International Journal of Automotive Technology, Vol. 8, No. 3, pp. 283−288 (2007)

1229−9138/2007/034−04

STATIC CHARACTERISTICS OF A UREA-SCR SYSTEM FOR NOx REDUCTION IN DIESEL ENGINES

J.-G. NAM*

Division of Marine Engineering, Mokpo National Maritime University, Geonnam 530-729, Korea

(Received 8 May 2006; Revised 17 May 2007)

ABSTRACT−This paper presents the static characteristics of a urea-SCR system. The static characterization of the urea-SCR system was generated by sweeping urea flow rates at common engine torque/speed operating points. Several experiments were performed using engine operating points at different raw NOx emission levels, space velocities, and SCR catalyst temperatures. The recorded NOx emissions from the engine exhaust outlet and engine tailpipe are then compared. The urea-SCR static system results indicated that a 50~60% NOx conversion is achievable at most engine operating points using the stoichiometric NH_3/NOx ratio, and a high 98% NOx conversion is possible by exceeding the stoichiometric NH_3/NOx ratio. The effect of the pre-oxidation catalyst volume was also investigated and found to have a profound impact on experimental results, particularly the static NOx conversion.

KEY WORDS : Space velocity, Stoichiometric NH_3/NOx ratio, Pre-oxidation catalyst, Static NOx conversion

1. INTRODUCTION

1.1. Motivation

Diesel engines offer significant advantages over spark-ignited engines in terms of peak torque production, carbon monoxide (CO) emissions, hydrocarbon (HC) emissions, and fuel consumption (and associated carbon dioxide (CO_2) emissions known to cause the greenhouse effect). However, lean exhaust conditions render conventional automotive three-way catalysts ineffective, making NOx reduction a considerable challenge (Kowalewicz, 2001; Lee and Choi, 2005). Urea-SCR is a technology which addresses this problem that has received much attention in recent years, and has shown the potential to meet the stringent regulations for NOx emissions for US 2007/2010 and Euro IV/V (Tennison *et al.*, 2004; Rinie *et al.*, 2002; Blakeman *et al.*, 2001).

1.2. Urea-SCR System

The functionality of a urea-SCR system is defined by the selective reduction of NOx in a lean exhaust environment using ammonia, which is generated from urea. This makes urea-SCR well suited to be used with diesel engines, which always operate significantly lean of stoichiometry. Four catalysts comprise a typical urea-SCR system, including pre-oxidation, hydrolysis, SCR, and post-oxidation catalysts (Gieshoff *et al.*, 2000).

The main function of the pre-oxidation catalyst is to balance the NO_2/NOx ratio for better low temperature NOx conversion efficiency, as well as to oxidize CO and HC emissions and prevent HC poisoning of the SCR catalysts (for zeolite formulations). The chemical reactions promoted at the pre-oxidation catalyst are listed in Equation (1).

$$CO+1/2O_2 \leftrightarrow CO_2 \qquad (1\text{-}1)$$

$$C_mH_n+(m+n/4)O_2 \leftrightarrow mCO_2+n/2H_2O \qquad (1\text{-}2)$$

$$NO+1/2O_2 \leftrightarrow NO_2 \qquad (1\text{-}3)$$

The toxic effect of ammonia prohibits its direct use in mobile applications, so a non-toxic chemical (urea) is substituted. The urea is typically carried in aqueous solution, and must react with the ammonia through a hydrolysis process. The hydrolysis catalyst (reactions listed in Equation 2) carries out this process, while limiting undesirable hydrolysis.

$$(NH_2)_2CO+H_2O \rightarrow 2NH_3+CO_2 \qquad (2)$$

The ammonia and exhaust gases then reach the SCR catalyst, where the reduction of NOx takes place. The chemical reactions for this catalyst are listed in Equation (3), and each reaction has a drastically different reaction rate, depending on operating conditions, which becomes an important system consideration. Unused ammonia either exits the SCR catalyst or is stored on the catalyst at active storage sites for further use.

**Corresponding author.* e-mail: jgnam@mmu.ac.kr

$$4NH_3+4NO+O_2 \leftrightarrow 4N_2+6H_2O \quad (3\text{-}1)$$

$$2NH_3+NO+NO_2 \leftrightarrow 2N_2+3H_2O \quad (3\text{-}2)$$

$$8NH_3+6NO_2 \leftrightarrow 7N_2+12H_2O \quad (3\text{-}3)$$

Finally, the exhaust gases and excess ammonia reach the post-oxidation catalyst, where excess ammonia is oxidized, as outlined in Equation (4). Any remaining ammonia exiting the post-oxidation catalyst is known as ammonia slip, and is highly undesirable due to toxicity and foul odor at concentrations as low as 10 parts per million (ppm).

$$4NH_3 + 3O_2 \leftrightarrow 2N_2 + 6H_2O \quad (4)$$

2. EXPERIMENTAL APPARATUS AND METHOD

2.1. Apparatus

The research engine used for these experiments was a 103 kW turbocharged, intercooled, 2.5L VM-Motori compression-ignition, direct-injection (CIDI) engine equipped with a cooled exhaust gas recirculation (EGR) system.

The engine is calibrated to meet the Euro III emissions certification level, and is representative of a modern passenger car diesel engine. Emissions measurements were performed using a Horiba MEXA-7500 exhaust gas analyzer, with NOx measurements available on two separate lines (for raw and post-catalyst measurements). Figure 1 shows a schematic diagram of the experimental measuring apparatus. Photographs of the test equipment are shown in Figure 2.

2.2. Method of Testing

This experiment adapted the state for a cooled EGR system. The urea solution was created using reagent-grade urea pellets and distilled water. The urea solution concentration selected for this work was 33% by weight, which is the eutectic solution. The static characterization of the urea-SCR system, specifically the NOx conversion capability of the catalyst, consisted of sweeping through multiple urea flow rates at fixed engine operating points. A total of 29 engine operating points were selected, ranging from 40 to 200 Nm at intervals of 40 Nm and 1250 RPM to 2500 RPM at intervals of 250 RPM, based on common operating points for the 2.5L VM-Motori diesel engine over urban and highway driving schedules in a mid-size sport utility vehicle. The urea flow rates were selected based on the stoichiometric urea flow rate, which is calculated as a function of raw NOx emissions from the engine and the chemical and physical properties of urea, NOx, and ammonia in Equation (5).

$$m_{urea,stoich}= (m_{NO}/FW_{NO})(FW_{NH3})(1/[U : NH_3])(1/Urea) \quad (5)$$

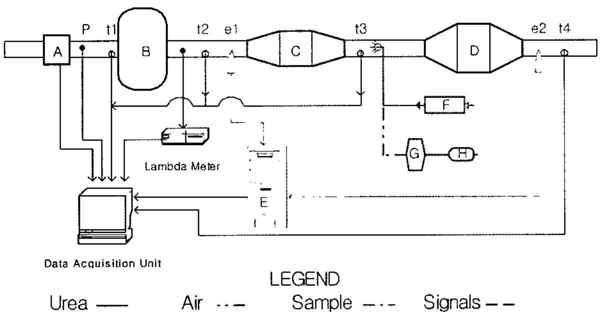
Where: m_{NO}; the raw NO flowrate in [g/s],

FW_{NO}; the formula weight of NO in [g/mol],

FW_{NH3}; the formula weight of NH_3 in [g/mol],

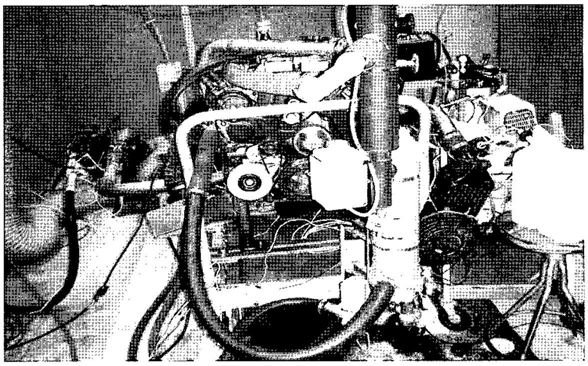
$U:NH_3$; the NH_3 produced from a unit mass of urea,

Urea; the concentration of the urea solution.

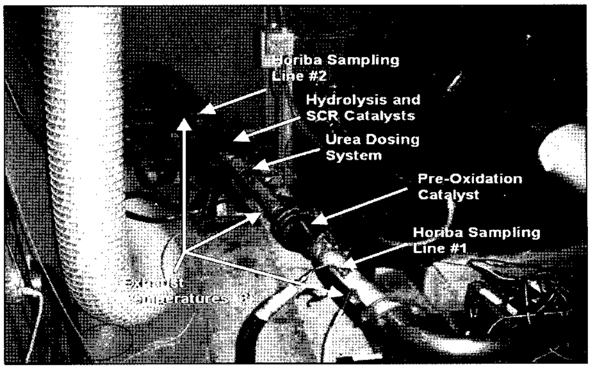


A. MAF Sensor, B. VM 2.5L CIDI Engine
C. Oxidation Catalyst
D. Hydrolysis & SCR Catalyst
E. Horiba MEXA-7500
(e1: NOx, THC, CO, CO_2, O_2, e2: NOx, THC)
F. Urea Syringe Pump G. Air Regulator
H. Compressed Air Tank P. Pressure Sensor
t1 – t4 : Temperature Sensors

Figure 1. Schematic diagram of experimental measuring apparatus.



(a) View of engine equipped with a urea-SCR system



(b) Urea-SCR system experimental setup

Figure 2. Photographs of test equipment.

3. RESULTS AND DISCUSSION

3.1. Urea Flow Rate Mapping

The urea-SCR system was tested at multiples of the stoichiometric urea flowrate, known as the ammonia-to-NOx ratio (ANR), or α, at each engine operating point (Walker *et al.*, 2004). α equal to one (α=1) corresponds to the stoichiometric urea flowrate, and α greater than one (α>1) represents urea flow in excess of stoichiometric flow. The stoichiometric urea flowrate of α equal to one could be delivered without a significant ammonia slip, where-as non-stoichiometric urea flowrate (α>1) can deliver an ammonia slip. Plots of selected cases of the urea flowrate mapping are included in Figures 3 through 5 in terms of the NOx flowrate as a function of α at engine-out and post-catalyst locations. Key factors affecting the NOx conversion efficiency of the catalysts, including space velocity and catalyst temperature, are listed on the plots as well. The three general trends in the data collected are exemplified in the figures above.

Figure 3 represents the case where relatively low NOx conversion efficiency (~56%) is achieved, despite exceeding the stoichiometric urea flow rate (α=4.46) significantly. This can likely be attributed to the low equilibrium catalyst temperature (~185°C) at the engine operating point (1250 RPM, 40 Nm).

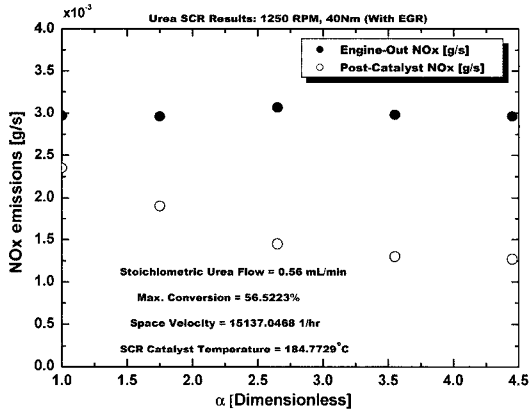


Figure 3. Urea flow rate mapping - 1250 rpm, 40 Nm.

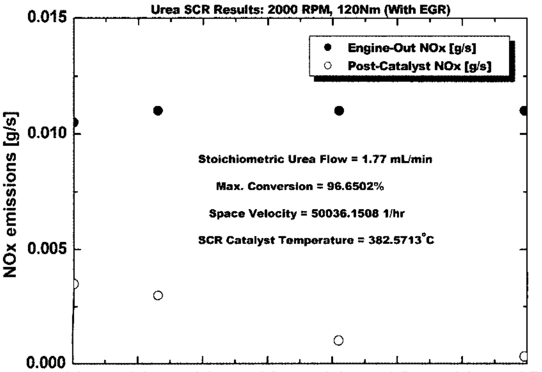


Figure 4. Urea flow rate mapping - 2000 rpm, 120 Nm.

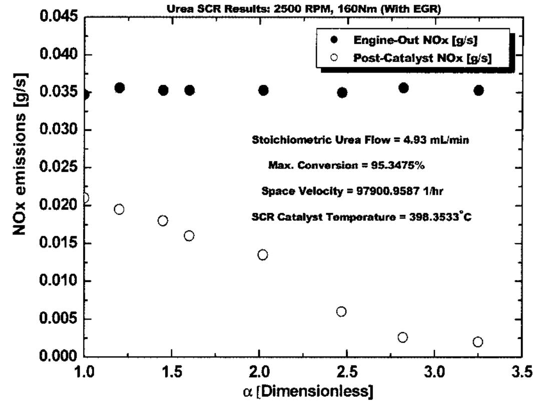


Figure 5. Urea flow rate mapping - 2500 rpm, 160 Nm.

Figure 4 is representative of a second case, where a high NOx conversion efficiency is achieved, even when α is not significantly greater than one. In this case, a 96.6% NOx conversion efficiency was achieved at an α of 1.7 only. This is likely due to the resulting combination of a relatively high catalyst temperature and a low-to-mid space velocity at the engine operating point (2000 RPM, 120 Nm).

Finally, Figure 5 represents cases where high a NOx conversion efficiency is realized, but only when it significantly exceeds the stoichiometric urea flow rate (α =3.26). The catalyst temperature is relatively high at this engine operating point (2500 RPM, 160 Nm), so the high space velocity, which limits the time the exhaust gases are in contact with the SCR catalyst, is the limiting factor for the NOx conversion efficiency. In general, NOx conversion efficiencies for all engine operating points ranged from 50~60% for α= 1 and reached as high as 98% for α > 1.

3.2. NOx Conversion from Urea-SCR

The NOx conversion potential of the urea-SCR system for cases with and without EGR was compiled. This included the NOx conversion potential using stoichiometric urea flow rates and beyond stoichiometric urea flow rates. The results for the urea-SCR system without EGR for stoichiometric and above stoichiometric urea flow rates are displayed in Figure 6 and Figure 7, respectively. The result for the SCR system with EGR for stoichiometric urea flow rates is displayed in Figure 8. Table 1 shows the relationship of the ammonia-to-NOx ratio (ANR) and the maximum value of the stoichiometric urea flow rates. This shows that exceeding the ANR will decrease the NOx reduction efficiency and

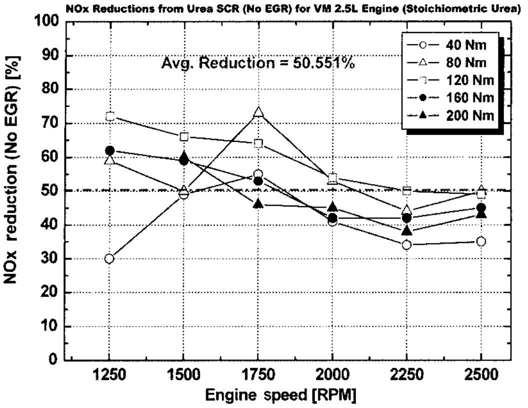


Figure 6. NOx conversion efficiency from urea-SCR (no EGR, stoichiometric urea).

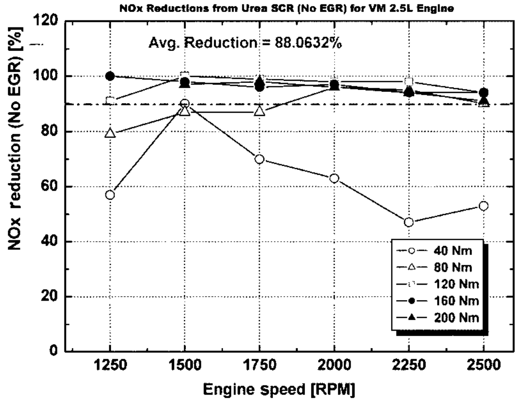


Figure 7. NOx conversion efficiency from urea-SCR (no EGR).

increase the ammonia slip.

The NOx conversion efficiency is typically very good for the urea-SCR system when the stoichiometric urea flow rate is exceeded, with conversion efficiencies approaching 90% for the case without EGR. Also, the NOx conversion efficiency is generally high across the range of engine speeds and torques. Conversely, use of the stoichiometric urea flow rate only introduces significant sensitivity to torque, with the highest conversion efficiency realized for the mid-load operating points (80~160 Nm).

The average conversion efficiency is also significantly lowered for the urea-SCR system using only the stoichiometric urea flow rate. The NOx conversion efficiencies for these cases (EGR active and inactive) were generally limited to 50~60%.

3.3. Space Velocity Effects

Space velocity is a key consideration in catalyst design, and it has a significant impact on the NOx conversion efficiency of a urea-SCR system. Space velocity is defined as the inverse of space time, which is equivalent to the time an exhaust gas takes to move through one catalyst volume. The significance of space velocity is that it defines the time period that the exhaust gases are in contact with the catalyst. As a design consideration, a balance must be reached between time for catalytic activity and excessive by-product formation and/or heat transfer. Space velocity is defined mathematically in Equation (6).

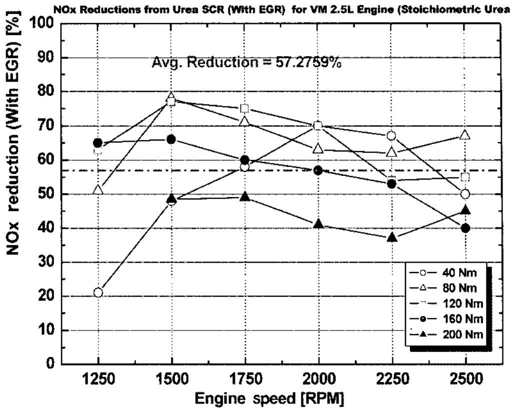


Figure 8. NOx conversion efficiency from urea-SCR (with EGR, stoichiometric urea).

$$SV = (m_{exhaust}/\rho_{exhaust})(1/V_{cat}) \qquad (6)$$

where: SV; space velocity in [1/hr],
$m_{exhaust}$; the exhaust mass flowrate in [g/hr],
$\rho_{exhaust}$; the exhaust gas density in [g/L],
V_{cat}; the catalyst volume in [L].

A map of the NOx conversion efficiency as a function of space velocity and catalyst temperature was generated based on the static urea mapping results presented previously, and it is displayed in Figure 9. The figure shows the trends in NOx conversion efficiency for varying catalyst temperatures and space velocities. As expected, the NOx conversion efficiency increases greatly with increasing catalyst temperature.

The secondary effect of varying the space velocity is also displayed, and the NOx conversion efficiency is adversely affected by an increasing space velocity above the threshold of 40,000~50,000 1/hr. This was anticipated because of the decreased time available for the catalytic reduction of NOx over the catalyst as the space velocity increased.

3.4. Effect of Pre-Oxidation Catalyst Volume

The pre-oxidation catalyst is a vital component of an effective urea-SCR system, and is necessary for high NOx conversion efficiency across a wide range of SCR catalyst temperatures. This is particularly true at low

Table 1. Stoichiometric urea flow rates (SUF), maximum urea flow rates (MUF), and rich ANR.

	rpm		40Nm	80Nm	120Nm	160Nm	200Nm
1	1250	SUF(ml/min.)	–	1.5	2.6	3.5	–
		MUF(ml/min.)	–	6.0	9.1	7.0	–
		Rich ANR	–	4.0	3.5	2.0	–
2	1500	SUF(ml/min.)	1.0	1.3	2.3	4.0	6.4
		MUF(ml/min.)	5.0	9.0	5.1	8.0	20.5
		Rich ANR	5.0	6.9	2.2	2.0	3.2
3	1750	SUF(ml/min.)	1.2	1.9	2.9	4.5	7.5
		MUF(ml/min.)	5.0	6.1	6.1	12.2	21.8
		Rich ANR	4.2	3.2	2.1	2.7	2.9
4	2000	SUF(ml/min.)	1.2	1.8	3.1	4.6	8.3
		MUF(ml/min.)	4.1	5.0	8.1	15.2	22.4
		Rich ANR	3.4	2.8	2.6	3.3	2.7
5	2250	SUF(ml/min.)	1.3	1.9	3.3	5.1	8.2
		MUF(ml/min.)	6.0	7.0	11.9	18.4	24.6
		Rich ANR	4.6	3.7	3.6	3.6	3.2
6	2500	SUF(ml/min.)	1.6	2.5	4.0	5.3	7.7
		MUF(ml/min.)	6.2	8.0	12.0	20.1	25.4
		Rich ANR	4.4	3.2	3.0	3.8	3.3

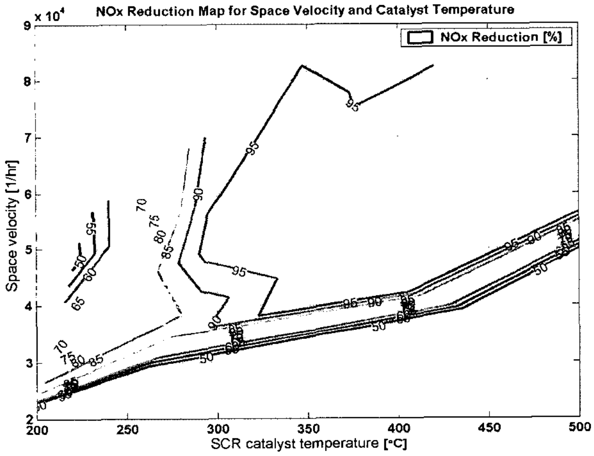


Figure 9. NOx conversion efficiency map as a function of space velocity and catalyst temperature.

Table 2. NO_2/NOx ratio for varying pre-oxidation catalyst volumes.

Engine operating point	NO_2/NOx ratio (V_{cat}=1.2 L)	NO_2/NOx ratio (V_{cat}=0.6 L)
1250 RPM, 40 Nm	0.727	0.179
1250 RPM, 160 Nm	0.131	0.140
1750 RPM, 120 Nm	0.332	0.085
2000 RPM, 120 Nm	0.255	0.071
2000 RPM, 160 Nm	0.285	0.156
2250 RPM, 200 Nm	0.188	0.074
2500 RPM, 80 Nm	0.427	0.130
2500 RPM, 120 Nm	0.295	0.042

SCR catalyst temperatures, where the pre-oxidation catalyst is designed to oxidize NO to NO_2 (to an optimal ratio of 1:1) to allow coupling of the three SCR reduction reactions to maximize the NOx conversion efficiency.

To investigate the effects of the pre-oxidation catalyst volume on the static NOx conversion efficiency, the urea flowrate mapping experiments outlined previously were repeated with the pre-oxidation catalyst volume decreased by 50%. These experiments were conducted at selected engine operating points on different raw NOx emission levels, SCR catalyst temperatures, and SCR catalyst space velocities. To quantify the effect of varying the pre-oxidation catalyst volume, the NO_2/NOx ratio was calculated from measurements at a position just downstream of the catalyst, and the results are listed in Table 2.

Based on Table 1, reducing the pre-oxidation catalyst volume by 50% dramatically decreases the NO_2/NOx ratio, particularly at low-to-mid load engine operating points. Therefore, significant degradation in the performance of the SCR catalyst, particularly at low-to-mid load engine operating points, was anticipated. The results of the repeated urea flow rate mapping experiments are presented in Figures 10 and 11.

The two cases presented in the figures above are

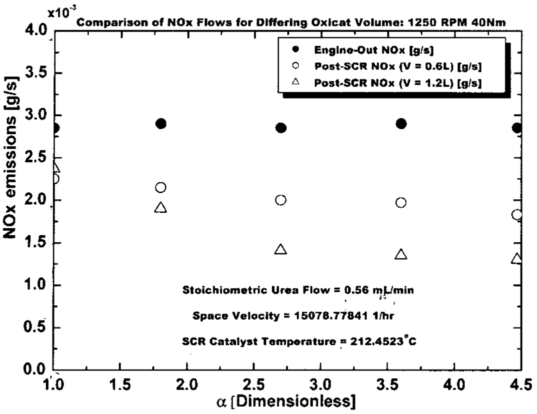


Figure 10. Urea flow rate mapping for varying pre-oxidation catalyst volumes - 1250 rpm, 40 Nm.

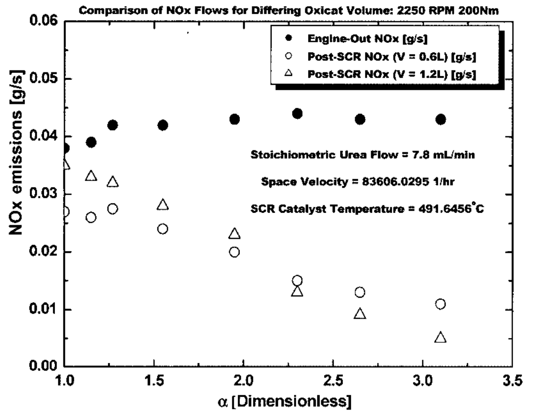


Figure 11. Urea flow rate mapping for varying pre-oxidation catalyst volumes - 2250 rpm, 200 Nm.

representations of the possible effects of the changes in the pre-oxidation catalyst volume. Figure 10 represents a case where the NOx conversion efficiency is adversely affected by the smaller catalyst size. This is largely due to the low SCR catalyst temperature encountered at the operating point (1250 RPM, 40 Nm).

Higher NO_2/NOx ratios are required at low SCR catalyst temperatures to allow for high NOx conversion efficiency through a coupling of all of the SCR reactions. The half-volume pre-oxidation catalyst does not produce sufficient NO_2 for this to take place.

Figure 11 is the representation of cases where the pre-oxidation catalyst volume does not drastically impact the NOx conversion efficiency. In this case, the likely cause is the high SCR catalyst temperature at the operating point (2250 RPM, 200 Nm). This makes the NO_2/NOx ratio, which is of the utmost importance at low catalyst temperatures, less crucial for a high NOx conversion efficiency, as other SCR reactions become dominant.

4. CONCLUSIONS

The NOx emissions limit for US 2007/2010 and Euro IV/V was set at 0.27 g/kWh and 2.0 g/kWh, respectively. These stringent measures calls for further after treatment methods for NOx reduction.

The static characterization results indicate that 50~60% NOx conversion is achievable at most engine operating points tested using the stoichiometric ammonia/NOx ratio, and a NOx conversion as high as 98% is possible by exceeding the stoichiometric NH_3/NOx ratio significantly. The NOx conversion efficiency of the catalysts has proven to be very sensitive to the engine operating point. Factors such as space velocity and, specifically, the catalyst temperature indicated a direct proportionality to the NOx reduction percentage. The pre-oxidation catalyst volume was also found to have a profound impact on the experimental results, particularly for static NOx conversion.

Hence, the results of the static characterization of a urea-SCR system for NOx reduction in diesel engines comply with the US 2007/2010 and Euro IV/V regulations.

REFERENCES

Blakeman, P. G., Chandler, G. R., John, G. A. and Wilkins, A. J. (2001). Investigations into NOx after treatment with urea SCR for light-duty diesel vehicles. *SAE Paper No.* 2001-01-3624.

Gieshoff, J., Schäfer-Sindlinger, A., Spurk, P. C., Van Den Tillaart, J. A. A. and Garr, G. (2000). Improved SCR systems for heavy duty applications. *SAE Paper No.* 2000-01-0189.

Helden, R. Van, Genderen, M. Van, Aken, M. Van, Verbeek, R., Patchett, J., Kruithof, J., Straten, T. and Gerentet de Saluneaux, C. (2002). Engine dynamometer and vehicle performance of urea SCR-system for heavy-duty truck engines. *SAE Paper No.* 2002-01-0286.

Kowalewicz, A. (2001). Lean-burn engine-potential analysis. *Int. J. Automotive Technology* **2**, **4**, 147–155.

Lee, C. H. and Choi, B. C. (2005). Evaluation of NOx reduction catalyst by model gas for lean-burn natural gas engine. *Int. J. Automotive Technology* **6**, **6**, 591–598.

Tennison, P., Lambert, C. and Levin, M. (2004). NOx control development with urea-SCR on a diesel passenger car. *SAE Paper No.* 2004-01-1291.

Walker, A. P., Balkeman, P. G., Ilkenhans, T., Magnusson, B., McDonald, A. C., Kleijwegt, P., Stunnenburg, F. and Sanchez, M. (2004). The development and in-field demonstration of highly durable SCR catalysts systems. *SAE Paper No.* 2004-01-1289.