

Twin-LNT System for Advanced Diesel Exhaust Gas Aftertreatment

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ABSTRACT

The most significant challenge in emission control for compression ignited internal combustion engines is the suppression of NO_x . In the US, NO_x -levels have faced a progressive reduction for several years, but recently the introduction of the Real Driving Emissions legislation (RDE) in Europe has not only significantly increased the severity of the required emission reduction but now is in the advent of stretching technology to its limits. Emission control is based on engine-internal optimization to reduce the engine-out emissions in conjunction with aftertreatment technologies, that are either Selective Catalytic Reduction (SCR) or Lean NO_x Trap (LNT) based systems. Due to its ability to control high amounts of NO_x , SCR is widely used in heavy-duty applications and is becoming more popular in light-duty and passenger car applications as well. This work in contrast shows that the LNT concept can be enhanced significantly to also offer robust emission control, providing good cold-start capabilities, package advantages and the lack of customer-interaction for refill of the diesel exhaust fluid. As an advanced engineering solution to the problem described, a twin LNT technology package has been designed to provide a wide emission control window, ideal for high and low load dynamic driving. The interactions when cleaning both LNTs from stored NO_x are investigated, the requirements of purges to clean the LNTs from stored NO_x and their performance are analyzed; coupled with an intensive investigation of sulfur storage and release.

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INTRODUCTION

Emission standards are subject to constant revision in order to improve the overall global air quality. Whilst for passenger cars and light duty vehicles these standards were previously based on a defined and evaluated test cycle driven on a vehicle chassis dynamometer, this will be complemented in Europe with the introduction of the Real Driving Emissions (RDE) legislation in 2018 [1], covering a much broader range of vehicle operation conditions. Compared to previous defined test conditions, RDE legislation challenges the emission control with unpredictable drive profiles in terms of vehicle speed, acceleration, ambient conditions, altitude gain etc. Furthermore, cold start requirements are currently subject of discussion and will potentially be added to this legislation in the near future.

One of the biggest challenges in emission control for vehicles with internal combustion engines is the suppression of oxides of nitrogen (NO_x). This holds especially for Diesel engines as their exhaust gas contains an excess of oxygen in its normal mode of operation. This inhibits the basic functionality of a three-way-catalyst as used on spark-ignited gasoline engines, which are typically operating at a stoichiometric air-fuel ratio ($\lambda=1$). Therefore, for the conversion of NO_x on a catalyst in a Diesel engine environment, the supply of an additional reductant is required. The two main aftertreatment technologies to suppress NO_x are Selective Catalytic Reduction (SCR) and Lean NO_x Trap (LNT) or combinations of both. SCR uses an additional liquid as reductant source, the Diesel Exhaust

Fluid (DEF), an aqueous urea solution, which is injected into the exhaust system and generates NH_3 in-situ that is then used to mitigate the NO_x emissions over a dedicated catalyst. The SCR concept can handle large quantities of NO_x without a fuel penalty by increasing the amount of injected DEF and is therefore widely used on heavy duty applications. Drawbacks include the fact that SCR systems are difficult to package due to the required additional tank and dosing system. It also adds weight to the vehicle and requires the customer to refill the DEF-tank. As an alternative, Lean NO_x Traps (LNT) are also widely used, especially, but not exclusively in smaller vehicles with lower feed gas NO_x levels. An LNT stores NO_x on a suitable catalytic surface during the normal lean operation of the engine in form of surface nitrates [2]. When the storage limit is reached, the stored NO_x needs to be converted. This is achieved by a modification of the engine operation parameters to generate a sub-stoichiometric, rich exhaust gas, hence with an excess of hydrocarbons ($\lambda < 1$) for a few seconds until the trap is cleaned. This procedure is called purging and - depending on the feed gas NO_x levels and the storage capability of the LNT - is usually required every few minutes. The additional reductant used to convert the NO_x is fuel, hence each LNT purge deteriorates fuel economy.

The ability of LNTs to extract NO_x from the exhaust mass flow is limited, amongst others, by space velocity. When the exhaust flow is high, e.g. during high load operation of the vehicle, residence time of the gas in the catalyst is short and adsorption efficiency is reduced.

This can be avoided by designing the LNT volume to accommodate the gas volumes that it will be exposed to. Another limitation is based on temperature; for hot exhaust gas, LNT storage efficiency is reduced, at very high temperatures it gets eliminated completely [3]. This report shows how this limitation can be mitigated by adding discrete LNT catalysts further downstream of an LNT close-coupled to the engine, where the exhaust gas temperature is lower.

This approach creates significant challenges, one of which is based on the sensitivity of LNTs to chemical poisoning, especially by sulfur. Sulfur is a constituent of Diesel fuel and is also found in the engine oil; it can deactivate LNTs by forming stable sulfates that block the sites required for NO_x absorption [4]. Even though the sulfur content of fuel in Europe is limited to 10 ppm, sulfur poisoning remains one of the most dominant deactivation mechanism for LNTs. The effect can be mitigated by removing the sulfur from the LNT using a deSO_x strategy, which requires rich exhaust conditions in combination with high temperatures at the LNT (typically >600°C) [5]. Achieving such temperatures in a position far away from the engine may be difficult or even impossible without exceeding temperature limits of engine components (e.g. turbocharger) or catalysts located close to the engine.

The work presented here investigates the performance potential of a twin LNT system. The analysis consists of a combination of tests: vehicle customer usage cycles are used to develop a working performance metric, Synthetic Gas Bench (SGB) investigations determine NO_x storage efficiency and sulfur loading impact and experiments on a transient engine dynamometer demonstrate realistic system performance as function of thermal aging and sulfur poisoning.

All tests have been carried out on LNT samples with identical specification: a fully formulated washcoat, containing oxygen- and NO_x-storage materials as well as precious metals on a ceramic flow-through substrate with 1.3 mm cell pitch (cell density of 400 cpsi) and 0.11 mm (4 mil) wall thickness. A Cu-SCR catalyst was used.

System Configuration

The experiments have been performed on a generic reference layout, consisting of a four-cylinder direct injection Diesel engine with 2.0 L displacement volume and high-pressure EGR. The layout of the aftertreatment is shown in Figure 1 along with the sensor set used, emission lines L1 to L3 and the NO_x sensors S1 to S4 have been installed for analytical purposes only. The lambda sensors are also used to control the actual LNT operation by the engine control unit and can be used for on-board diagnostic purposes as well.

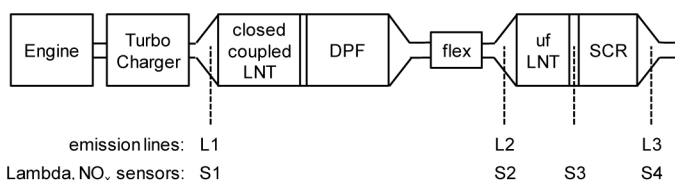


Figure 1. Aftertreatment configuration

The system uses a close-coupled LNT (cc LNT) followed by a Diesel Particulate Filter (DPF). This hot-end configuration is connected via a flexible connection to the underfloor sub-system that holds another LNT (uf LNT) and an SCR catalyst. The SCR is used passively, no urea solution is injected; the NH₃ required is generated by the LNTs located upstream. The dimensions of the components are listed in Table 1.

Table 1. Dimensions of aftertreatment elements

close-coupled LNT	diam. 132 mm, length 136 mm, vol. 1.9 L
DPF	diam. 132 mm, length 146 mm, vol. 2.0 L
underfloor LNT	diam. 144 mm, length 62 mm, vol. 1.0 L
SCR	diam. 144 mm, length 62 mm, vol. 1.0 L

VEHICLE TEMPERATURE TRACES

A vehicle equipped with the aftertreatment system as shown in Figure 1 was instrumented with temperature sensors on all relevant positions. While the vehicle was driving on a road, drive conditions and temperatures were recorded with results displayed in Figure 2. Significant differences in heat-up dynamics and peak temperatures for the positions upstream cc LNT and upstream uf LNT can be seen.

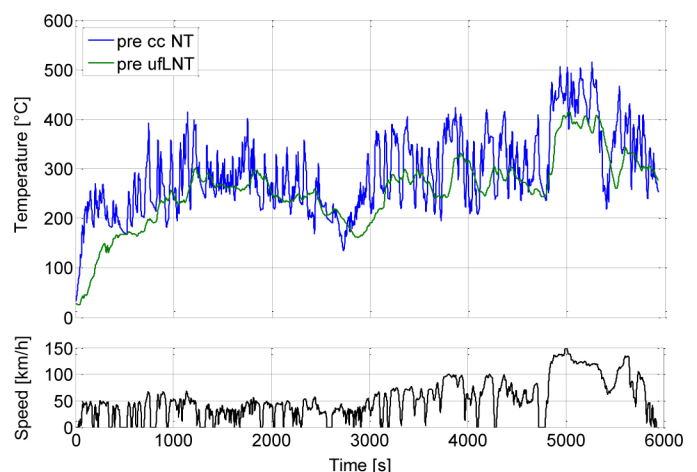


Figure 2. Temperatures in front of the cc LNT and the uf LNT during a customer usage cycle test

For more detailed analysis, temperature histograms are plotted in Figure 3 for three different vehicle speed regimes: < 60 km/h low speed “City”, 60 - 90 km/h mid-speed “Rural” and > 90 km/h high-speed “Motorway”. Except for the cold start phase (City), where the cc LNT has significantly less time below 150°C, the shapes of the graphs are relatively similar - with an offset on the x-axis as exhaust temperature gets lower further downstream. For the rural section, temperatures are higher with separation on the x-axis between the two locations being more pronounced. However, both LNTs are in a favorable temperature range in terms of NO_x storage and conversion. A similar separation is visible on the high speed section, but here the cc LNT is frequently subject to temperatures exceeding 425°C, where NO_x adsorption capability is typically reduced by high temperature. The uf LNT however, remains below 450°C all the time.

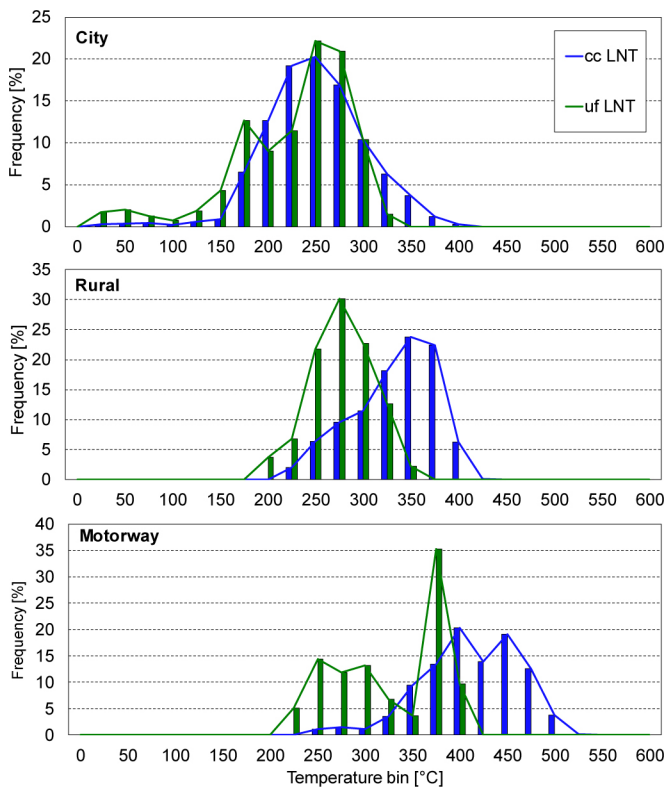


Figure 3. These charts show the temperature histograms for the ccLNT and the ufLNT derived from the real world drive shown in Figure 2. The data has been separated by vehicle speed: city covers points below 60km/h, rural 60-90km/h, motorway faster than 90 km/h.

PURGE CONDITIONS ON TWIN LNT

To improve understanding of the functional aspects of a twin LNT system and to derive relevant conditions for laboratory studies, a representative drive profile was transferred from the vehicle to a transient engine dynamometer. The programming of the dynamometer included engine speed/load and the purge pattern. A comparison of the exhaust temperatures of the vehicle with those recorded on the dynamometer installation showed good consistency. On the dynamometer, emissions are sampled at feed gas position, downstream of the cc LNT, downstream the uf LNT and downstream the SCR (tailpipe position). In addition, temperature, pressure, lambda and NO_x are measured by dedicated sensors upstream of both LNTs as well as upstream of the SCR and at tailpipe position as shown in Figure 1.

In a twin LNT system, both catalysts operate “hand in hand”: for low temperature, e.g. during cold start, the close-coupled LNT is dominant for NO_x control, as it reaches faster its light-off temperature. For high load operation the temperature at the ccLNT can get too high to allow NO_x storage. The slipped NO_x can then be stored by the colder ufLNT.

The effect on NO_x for a real world drive can be seen in Figure 4. The main reduction takes place on the close-coupled LNT. Later in the cycle, where higher temperatures occur, the increasing NO_x breakthrough from the cc LNT is compensated by the uf LNT. The contribution of the SCR is evident as well towards the end of the cycle.

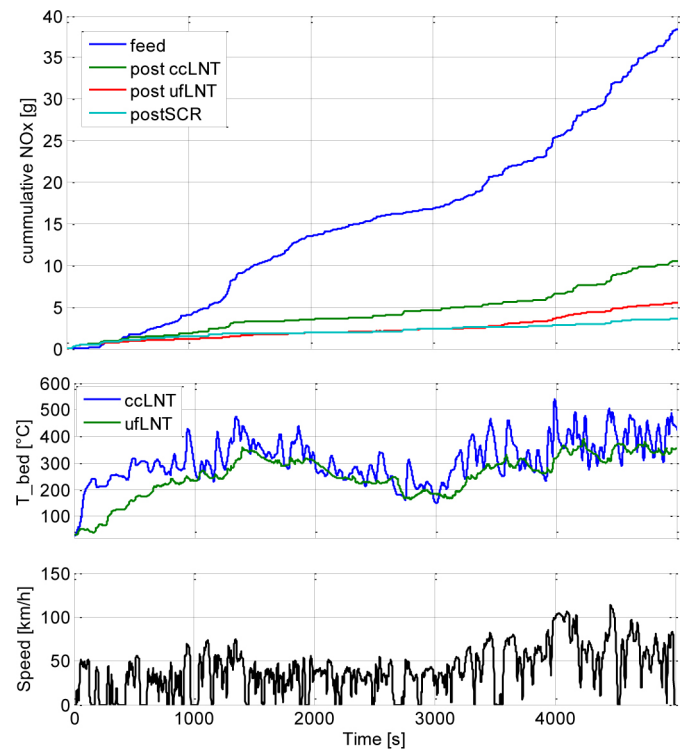


Figure 4. NO_x performance of a twin LNT system. Other than in Figure 2 the displayed temperatures are not measured in front but in the center of the LNTs (bed temperatures).

The sensor set on the dynamometer installation allows a deeper analysis of the performance aspects. Therefore, two typical purge events will be discussed in further detail; one purge at medium and one at high engine load are compared. The transient driving conditions and temperatures are shown in Figure 5, the time of the de NO_x operation is indicated by the vertical red lines.

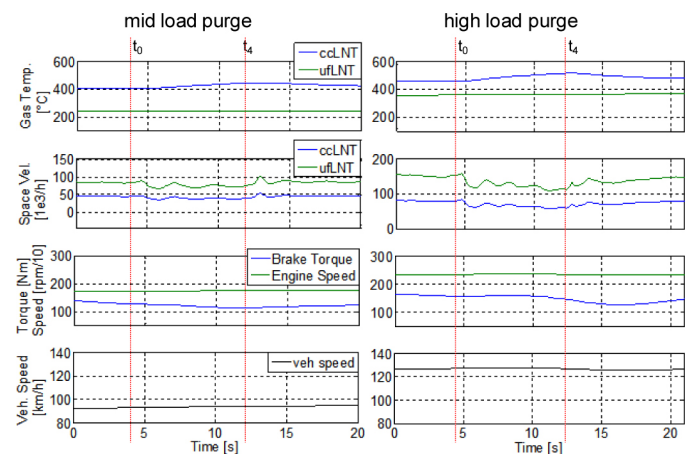


Figure 5. Boundary conditions of a typical mid and high load purge event. These examples are used for more detailed analysis in this report. The red lines denote the start (t_0) and the end (t_4) of the de NO_x purge events.

In Figure 6, lambda profiles of the two de NO_x operations are shown for the four locations in the exhaust system. At $t = t_0$ the engine is switched from conventional lean to rich combustion. This is achieved by engine measures minimizing the airflow and adding last fuel injection. The desired feed gas lambda target is reached at $t = t_1$. The lambda value downstream the LNT is lower than the feedgas after t_2 .

because of the higher sensitivity of the sensor to the produced hydrogen. In Figure 6 - Figure 8 the different emission analyzer response delays are compensated using the oxygen and NO_x sensor signals for each location.

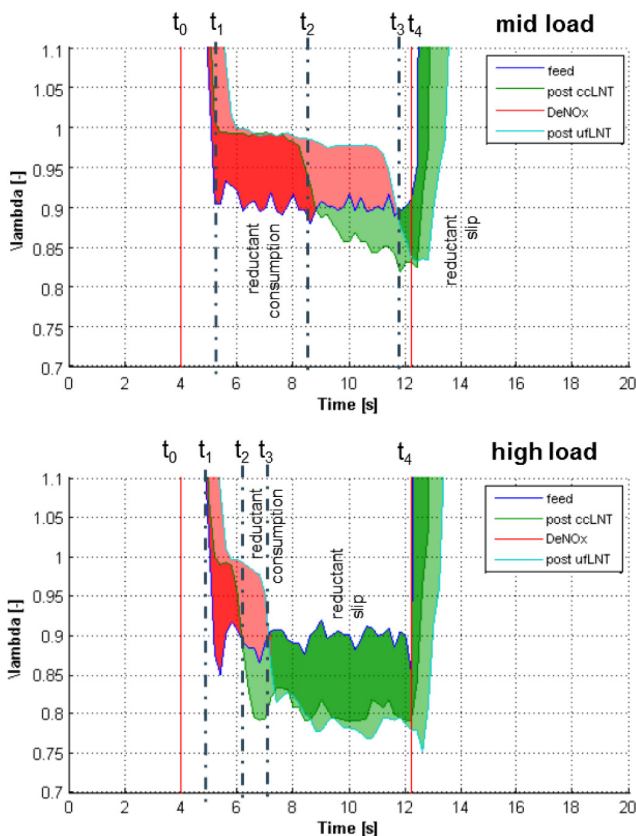


Figure 6. Lambda profiles during deNO_x purges over the twin LNT for mid and high load conditions.

The development of selected gaseous emissions during these events is shown in Figure 7 for the purge event at medium load and in Figure 8 for the high load scenario. The engine out emissions in rich operation conditions contain CO, H₂ and residual fuel (THC, respectively) as reductants as well as NO_x, O₂, CO₂ and water. As soon as rich feed gas emissions are established, at $t = t_1$ there is no more net O₂ measured downstream the cc LNT which is observed by the lambda (oxygen) sensor. The oxygen signal from the emission analyzer is not appropriate for the analysis as the response is too slow and accuracy is limited for such low level of oxygen. By using the details from the other reductant emissions as measured in conjunction with the oxygen sensor signal, the reductant utilization can be evaluated.

As LNT catalysts contains oxygen storage components (OSC) as well as NO_x storage components, the reductants in the rich feed gas start to reduce the stored NO_x and O₂. As this process consumes all reductants, there is only limited reductant slip to the uf LNT at this stage. This changes at $t > t_2$ when the cc LNT is fully reduced and reductants start to breakthrough and become available for reduction on the uf LNT.

The reductant composition that is fed into the uf LNT is different compared to the engine out reductant composition that reached the cc LNT. During the purge, the first LNT emits a certain level of NH₃, which is a product of reduced nitrates.

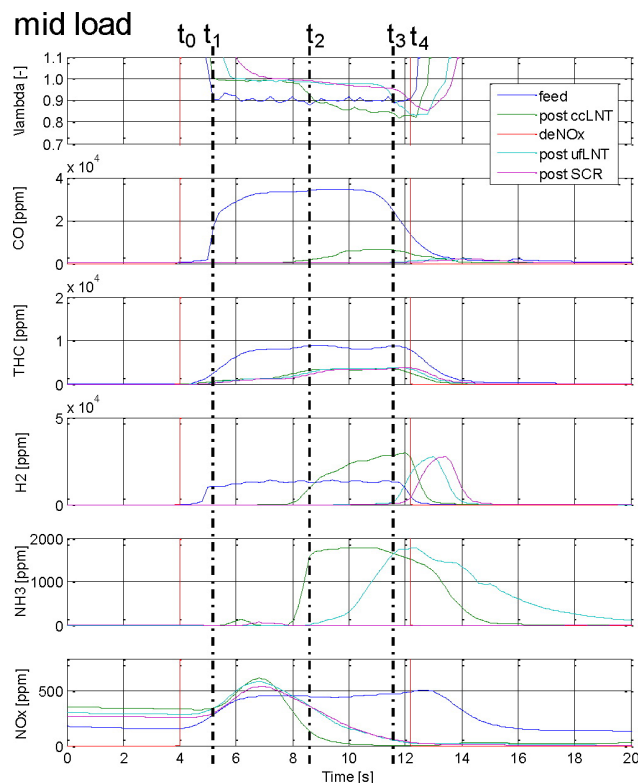
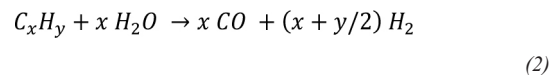
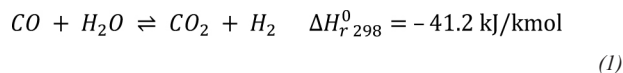


Figure 7. Lambda, CO, THC, H₂, NH₃ and NO_x in deNO_x over the twin LNT system for a purge at medium load conditions. Note that the NH₃ analyzer is saturated at 1800 ppm.

Carbon monoxide and water that is produced during rich operation of the engine is partly oxidized and converted to hydrogen in the LNT by the water-gas-shift (WGS) reaction (Equation 1). This exothermic reaction is the source of the increased hydrogen concentration downstream of the first LNT. In addition, the steam reforming reaction (SR) starts to play a role at higher temperatures, where hydrocarbons are reformed to carbon monoxide and hydrogen (Equation 2). This is a strongly endothermic reaction where higher temperature raises both the kinetic rates as well as the thermodynamics driving the reaction toward production of hydrogen and carbon monoxide.



During the phase of reductant consumption in the cc LNT there is still a NO_x slip into the uf LNT. After the reductant breakthrough ($t > t_2$), NH₃ emission is measured downstream of the cc LNT. At $t > t_3$, also the uf LNT is reduced and starts to emit NH₃. Shortly after this (t_4), the engine operation mode is swapped back to lean and the purge is being stopped. The NH₃ produced by the uf LNT is stored in the passive SCR and utilized for further NO_x reduction in the lean operation state afterwards. There is no NH₃ breakthrough downstream of the SCR at any time.

Under high load conditions (Figure 8), the reductant breakthrough is much faster than for the mid load condition due to higher mass flow and increased space velocity.

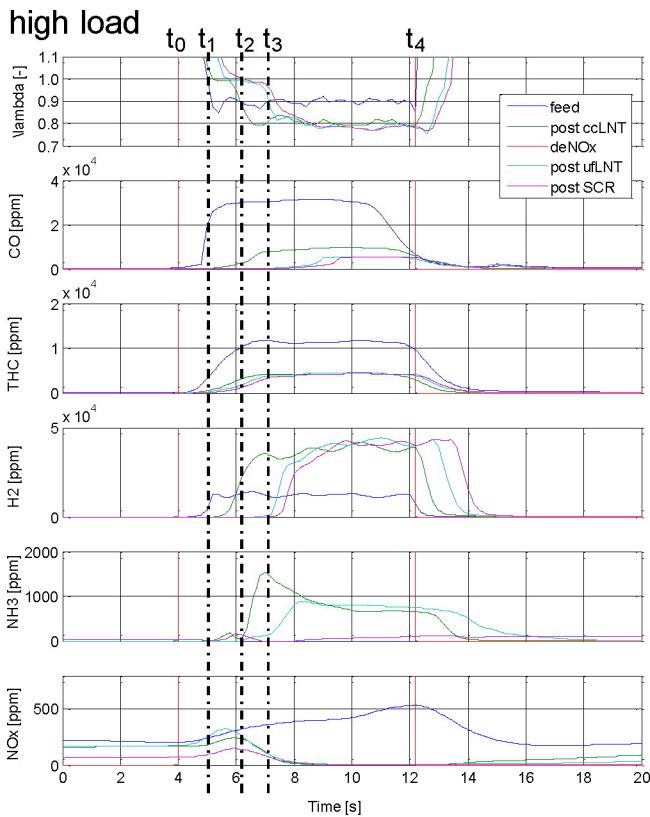


Figure 8. Lambda, CO, THC, H₂, NH₃ and NO_x in deNO_x over the twin LNT system for a purge at high load conditions

Analysis of Rich Purges

A detailed breakdown of the rich purge transformation under medium and high load is presented in Figure 9 and Figure 10 where all reductant amounts are converted to their O₂ equivalents for full oxidation. The oxygen content of the feed gas could not be measured directly because of too slow detector response and lack of accuracy for such low concentrations. Instead, the O₂ in the feed gas is calculated using backward correction for NO_x removal and oxygen storage capacity for the cc LNT and the uf LNT. This method resulted in reasonable O₂ feed gas levels of 0.95 vol% and 0.34 vol% for the medium and high load purge, respectively.

During the medium load purge (Figure 9), 70% of the hydrocarbons are converted over the cc LNT, but no further conversion takes place over the catalysts further downstream. Also, almost 90% of the CO is converted over the cc LNT, whilst the amount of H₂ remains constant, likely as a result of WGS and SR activity that balances its consumption as H₂ is the most reactive reductant to convert. The uf LNT consumes almost all CO and 50% of the H₂ that is emitted by the cc LNT. For both LNTs, about half of the consumed reductants are used for NO_x conversion to N₂ and the other half is consumed to reduce the OSC. There are also significant amounts of NH₃ generated over the LNTs and consumed by the SCR. More detail on the NO_x balance is given in the paragraph on NO_x cycles. Overall, 32% of the reductant remains unused, some of that being CH₄ in the total hydrocarbon part.

In contrast, the high load purge (Figure 10) delivers more than double the amount of reductants compared to the medium load purge due to the higher space velocity. The cc LNT operates in a very favorable

regime for SR and WGS, as 66% of the THC and 73% of the CO are converted, mainly to form a large amount of H₂. The second LNT again does not convert additional hydrocarbons, but shifts the WGS equilibrium even more to H₂, meanwhile converting 60% of CO and only removing 5% H₂. Because of the higher temperatures and larger amount of reductant, more reductant is consumed by the OSC. Only 27-31% of the reductant consumption leads to NO_x conversion and hence N₂. Overall, 70% of the reductants remain unused, even though a large amount of H₂ is available. Clearly, the length of the purge is not sufficient to convert the amount of NO_x stored and further optimization is possible. However, as an advantage of the large reductant breakthrough, production of NH₃ is also larger (Figure 8), mainly from the reduction of engine out NO_x. The amount of reductants consumed during the medium and high load purges over the cc LNT and uf LNT are almost identical.

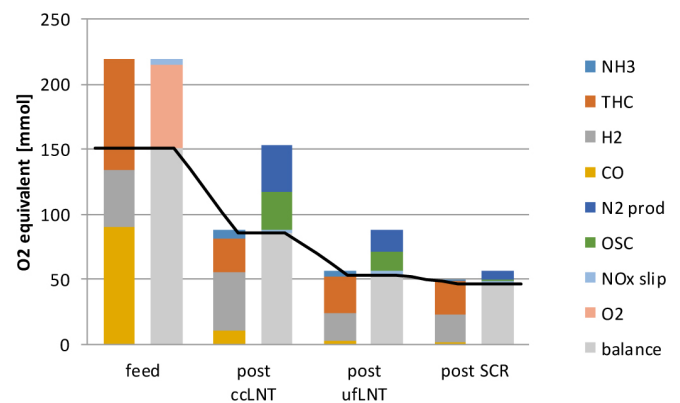


Figure 9. Analysis of medium load rich purge, all reductant amounts are converted to their O₂ equivalents for full oxidation. The first stacked bar shows reductant distribution, the second stacked bar shows the reductant/O₂ balance and consumption during the purge over the specific element. The black line highlights the balance.

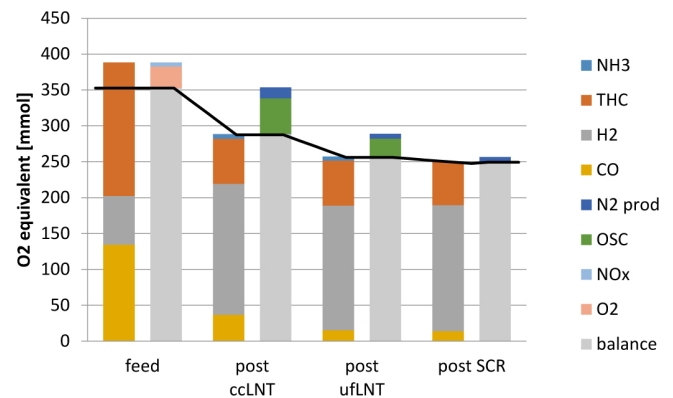


Figure 10. Analysis of the high load rich purge, analog to Figure 9

Analysis of the NO_x Lean Plus Rich Cycles

In order to discuss NO_x performance of the three catalytic elements in more detail, the NO_x mole balances over the LNTs are depicted in Figure 11 and Figure 12. In these mole balances, the amounts of N₂ produced are derived from the mole balance calculation in Equation 3.

$$NO_x^{\text{stored}} + NO_x^{\text{rich,in}} + NH_3^{\text{rich,in}} = N_2^{\text{produced}} + NO_x^{\text{rich,out}} + NH_3^{\text{rich,out}} + NH_3^{\text{stored,SCR}}$$

(3)