B), the increase in N₂O emissions was substantial from ~23 ppm (no additives) to ~45 ppm for both additives, but other species emissions (CO, UHC and NO₂) remained surprisingly very low because there were relatively enough temperatures for oxidation. However, at the lower temperatures (1000~1100K of flow #6~#4), diesel fuel produced higher CO, UHC, N₂O and NO₂ emissions than C₂H₆ because of the higher carbon content of diesel fuel (6~9 times).

After all, the injection of C₂H₆ and diesel fuel into the exhaust pipe is believed to have promoted the production of OH/O/HO₂/H radicals in N/H/O/hydrocarbon reactions which certainly contributed to further NO_x reduction at lower temperatures. In addition, the existence of higher CO/UHC levels would accelerate the rate of NO_x reduction in short residence times (~50 msec), but decrease the selectivity for the reaction of NH₃ with NO_x, resulting in overall slightly lower NO_x reduction, and contribute to higher CO/N₂O/NO₂ emission levels.

Nevertheless, Injecting a small amount of diesel fuel together with a primary reducing agent (NH₃) seems to be more encouraging for practical reason and could be suggested as an alternative SNCR DeNO_x strategy under diesel exhaust systems,

following further strict optimization of chemicals used for lower emission levels of byproducts.

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