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ABSTRACT

The 2007 emission standards for both light-duty and heavy-duty diesel vehicles remain a challenge. A level of about 90% NO_x conversion is required to meet the standards. Technologies that have the most potential to achieve very high NO_x conversion at low temperatures of diesel exhaust are lean NO_x traps (LNTs) and Selective Catalytic Reduction (SCR) of NO_x using aqueous urea, typically known as Urea SCR. The LNT has the advantage of requiring no new infrastructure, and does not pose any new customer compliance issues. However, Urea SCR has high and durable NO_x conversion in a wider temperature window, a lower equivalent fuel penalty, and lower system cost. On a technical basis, Urea SCR has the best chance of meeting the 2007 NO_x targets. This paper reviews the results of some demonstration programs for both light- and heavy-duty applications.

INTRODUCTION

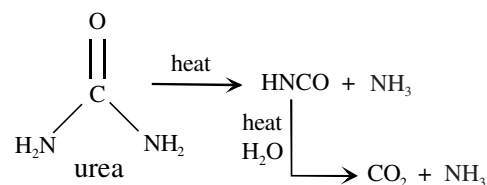
Reduction of NO_x in the lean exhaust gas of diesel engines is not trivial. The 2007 NO_x standards represent a 90+% reduction from previous standards as shown in Table 1. Also shown are NMOG (Non-Methane Organic Gases), NMHC (Non-Methane Hydrocarbon), CO (Carbon Monoxide) and PM (Particulate Matter) standards. In general, the two leading technologies for very high NO_x conversion are Lean NO_x Traps (LNTs) and Selective Catalytic Reduction of NO_x using aqueous urea (Urea SCR).

LNTs contain an oxidative component such as Pt that oxidizes engine-out NO to NO₂ and a storage component (typically an alkali metal salt) that forms a nitrate

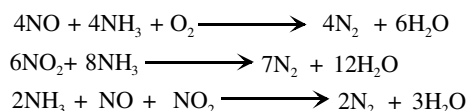
compound releases NO_x that is then reduced to N₂.

The reduction of NO_x with either ammonia (NH₃) or urea has been used extensively for stationary source emission control. NO_x reduction is possible due to the high selectivity of the NH₃ and NO_x reaction to form elemental N₂. The typical reaction scheme using urea is as follows:

urea decomposition:



NO_x reduction:



Urea is the preferred means of delivering ammonia onboard a vehicle because it is safely transported and can be easily injected as an aqueous solution. Urea has a very low toxicity and is widely used as a fertilizer. The mixture with the lowest freeze point (eutectic) with about 32.5 wt% urea in water is preferred.

There have been successful light-duty (LD) and heavy-duty (HD) testing of both LNT and Urea SCR on US emission cycles. Table 2 summarizes the most recent results.

Table 1
2007 standards for LD and HD diesel vehicles.

	NMOG/NMHC	CO	NOx	PM
LD Tier 1 diesel (100k mi)^a	0.31-0.56 g/mi	4.2-7.3 g/mi	0.97-1.53 g/mi	0.10-0.12 g/mi
LD Tier 2 Bin 5 (120k mi)	0.090 g/mi	4.2 g/mi	0.07 g/mi	0.01 g/mi
HD 2004 MY	0.5 g/hp-hr	15.5 g/hp-hr ^b	2.0 g/hp-hr	0.10 g/hp-hr
HD 2007 MY	0.14 g/hp-hr ^c	15.5 g/hp-hr ^b	0.20 g/hp-hr ^c	0.01 g/hp-hr

^a Tier 1 standards vary according to vehicle weight.

^b HD CO standard is carried over from 1998 MY.

^c 2007 NMHC and NOx standards to be phased in from 2007-2010.

Table 2

Summary of reported results from recent diesel technology testing with fresh catalysts.

Application	Technology	Cycle	NOx Conv.	Tailpipe NOx	Ref.
PC	Urea SCR	FTP-75	90+%	0.05 g/mi	1
PC	Urea SCR	US06	90+%	0.05 g/mi	1
PC	LNT (DPNR)	FTP-75	80+% [2]	0.05 g/mi	3
PC	LNT (DPNR)	US06	80+% [2]	0.14 g/mi	3
LDT	Urea SCR	FTP-75	82%	0.17 g/mi	4
LDT	LNT	FTP-75	72%	not reported	5
HDT	Urea SCR	HD FTP	85%	0.86 g/hp-hr	6
HDT	Urea SCR	SET	86%	0.85 g/hp-hr	6
HDT	Urea SCR	HD FTP	90%	0.22 g/hp-hr ^a	7
HDT	Urea SCR	SET	90%	0.18 g/hp-hr	7
HDT	LNT	HD FTP	95%	0.13 g/hp-hr	8 ^b
HDT	LNT	SET	94%	0.12 g/hp-hr	8 ^b

Notes:

All results obtained with very low sulfur diesel fuel (< 30 ppm).

PC = Passenger Car

LDT = Light-Duty Truck

HDT = Heavy-Duty Truck

DPNR = Diesel Particulate - NOx Reduction

FTP-75: Federal Test Procedure for LD vehicles; cold-start three-bag cycle.

US06: High speed, high load cycle for LD vehicles; part of Supplemental FTP.

HD FTP: Heavy-Duty Federal Test Procedure; transient dynamometer cycle.

SET: Supplemental Emission Test for HD; steady-state points.

^a Composite results for HD FTP (1/7 cold, 6/7 hot start).

^b Results obtained with catalyst preconditioning.

The case against using Urea SCR for vehicle applications is twofold: (1) an infrastructure is required to deliver the reductant onboard the vehicle and (2) customer compliance is required to maintain adequate reductant for continuous, high NOx conversion. These issues make Urea SCR difficult to implement, but not

chosen by HD manufacturers to meet Euro IV and Euro V standards [9, 10]. Urea SCR does not have a direct fuel penalty because the engine can be tuned for optimum fuel consumption rather than minimum engine-out NOx, and durability is confirmed for over 500,000 km (> 300,000 mi) [9]. Development of an aqueous urea

not impossible, especially if an approach like co-fueling of diesel and urea simultaneously is adopted [11,12]. Such an approach requires no extra action by the customer other than normal refueling. In fact, refueling a vehicle equipped with either SCR or LNT emission control technologies can be transparent to the end user.

This paper will focus on the technical advantages of Urea SCR over LNT that include wider temperature window for very high NO_x conversion, higher resistance to sulfur poisoning, better thermal durability, lower fuel economy penalty, lower system HC emissions, lower greenhouse gas emissions, and lower system cost.

EXPERIMENTAL

LABORATORY TESTING & AGING CONDITIONS: UREA SCR

Fundamental catalyst activity data were obtained at Ford using a laboratory-scale flow reactor system. A round sample core with dimensions of 1" diameter and 1.5" length was taken from a washcoated cordierite monolith obtained from a supplier. The catalyst was a base metal/zeolite type that did not contain vanadium. Simulated diesel exhaust gas flowed through the sample core at a space velocity of 30k h⁻¹, measured at standard conditions. The composition of the feedgas is shown in Table 3. The composition of the inlet NO_x was varied from 0 to 80% NO₂ (balance NO).

Table 3

Composition of simulated diesel exhaust gas for SCR activity measurement.

Component	Concentration
O ₂	14%
H ₂ O	4.5%
CO ₂	5%
NO _x	350 ppm
NH ₃	350 ppm
N ₂	Balance

Catalyst temperature was maintained with a tube furnace. An FTIR (infrared) spectrometer was used at the reactor outlet to measure NO_x and NH₃. Data were taken at catalyst temperatures from approximately 170 to 600°C in order to cover the normal operating range expected on a diesel vehicle. NO_x conversion was allowed to equilibrate before raising the catalyst temperature to the next level.

SCR catalysts were aged to represent 120k miles via two

core was installed into a tube furnace that was set at 350°C. N₂, O₂, H₂O and CO₂ at the appropriate levels for diesel exhaust were flowed through the catalyst at a space velocity of 30k h⁻¹. SO₃ was generated from SO₂ over a Pt catalyst and added to the gas stream at a level to represent 120k miles of exposure over 24 hours for a range of diesel vehicles from PC to LDT. A future fuel sulfur level of 10 ppm was assumed for this calculation. After aging, NO_x performance was measured without any attempts to remove sulfur from the catalyst. Hydrothermal aging was performed at 670°C and 30k h⁻¹ with N₂, O₂, H₂O, CO₂ and SO₂ at the appropriate levels. An aging time of 64 hours was chosen to represent well over 120k miles based on Ford's projection of accumulated time at high temperature if a diesel particulate filter is periodically regenerating in the system.

LABORATORY TESTING & AGING CONDITIONS: LNT

Monolith cores of LNT samples were tested at Ford in a similar manner to the SCR catalysts except that the reactor feed gas was operated in a cyclic fashion of lean and rich durations. The feed gas concentration and the duration of lean and rich stages were controlled. A typical cycle for the LNT performance measurement contained 25 s of lean condition and 5 s of rich condition. The lean and rich feedgas conditions are shown in Table 4. Total gas flow was 30k h⁻¹, measured at standard conditions.

Table 4

Composition of simulated diesel exhaust gas for LNT activity measurement.

Component	Concentration (lean)	Concentration (rich)
CO	500 ppm	4%
H ₂	167 ppm	1.3%
C ₃ H ₆	300 ppm C ₁	5000 ppm C ₁
NO	500 ppm	500 ppm
O ₂	10%	1%
CO ₂	5%	5%
H ₂ O	5%	5%
N ₂	Balance	Balance
Lambda	1.96	0.90

LNTs were aged under the conditions that may occur onboard a vehicle when removing sulfur from the catalyst (deSO_x). The deSO_x operation is typically done at high temperature (> 600°C) and predominantly rich conditions. For laboratory aging of LNTs, an inlet temperature between 600-700°C was chosen.

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