DIESEL ENGINE NOx REDUCTION BY SNCR UNDER SIMULATED FLOW REACTOR CONDITIONS

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Abstract : NOx reduction experiments were conducted by direct injection of urea into a diesel fueled, combustion-driven flow reactor which simulated a single engine cylinder ($966 cm^3$). NOx reduction tests were carried out over a wide range of air/fuel ratios (A/F=20-40) using an initial NOx level of 530ppm, and for normalized stoichiometric ratios of reductant to NOx (NSR) of 1.5 to 4.0. The results show that effective NOx reduction with urea occurred over an injection temperature range of 1100 to 1350K. NOx reduction increased with increasing NSR values, and about a 40%-60% reduction of NOx was achieved with NSR=1.5-4.0. Most of the NOx reduction occurred within the cylinder and head section (residence time <40msec), since temperatures in the exhaust pipe were too low for additional NOx reduction. Relatively low NOx reduction is believed to be due to the existence of higher levels of CO and unburned hydrocarbons (UHC)inside the cylinder,and large temperature drops along the reactor. Injection of secondary combustible additives (diesel fuel/C_2H_6) into the exhaust pipe promoted further substantial NOx reduction (5%-30%) without shifting the temperature windows. Diesel fuel was found to enhance NOx reduction more than C_2H_6, and finally practical implications are further discussed.

Key Words : Diesel NOx, SNCR, NOx reduction, Diesel engine, N_2O

INTRODUCTION

As future emission regulations become more stringent, the reduction of diesel NOx emissions presents new challenges, since typical noble metal three-way catalysts show little activity towards NOx reduction under oxidizing conditions.[1] Over the last decade, many studies and research projects have focused on the selective catalytic reduction (SCR) by NH_3/urea and hydrocarbons as reducing agents for practical diesel NOx reduction.[2-6] However, poor durability of catalysts and low NOx reduction (10%-40%) with hydrocarbons in the actual exhaust gases still remain outstanding problems prior to any potential com-mercialization.

In the present work, the alternative, gas-phase selective noncatalytic reduction (SNCR) technologies using NH_3/urea[7-8]have been considered for diesel NOx reduction. The SNCR process has been successfully used as a NOx control technology mostly in stationary power plants and industrial boilers. Lyon[7] found that the NH_3 selectively reduces the NO in the presence of oxygen without a catalyst over the temperature range from 1,100 to 1,400 K. Further extensive investigations including experimental observations and kinetic calculations have been reported under mostly power plant conditions by which it proved that many reaction parameters such as temperature, molar ratio (NH_3 /NOx), residence time, oxygen level and initial NOx would simultaneously affect the NOx reduction potential.[9-12] However, only a few inve-

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stigations[5,13] have been applied to diesel engines, based on this SNCR concept, and basic experimental data are further required. Therefore, the objectives of this work are to report the application of SNCR for DeNOx of diesel engines through direct injections of urea into a simulated cylinder and also when in-cylinder SNCR is combined with the secondary addition of hydrocarbons into the exhaust pipe. In particular, diesel engine environments that exhibit high rates of gas phase quenching from the cylinder to the exhaust pipe, relatively high CO/UHC and a wide range of oxygen levels and a shortage of effective residence time are different from those in stationary sources, and will be the main focus of this investigation, including the implications of the experimental results.

EXPERIMENTAL

Flow Reactor and Ancillaries

To perform diesel DeNOx 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 (quench rates), residence times and aerodynamics of a diesel engine cylinder and exhaust. The system design, previously described in detail by Nam and Gibbs,[5] was based on a Perkins 4.236 single cylinder diesel engine (966 cm^3 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 was bolted onto an engine cylinder head/exhaust manifold (cut from a real engine) and finally an exhaust pipe, a 2 m long insulated tube (stainless steel, 50mm diameter). Initial NOx was established by NH$_3$ doping of the combustion air. Primary reductants were directly injected into the simulated cylinder whilst secondary hydrocarbon additives could be injected into the inlet of the exhaust pipe. Gas temperatures were measured by shielded thermocouples and were corrected for radiation losses.

The gas analyzer system was attached to the

combustion rig along the exhaust pipe. Concentrations of NOx were measured continuously by a chemiluminescent NOx analyser (Rotork Model 440), whilst N$_2$O was monitored by an on-line N$_2$O analyzer (Hartmann and Braun). The CO and CO$_2$ measurements were conducted using nondispersive infrared continuous analysers (NDIR, ADC type 370), and oxygen levels were determined by a paramagnetic analyser (Servomex 570). For UHC detection, a flame ionisation detector (FID) was employed. The NH$_3$ slip was separately measured by a wet chemical method using dilute H$_2$SO$_4$ solution. In an actual diesel engine system, a possible diagram of the engine cylinder for diesel DeNOx experiments can be described as in Figure 1. The main chamber should have an additional nozzle for reductant and also indicate its injection direction. Detailed discussion is further introduced in practical implication section.
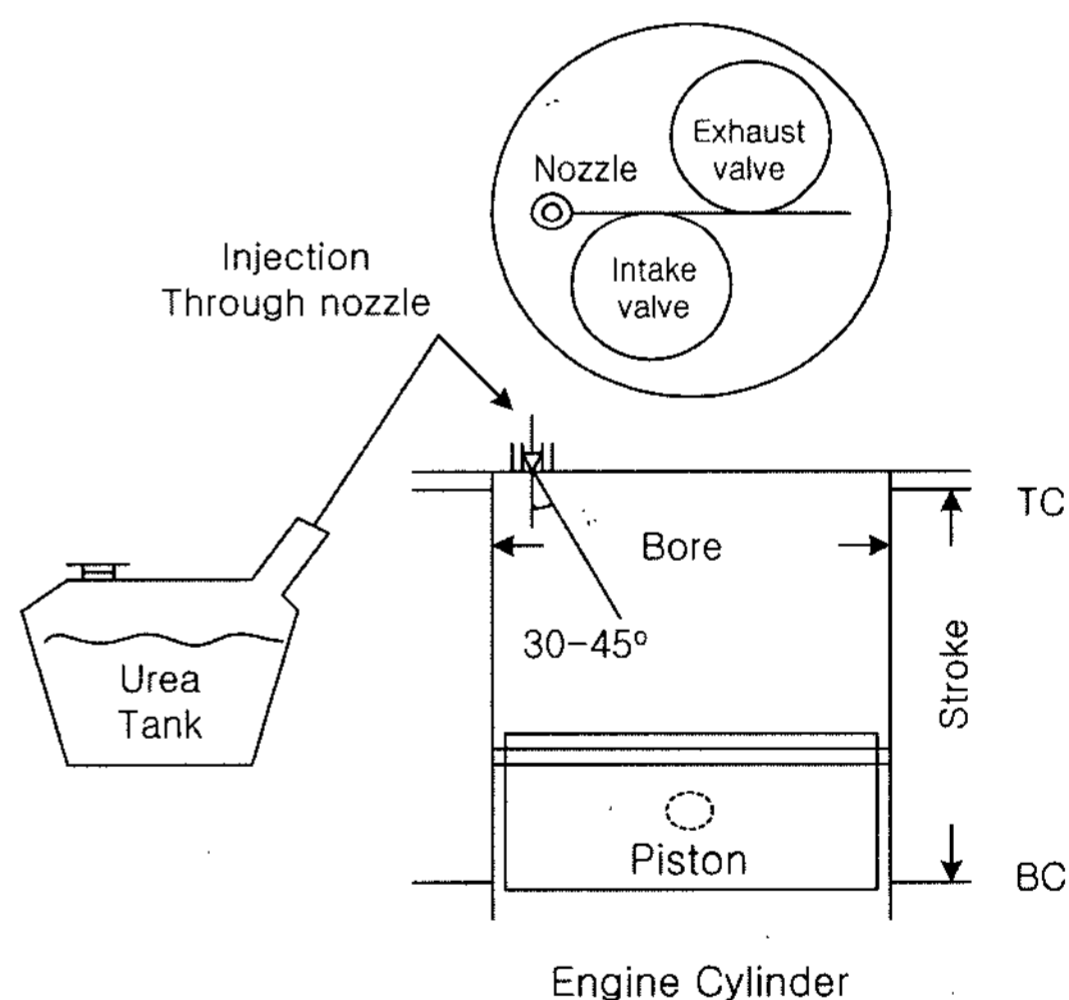

Figure 1. A possible schematic of injection direction of reductants at actual diesel engine cylinder: TC=top center, BC=bottom center.

Procedures and Typical Conditions

The air flow 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 (A/F's) of 20-45 (=0.72-0.32). Gas temperatures in the simulated cylinder were typically in the range of 1,050 to

1,400K with oxygen levels varying from 6.6 to 12.8% according to the air/fuel ratio. The initial NOx level was maintained at 530 ppm. Urea was used as the primary reductant and directly injected into the simulated cylinder. DeNOx reactions proceeded mainly in this simulated cylinder where large quenching rates (-7,880 K/sec) were achieved because of water-cooling. The residence time reached about 20 ms at a typical air/fuel ratio of 27.5. Additional NOx reduction also took place in the cylinder head region 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 the exhaust pipe, and were normally less than 150 and 10ppm respectively, except for flow # 5 and # 6, as in Figure 2. However, at the cylinder injection point, these concentrations reached about 1,700ppm CO and 400ppm UHC (although they are eventually oxidized to exhaust concentrations) and are significant as they can influence DeNOx performance.
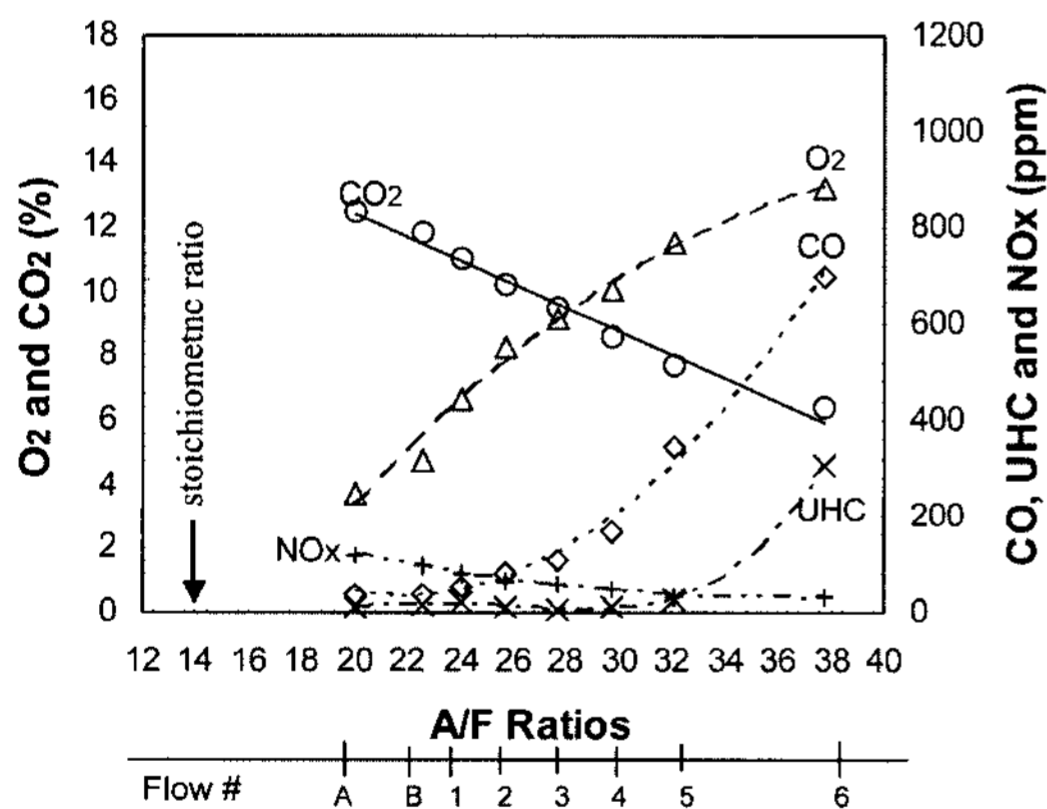
3 shows the NOx reduction as a function of injection temperature with varying urea NSRs from 1.0 to 4.0 for an initial NOx level of 530 ppm. The curves show temperature windows, formed between 1,100 and 1,350 K, where the NOx reduction effectively occurred, and the optimum temperature was located at about 1,290K (O_2=8.3%). The reduction of NOx increases with increasing NSR, and about a 40%-60% reduction of NOx was achieved at NSR=1.5-4.0. NOx reduction continues to take place up to the optimum temperature, but it gradually decreases over the high temperature range. These experimental data are qualitatively in good agreement with those in the literature[14-15] in which optimum temperatures were usually centered at around 1,270K ($\pm$ 100K). However about 60%-80%, NOx reduction was reported with NSR=1-1.6, which might be explained by different conditions, especially low quench rates of -200 to -290 K/sec under furnace conditions compared with -5,800 to -8,000K/sec developed in the cylinder section. Furthermore, higher CO/UHC levels (2,000/400ppm) inside the simulated cylinder could also cause a decrease in NOx reduction, whilst the effects of higher oxygen levels (8.3% to 10.1%) would be negligible.[5]
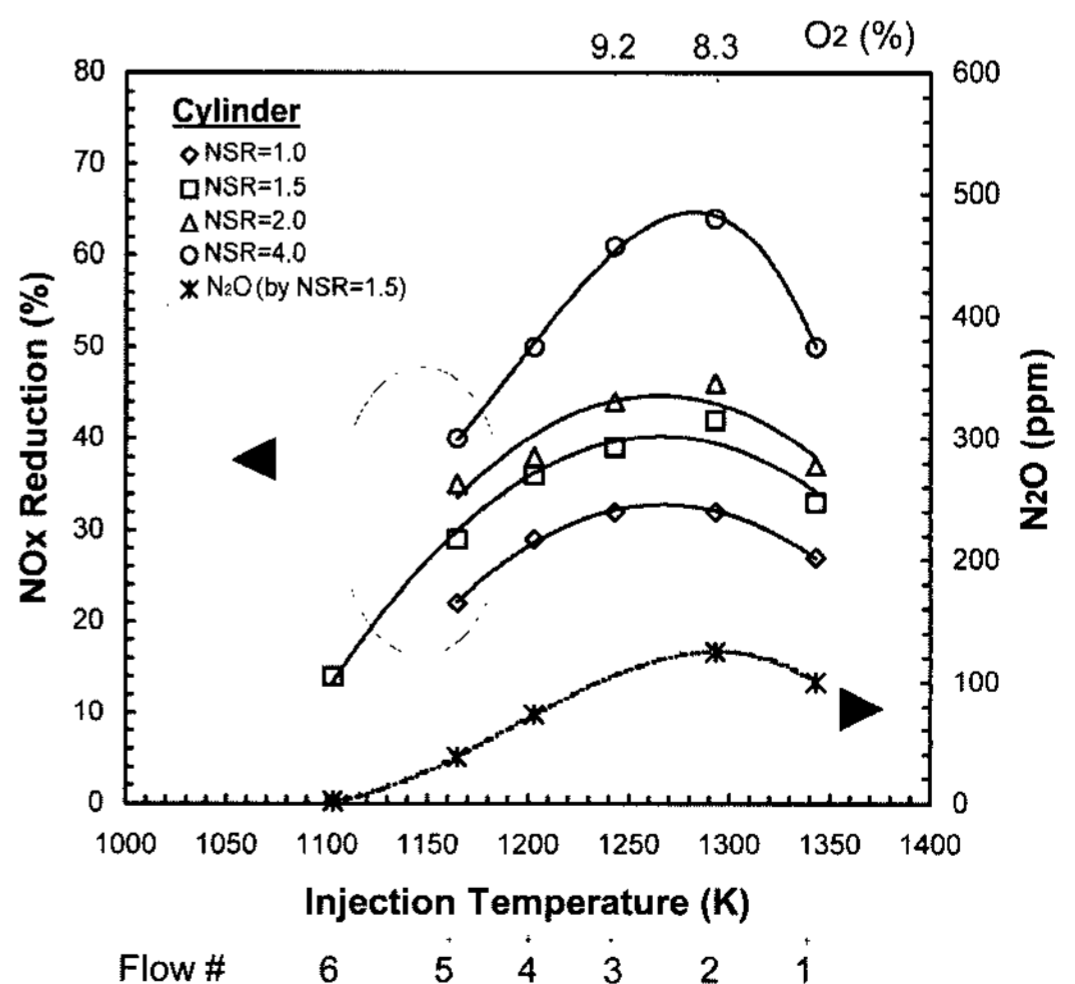

Figure 2. Combustion products emitted from the flow reactor over the range of air fuel/ratios and effective diesel fuel flows utilized in the SNCR tests.

RESULTS AND DISCUSSION

Direct Injection into the Cylinder

The selective noncatalytic NOx reduction experiments under diesel engine conditions were performed through direct injection of urea into the cylinder inlet at various air/fuel ratios. Figure

Figure 3. Temperature characteristics of NOx reductions and N_2O formation for direct injection of urea into the cylinder at various NSR values; NOx=530ppm.

The mechanism of urea decomposition reactions has been discussed rarely. According to Caton and Siebers,[16] urea would firstly be decomposed at less than 720 K as follows;

$$H_2NCONH_2 = NH_3 + HNCO \qquad (1)$$
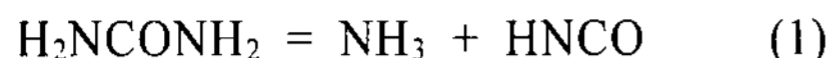
where NH_3 follows the complicated NH_3 oxidation routes for NOx reduction,[11,18] and the isocyanic acid (HNCO) is further decomposed to form mainly isocyanate radical (NCO) and other minor radicals (NH_2, HNO);

$$HNCO + OH = NCO + H_2O \qquad (2)$$

or as minor reactions

$$HNCO + H = NH_2 + CO \qquad (3)$$
$$HNCO + O = HNO + CO \qquad (4)$$
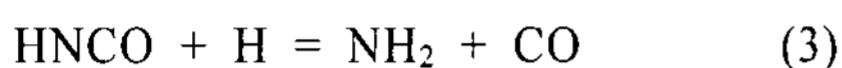
As far as fuel-lean conditions are involved, reaction 2 is dominant, so that NCO radicals react with NO to form N_2O and CO as follows;

$$NCO + NO = N_2O + CO \qquad (5)$$
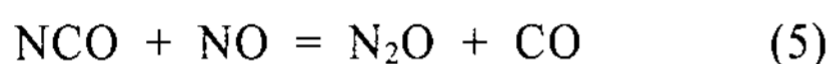
Any N_2O formed can be decomposed to form N_2, depending on the temperature, which influences the total NOx reduction.

Therefore, the major pathways of NO reduction as well as N_2O formation by urea must be reactions 2 and 5, and N_2O decomposition reactions. This HNCO related mechanism describes the key, different experimental phenomena such as the shift in the temperature windows and N_2O formation, compared with general NH_3 deNOx characteristics.[16-17]

Residence Time

Figure 4 shows the NOx reduction behavior at different NSR of 1.5 and 4.0, as well as the temperature profile along the reactor positions at optimum flow #2 (T_{in}=1,290K, O_2=8.3%). As expected, most of the NOx reduction occurred within the simulated cylinder and head section (residence time <40msec), and the rest of the NOx reduction took place in the exhaust section, reaching a maximum of around 40% and 65% at NSR=1.5 and 4.0, respectively. The temperature profile for flow #2 not only indicates good agreement with NOx reduction and CO/UHC oxidation profiles (not shown), but also shows that exhaust temperatures are too low for further NOx reduction. An interesting observation is that

NOx reduction seems to be related to both temperature and CO/UHC oxidation profiles, since they simultaneously occur in the higher temperature cylinder section. In particular, the existence of CO/UHC species accelerates the rate of NOx reduction, but too much CO/UHC decrease the selectivity for NH_3 with NOx, resulting in overall lower NOx reduction.
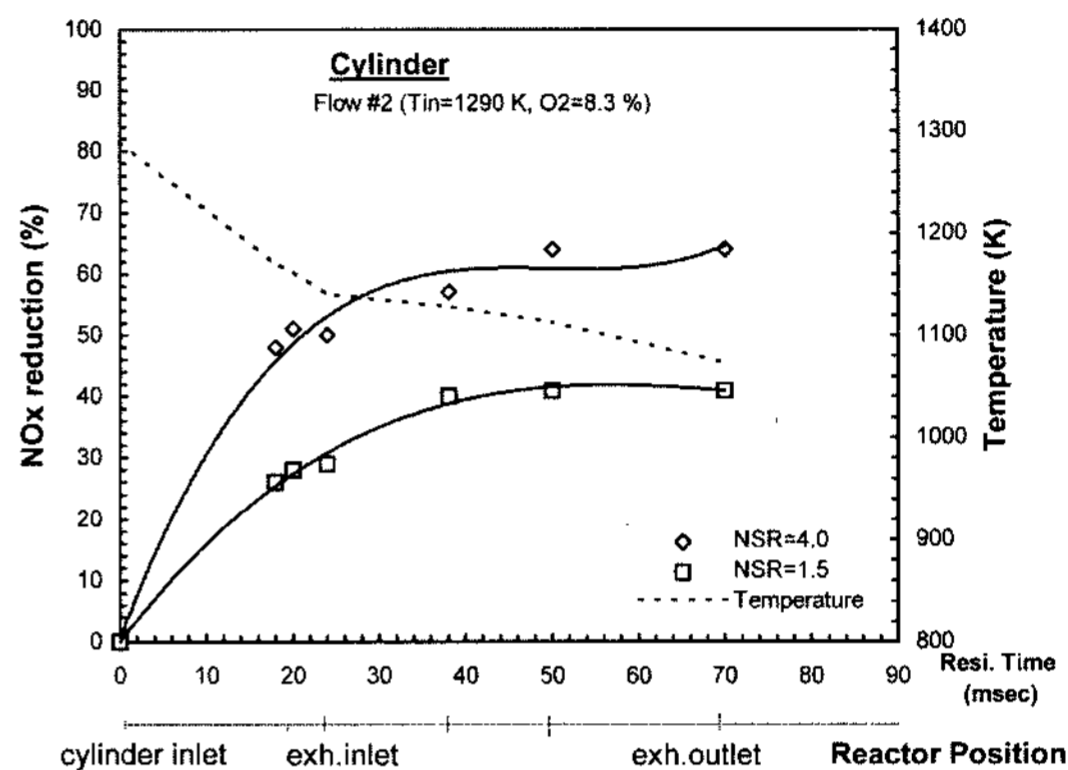

Figure 4. Effect of residence time on NOx reduction and gas temperature during urea injection into the cylinder at the optimum flow #2; NOx=530ppm.

Staged Injection with Hydrocarbons:

It was found that most of the NOx reduction would occur in the cylinder section, while the exhaust section, with sufficient residence time, was of little use to achieve extra NOx reduction because of too low temperatures. Injection of combustible additives together with the primary additive has been found previously to shift temperature windows downwards by about 100 -200 K.[19] Hence further NOx reduction at lower temperatures could potentially be achieved by the separate injection of secondary combustible additives in a lower temperature region. Therefore, urea was injected into the cylinder as a primary reductant, whilst C_2H_6 or diesel fuel was injected simultaneously into the inlet of the exhaust pipe. Figure 5. shows the effects of "staged injection" on NOx reduction with varying hydrocarbon mass ratios (HC/NOx) at a NSR=4.0. The NOx reduction was substantially increased over the whole temperature range by an additional 5%-30%, compared to that with no secondary additive. In particular, diesel

fuel turned out to be very effective at the lower temperatures where NOx reduction reached almost 65%-70% for mass ratios of 1.6 and 5.4. C_2H_6 showed around a 5%-15% increase for mass ratios from 0.2 to 1.0, but did not enhance NOx reduction as much as diesel fuel did. In fact, these trends demonstrated that staged injection did not shift temperature windows at all, compared with simultaneous injection of additives, but enhanced the NOx reduction at all temperatures.
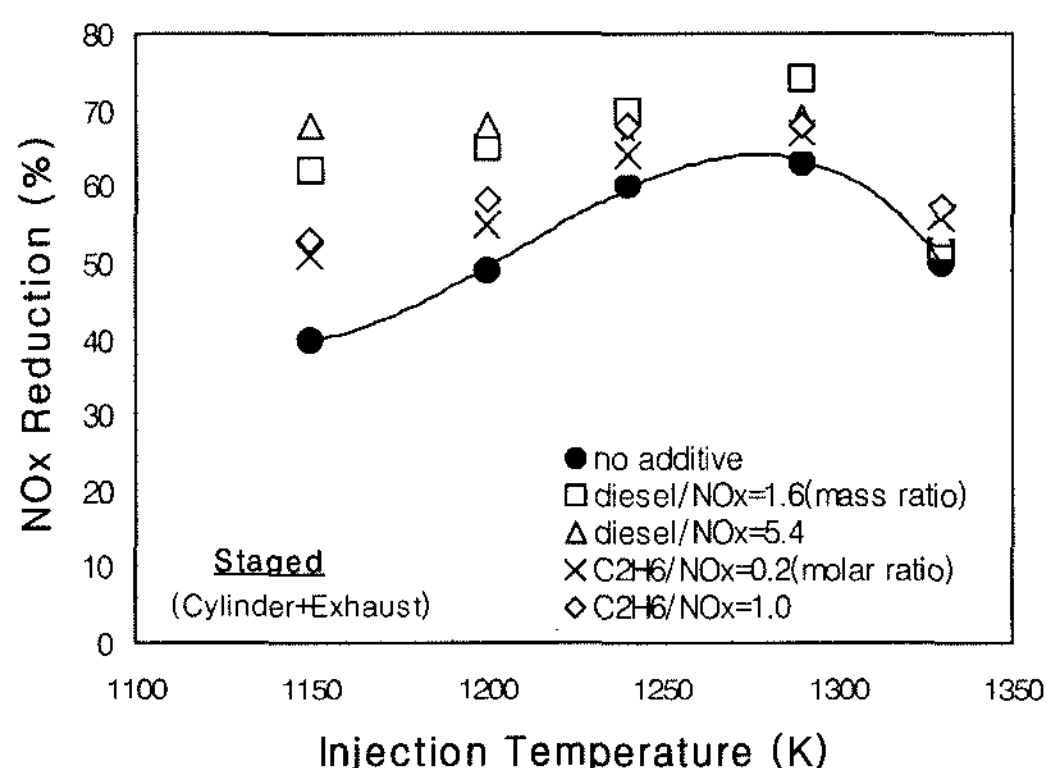

Figure 5. Effect of C_2H_6/diesel fuel staged addition at the exhaust on NOx reduction with urea injection into the cylinder; 530 ppm NOx, NSR=4.0.

Staged injection in SNCR process has already been conducted mostly in stationary power plants, in order to follow various load changes (temperatures), and sometimes to burn out the unreacted NH_3 in the downstream region. OH/O/H radicals play an important role in the SNCR process.[18] Injection of additives is believed to have promoted the above radical production at low temperatures, which caused further NOx reduction in the exhaust pipe.

Practical Implications

While the majority of diesel DeNOx studies have focused on the SCR process (i.e.,on the search for catalyst materials), few investigations based on the SNCR concept have been adapted for diesel engines. With respect to the narrow temperature windows, it is necessary to find appropriate high temperature ranges for injection

of reductants in diesel engines. In practice, the temperatures within actual engine cylinders at 40-50° Crank angle, after top dead center (CA ATDC) range from approximately 1,700-2,000K depending on the power outputs.[20] However, at around 70-90° CA ATDC, the temperatures are typically within 1,100-1,600K 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. Provided that injection temperatures for the primary additive are maintained at or above the optimum, NH_3 slip will be acceptable. In case of urea DeNOx, N_2O emissions can be significant and may need to be reduced if the technique is to be successfully applied to a real engine.

Miyamoto *et al.*[13] applied the SNCR process for engine DeNOx by directly injecting various reductants (NH_3, urea or ammonium acetate) into an actual diesel engine (bore-stroke of 96 mm x 110 mm). Optimum NOx reduction was achieved at the injection timing of about 90° CA ATDC, where the pressure of several atmospheres would also be involved. Fortunately, previous 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.[21] Therefore, the present experimental results should be not only directly applicable to diesel engine conditions, but also provide a valuable basis for future studies on actual engines.

CONCLUSIONS

NOx reduction experiments under diesel engine conditions were conducted using the selective non-catalytic method in a stainless steel flow reactor, which closely simulated the cylinder and head, exhaust pipe section and combustion products (CO, UHC and O_2 levels) that occur in actual diesel engines. The major findings were as follows: i) About 40%-60% NOx reduction can be achieved using urea as the reductant over the temperature range 1,100-1,350K and with a NSR of 1.5-4.0. ii) Most of the NOx reduction occurred

within the cylinder and head section (residence time <40 msec), since exhaust temperatures were too low for further reduction. It is believed that the NOx reductions in the cylinder are limited by both the extent of gas quenching and high concentrations of CO and UHC, while high oxygen levels (around 10%) have a negligible influence on NOx reduction with urea. iii) Staged injections using diesel fuel as the secondary additive in the exhaust increased NOx reduction by 5%-30% compared with in-cylinder DeNOx without shifting temperature windows. This demonstrates the potential of staged SNCR for DeNOx in diesel engines. iv) Urea DeNOx performance turned out to be overall promising at higher oxygen levels of diesel conditions, whereas some amount of N_2O (above 100ppm) emission became worried. NH_3 slip was negligible at or above the optimum DeNOx temperature. v) The experimental data from the flow reactor are directly applicable to actual diesel engine conditions.

ACKNOWLEDGEMENT

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