THE NEW EXHAUST AFTERTREATMENT SYSTEM FOR REDUCING NO_X EMISSIONS OF DIESEL ENGINES: LEAN NO_X TRAP (LNT). A STUDY

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Abstract: *In nowadays, reducing emissions of the nitrogen oxide (NO_x) in diesel engines become a principal goal for the future. The new technology Lean NO_x Trap (LNT, is also known like NO_x adsorber catalyst (NAC) or NO_x Storage and Reduction (NSR) catalyst) can be applied on passenger cars, light and heavy-duty diesel engines to reduce NO_x emissions substantially. The NO_x emissions are absorbed onto a catalyst during lean engine operation. After the catalyst is saturated, the system is regenerated in short periods of fuel rich operation during which NO_x is catalytically reduced. This paper presents a literature review about the function and importance of LNT as the new aftertreatment exhaust system for reducing the NO_x emissions of the new generation of diesel engines.*

Keywords: EMISSIONS, NITROGEN OXIDE (NO_X), DIESEL ENGINES, LEAN NO_X TRAP (LNT), AFTERTREATMENT, EXHAUST SYSTEM

1. Introduction

Lean-burn engines provide more efficient fuel combustion and lower CO_2 emissions compared with traditional stoichiometric engines. However, the effective removal of NO_x from lean exhaust represents a challenge to the automotive industry. In this context, lean NO_x traps (LNTs), also known as NO_x storage-reduction (NSR) catalysts, represent a promising technology, particularly for light duty diesel and gasoline lean-burn applications. Moreover, recent studies have shown that the performance of LNTs can be significantly improved by adding a selective catalytic reduction (SCR) catalyst in series downstream [1].

The lean NO_x trap (LNT) technology is considered as one of the aftertreatment solutions to reduce NO_x emissions from lean burn or diesel engines, those that operate under highly oxidizing conditions. Typically, LNT catalysts usually consisting of precious metals (e.g. Pt, Pd, Rh), a storage element (BaO) and a high surface area support material (e.g. Al_2O_3, CeO_2, ZrO_2), operate under transient conditions that include lean and rich phases. Pt material properties, including dispersion and particle size, are known to be important factors in determining NO_x uptake performance, since Pt provides active sites for NO oxidation to NO_2 necessary for storing NO_x as nitrates, and for the reduction of nitrates to N_2 [2].

LNT catalysts are typically composed of at least one precious-metal component and one alkali or alkaline-earth component which are supported on a high surface area refractory oxide. These catalysts operate in a cyclic manner, whereby the catalyst stores or "traps" NO_x as nitrate species during lean period of operation. Periodically a short rich pulse is introduced so that the trapped NO_x is released and reduced to N_2, thereby regenerating the trapping capacity of the catalyst [3].

The LNT operates by storing NO_x during normal lean operation (when excess oxygen in the exhaust hinders the chemical reduction of NO_x). The LNT must be regenerated periodically by a rich excursion, a brief event in which the exhaust air/fuel ratio (AFR) is driven rich to achieve overall reducing conditions. The excess-fuel derived reductants (HCs, CO, H_2) cause the release and subsequent reduction of the stored NO_x [4].

Reducing emissions of the nitrogen oxide (NO_x) in diesel engines become a main goal for the future, because it's needed to maintain the diesel engine as a propulsion source with highest fuel economy. Due to strict legislation, the automotive manufacturers are forced to adjust to the new requirements on exhaust emissions.

This paper presents the necessity and importance of the LNT catalyst for reducing the NO_x emissions of the new generation of diesel engines. Also, this study wants to show the benefits of this new technology in combination with other catalytic systems.

2. Operating characteristics and performance

Under lean conditions, NO is oxidized to NO_2 in the gas phase over platinum. The resulting NO2 is adsorbed on an oxide surface as barium nitrate. Typical adsorbents include oxides of potassium, calcium, cerium, zirconium, lanthanum, calcium and barium. The sequence of steps is [5]:

Step I: $NO + ½ O_2 \Leftrightarrow NO_2$
Step II: $BaCO_3 + 2NO_2 \Leftrightarrow Ba(NO_3)_2$

At rich air fuel ratios, the adsorbed barium nitrate is released from the trap as barium oxide. In the presence of reducing agents such as CO, HC and H_2 and Pt/Rh catalyst, the NO_x is converted to nitrogen and the trapping constituent, barium carbonate is restored. The sequence of steps is [5]:

Step III: $Ba(NO_3)_2 \Leftrightarrow BaO + 2NO_2$
Step IV: $2\ NO_2 + 2\ CO/HC$ ==Pt/Rh=> $N_2 + 2CO_2$
Step V: $BaO + CO_2 \Rightarrow BaCO_3$

Sulfur present in the fuel acts as a poisoning agent. In the combustion process, the sulfur is oxidized to sulfur dioxide (SO_2). The sulfur dioxide is oxidized to sulfur trioxide in the presence of platinum. The sulfur trioxide is trapped as barium sulfate at the trap operating conditions [5].

NO_x adsorber technology removes NO_x in a lean (i.e. oxygen rich) exhaust environment for diesel engines. The mechanism involves (see figure 1 and figure 2) [6]:
- Catalytically oxidizing NO to NO_2 over a precious metal catalyst;
- Storing NO_2 in an adjacent alkaline earth oxide trapping site as a nitrate;

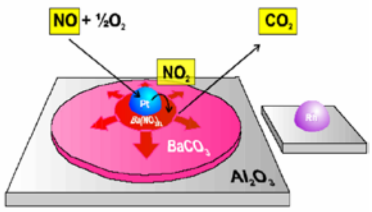

***Fig. 1** The lean NO_x trap running under lean conditions [6,7].*

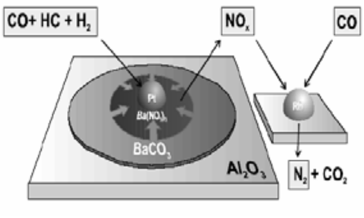

***Fig. 2** The lean NO_x trap running under period regeneration (rich) conditions [6,7].*

- The stored NO_x is then periodically removed in a two-step regeneration step by temporarily inducing a rich exhaust condition followed by reduction to nitrogen by a conventional three-way catalyst reaction.

In order to reduce the trapped NO_x to nitrogen, called the NO_x regeneration cycle, the engine must be operated rich periodically for a short period of time (a few seconds). This cycling is also referred to as a lean/rich modulation. The rich running portion can be accomplished in a number of ways including [6]:

- Intake air throttling;
- Exhaust gas recirculation;
- Post combustion fuel injection in the cylinder;
- In-exhaust fuel injection;

It is likely to dominate for small diesel vehicles, such as passenger cars, at least in the near term, as it is a more cost effective solution for these vehicles than SCR. In a NO_x trap, a NO_x storage component, usually an alkali or alkaline earth metal oxide, e.g. barium oxide, is added to the platinum and rhodium catalyst. Under normal lean diesel conditions this stores NO_x as nitrate, but every 60-120 seconds or so the nitrate regenerates by running the engine with more fuel for a few seconds, so that some carbon monoxide and hydrocarbon can reduce the nitrate to harmless nitrogen [7].

In the scientific work [8], are presented the typical application, estimated cost per vehicle, the advantages and limitations of LNT system. As typical application are the light-duty vehicles with engine displacements below 2.0 liters. Cost 320 $ for engines < 2.0 l and 509 $ for displacement of engines > 2.0 l.

Advantages [8]:

- 70-90% efficiency at low loads;
- Good durability and NO_x reduction performance;
- More economical for engines less than 2.0 l;
- No additional reductant tank is needed (lower packaging constraints);
- Reductant fluid not required (no refills needed).

Limitations [8]:

- NO_x storage capacity is limited by physical size of LNT; Highway and uphill driving can overwhelm the capacity of LNT, leading to high NO_x emission events;
- For engines > 2.0 l, more frequent trap regeneration events are required, leading to additional fuel penalties (around 2%);
- Precious metal usage is high (approximately 10 to 12 g for a 2.0 l engine);
- NO_x adsorbers also adsorb sulfur oxides resulting from the fuel sulfur content, and thus require fuels with a very low sulfur content (< 10 ppm). Sulfur compounds are more difficult to desorb, so the system has to periodically run a short "desulfation" cycle.

Application examples: VW Polo, VW Golf, BMW 2-Series [8].

The Lean NO_x Trap (Fig. 3) is also now known as a NO_x Storage Catalyst or NO_x Adsorber Catalyst [9]. It collects NO_x using compounds that form nitrates under stable conditions in lean operation.

***Fig. 3** The lean NO_x trap [9].*

The LNT was originally used on gasoline direct injection (GDI) engines which could switch between normal gasoline operation (at or around stoichiometric air/ fuel ratios) and lean mixtures. Any sulphur build-up is exhausted by running at an elevated temperature of between 600°C and 700°C. This is rather more easily achieved on gasoline engines which are able to run up to 900°C compared to the diesel engine's 700°C.

In a diesel engine use may be made of the very flexible "Common Rail" fuel system to create a "post" injection to effect the required temperature rise. An unwanted emission from the LNT is that of ammonia. This requires an oxidation catalyst to keep within the European limit of 10 ppm at tailpipe. The reducing chemical equations are [9]:

$$Ba(NO_2)_2 \Rightarrow Ba + N_2 + 2O_2 \quad (1)$$
$$Ba(NO_3)_2 \Rightarrow Ba + N_2 + 3O_2 \quad (2)$$

For diesel LNTs the future challenge is to maximize NO_x conversion at low speed driving conditions as well as providing high NO_x conversion during high speed driving [10].

The Selective Catalytic Reduction (SCR) system is proposed as first choice for large vehicles which require high NO_x conversion efficiencies over high vehicle mileage (such as SUVs for US Tier 2 Bin 5 emission standards). The LNT technology is considered as an attractive alternative for smaller vehicles with lower NO_x reduction efficiency demand (e.g. for EU5 and post EU5 legislation) [11].

A major challenge in the future for LNT technology is desulfurization and thermal aging and thus the long-term stability. Conversely, system packaging in the vehicle including the required SCR catalyst, tank volume and the low temperature activity will be important issues to be solved for SCR technology [11].

A second considerable challenge remains, which is the issue of the infrastructure for the urea distribution, especially in the U.S. The concerns of the EPA regarding this technology remain and have to be addressed by each manufacturer that attempts to launch a diesel vehicle in the U.S. using SCR exhaust aftertreatment [11].

3. System combination between LNT and SCR

The removal of NO_x and particulate emissions in light-duty diesel vehicles will require the use of aftertreatment methods like Diesel Particulate Filters (DPF) and Selective Catalytic Reduction (SCR) with urea and Lean NOx Trap (LNT). A new combination is between LNT and SCR, which enables on-board synthesis of ammonia (NH_3), which reacts with NO_x on the SCR catalyst [12].

The SCR may utilize any NH_3 emanating from the Lean NO_x system to eliminate further NO_x from the tailpipe. This has been used, for instance, on a Mercedes-Benz "Bluetec" vehicle system and may become a much more general approach as the diesel engine OEMs are faced with ever more stringent NO_x legislation [9].

In the case of the LNT/SCR dual bed, again the amounts of NO_x removed are lower at any temperature because of the inhibition of CO_2 on the storage of NO_x. The NO_x removal efficiency is always higher for the hybrid LNT–SCR systems, both dual bed and physical mixture compared to single LNT, in the absence and in the presence of CO_2 and H_2O. This is due to the contribution of NO_x stored onto the LNT catalyst and of N_2 produced by the SCR reactions over the Fe-ZSM-5 catalyst during the lean phase. The presence of CO_2 and H_2O reduces the NO_x removal efficiency over all the investigated systems [13].

J. Wang et al. have studied the effect of simulated road aging on the NO_x reduction performance of coupled Pt/Rh LNT and Cu-CHA SCR catalysts using H_2, CO and C_3H_6 as NO_x reductants [14].

Figure 4 shows the product selectivity for the LNT catalyst and LNT-SCR systems using 2.5% CO as the reductant. As was the case for H_2, the selectivity of NO_x reduction to NH_3 over the LNT is increased after aging. It is also noteworthy that after aging a decrease in the selectivity of NO_x reduction to N_2O over the LNT

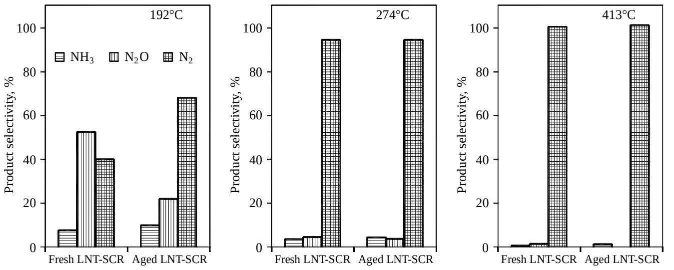

***Fig. 4** Comparison of product selectivity over LNT catalyst and LNT–SCR system using 2.5% H_2 as reductant; top: 192°C; middle: 274°C; bottom: 413°C [14].*

catalyst is observed [14].

The selectivity to N_2O is high at 192°C for both the fresh and aged LNT when CO is used as the reductant, although the low NO_x conversion at this temperature limits the N_2O emission from the LNT in absolute terms. In general, the factors controlling the selectivity of NO_x reduction to N_2O are poorly understood, although catalyst composition appears to play a major role. The nature of the reductant has also been highlighted; however, published data are conflicting on the subject of which reductant affords the highest selectivity to N_2O. This is presumably a consequence of differences in the composition of the catalysts used in these studies, as well as the use of different reaction conditions [14].

In figure 5 [15] is presented a LNT-SCR system for NO_x reduction.

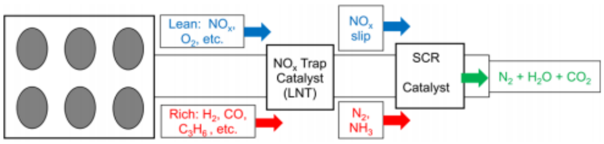

Fig. 5 *Coupled LNT-SCR System for NO_x reduction [15].*

The LNT-SCR system has several significant benefits in comparison with NO_x reduction technologies. Most importantly, the LNT-SCR system requires only fuel as the reductant and therefore eliminates the need and associated cost for the urea infrastructure.
The LNT-SCR system also has several advantages over an LNT-only system. First, the SCR catalyst eliminates NH_3 slip from the LNT by storing it and subsequently catalyzing its reaction with unreacted NO_x from the LNT. Second, the presence of the SCR catalyst relaxes the NO_x conversion requirements of the LNT. Consequently, the LNT catalyst volume in the LNT-SCR system can be lower than for an LNT only system, reducing the precious metal costs for the system. Third, the durability of the LNT-SCR should be superior since the system requires both less frequent and shorter desulfations than an LNT-only system owing to its higher overall efficiency and mitigation of H_2S emissions, respectively [15].

Figure 6 shows an SCR deNO_x system in its most extensive layout. SCR systems for Euro 4 (requiring about 60% NO_x reduction) will generally not have the NO to NO_2 catalysts. Also the hydrolysis catalyst is optional, since the SCR catalyst itself is very effective for hydrolysis. An NH_3 clean-up catalyst may be applied as a safeguard measure. The urea dosage control will be open-loop with look-up tables for NO_x or urea quantity as a function of engine speed and load and catalyst temperature [16].

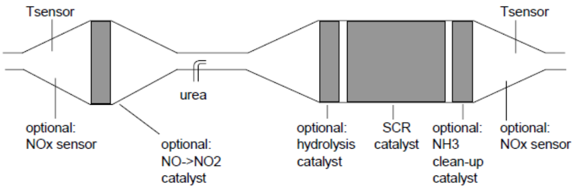

Fig. 6 *Layout of urea SCR deNO_x system [16].*

Primary advantage of a closed-loop control strategy with a NO_x sensor is that urea dosage can be adapted to engine-out NO_x variations due to variations in ambient conditions and fuel quality [16].

Some key differences between EU and US NO_x technology control choices (e.g., the prevalence of LNT in Europe, and the emergence of combined SCR+LNT solutions in the US, likely because this type of solution is ultimately required for compliance with the low-emission bins of US Tier 2 regulations) seem to indicate that the different regulatory frameworks (the US has lower nominal emission limits, more demanding test cycles, and a robust enforcement and compliance program that the EU lacks) have a direct influence upon the technological choices made by diesel passenger car manufacturers [8].

4. System Combination Between LNT, SCR and DPF

Additionally a DPF (Diesel particle filter) may be added to the LNT+SCR system for treatment of particulates. DPFs will become necessary for Euro 6 and beyond as partical number legislation has been introduced for Diesel and DISI Gasoline types [9].

The combination system between Lean NO_x Trap (LNT), Selective Catalytic Reduction (SCR) and Diesel Particulate Filter (DPF) catalysts, is shown in figure 7. Engine NO_x is reduced by the LNT and SCR catalysts. The LNT stores NO_x and undergoes controlled periodic regeneration, releasing the NO_x as nitrogen and ammonia. The SCR collects the released ammonia and uses it to continuously treat the remaining NO_x. A Diesel Particulate Filter (DPF) traps Particulate Matter (PM) and undergoes periodic regeneration [17].

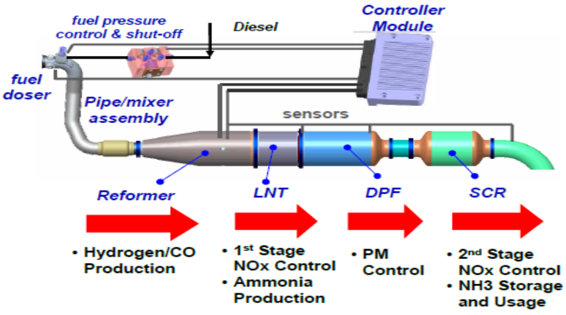

Fig. 7 *Combination system between LNT, SCR and DPF [17].*

5. Conclusions

The lean NO_x trap (LNT) technology is considered as one of the aftertreatment solutions to reduce NO_x emissions from lean burn or diesel engines, those that operate under highly oxidizing conditions.

LNT catalysts are typically composed of at least one precious-metal component and one alkali or alkaline-earth component which are supported on a high surface area refractory oxide.

LNT catalysts usually consisting of precious metals (e.g. Pt, Pd, Rh), a storage element (BaO) and a high surface area support material (e.g. Al_2O_3, CeO_2, ZrO_2), operate under transient conditions that include lean and rich phases.

NO_x adsorber technology removes NO_x in a lean (i.e. oxygen rich) exhaust environment for diesel engines.

For diesel LNTs the future challenge is to maximize NO_x conversion at low speed driving conditions as well as providing high NO_x conversion during high speed driving.

The LNT technology is considered as an attractive alternative for smaller vehicles with lower NO_x reduction efficiency demand (e.g. for EU5 and post EU5 legislation).

A major challenge in the future for LNT technology is desulfurization and thermal aging and thus the long-term stability.

The SCR catalyst eliminates NH_3 slip from the LNT by storing it and subsequently catalyzing its reaction with unreacted NO_x from the LNT.

The presence of the SCR catalyst relaxes the NO_x conversion requirements of the LNT. Consequently, the LNT catalyst volume in the LNT-SCR system can be lower than for an LNT only system, reducing the precious metal costs for the system.

The durability of the LNT-SCR should be superior since the system requires both less frequent and shorter desulfations than an LNT-only system owing to its higher overall efficiency and mitigation of H_2S emissions, respectively.

Further it's recommended more tests and experiments using catalyst systems combined LNT-SCR-DPF and LNT-SCR-DPF with Diesel Oxidation Catalyst (DOC), and the diesel engines tested to be fueled with alternative fuels, such as simple mixtures bodiesel-diesel (with different concentrations of biodiesel), bidoiesel-in-diesel fuel emulsions and water-in-diesel fuel emulsions.

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