

Development of a NO_x Storage-Reduction Catalyst Based Min-NO_x Strategy for Small-Scale NG-Fueled Gas Engines

Fino Scholl, Paul Gerisch, Denis Neher, and Maurice Kettner
Karlsruhe University of Applied Sciences

Thorsten Langhorst
Karlsruhe Institute of Technology

Thomas Koch
KIT Karlsruhe Institute Of Technology

Markus Klaissle
SenerTec Kraft-Wärme-Energiesysteme GmbH

ABSTRACT

One promising alternative for meeting stringent NO_x limits while attaining high engine efficiency in lean-burn operation are NO_x storage catalysts (NSC), an established technology in passenger car aftertreatment systems. For this reason, a NSC system for a stationary single-cylinder CHP gas engine with a rated electric power of 5.5 kW comprising series automotive parts was developed. Main aim of the work presented in this paper was maximising NO_x conversion performance and determining the overall potential of NSC aftertreatment with regard to min-NO_x operation.

The experiments showed that both NO_x storage and reduction are highly sensitive to exhaust gas temperature and purge time. While NO_x adsorption rate peaks at a NSC inlet temperature of around 290 °C, higher temperatures are beneficial for a fast desorption during the regeneration phase. Combining a relatively large catalyst (1.9 l) with a small exhaust gas mass flow leads to a low space velocity inside the NSC. This enabled long storage periods up to 40 min with purge times of around 40 s. At constant engine power, the NSC system allows reducing tailpipe NO_x emissions by up to 92 % (NO_x ≈ 22.5 ppm) compared to lean-burn operation at MBT spark timing, while showing a fuel penalty of < 2 %. An oxidation catalyst positioned upstream of the NSC only proved beneficial to reducing HC emissions, while not affecting neither NO_x and CO output but increasing fuel penalty due to reduced NO_x storage capacity.

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INTRODUCTION

Small cogeneration or CHP (combined heat and power) units below $P_{el} = 50$ kW have become an important pillar of energy supply in many countries worldwide. Most units use lean-burn ($\lambda > 1$) internal combustion engines to generate heat and electric power from natural gas, achieving high overall efficiencies, thus contributing to future CO₂ reduction targets. Lean-burn operation is characterised by a variety of advantages over stoichiometric operation ($\lambda = 1$): While attaining high thermal efficiency at relatively low emissions, heat losses, knock tendency, peak combustion pressure as well as combustion and exhaust gas temperatures are reduced. As a result, stress on the engine and its components is reduced, allowing for long life-cycle times. While reducing engine-out CO and HC emissions is manageable by the use of an oxidation catalyst (OC) allocated downstream, the steady tightening of NO_x limits is one of the main challenges that CHP engine developers are facing. NO_x can be

reduced by decreasing combustion temperatures through additional charge dilution (further leaning) but this usually leads to a drop in engine power and efficiency and increases cycle-by-cycle variations (CCV) for naturally aspirated engines and is limited by the lean-burn limit (see Figure 1). One promising way to achieve very low NO_x levels, beyond those obtainable by in-cylinder measures affecting the combustion, is reducing tailpipe emissions using a NO_x storage catalyst (NSC).

NO_x storage catalysts, also referred to as NO_x storage-reduction (NSR) catalysts, Lean NO_x Traps (LNT) or simply NO_x Absorbers were first introduced in series automotive engines by Toyota in the mid-90s to reduce NO_x emissions during lean-burn operation [1]. Ever since, they have been introduced in series aftertreatment systems for both diesel and petrol applications and have attracted much research activity. Their working principle is very similar to that

of a conventional three-way catalyst (TWC), the main difference being an additional coating material to adsorb NO_x during the lean, overstoichiometric phase. Typical NSC formulations contain precious metals such as platinum (Pt) and rhodium (Rh) and an alkali or alkaline earth metal storage component such as barium (Ba), potassium (K) or caesium (Cs), supported on a high surface area material, usually alumina (Al_2O_3) or cerium oxide (CeO_2). In most of today's NSC, BaO is used for adsorbing NO_x due to the good compromise between storage efficiency and resistance against thermal ageing [2].

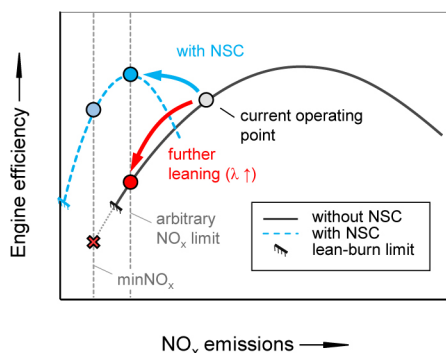


Figure 1. Qualitative trade-off between engine efficiency and NO_x emissions for lean-burn operation and target when operating the engine using a NO_x storage and reduction aftertreatment system.

The process of NO_x storage and regeneration is of very complex nature, being influenced by a large number of factors inherent to the choice of catalyst materials (e.g. type and ratio of noble metals and washcoat composition) and the operating conditions (employed fuel, catalyst temperature, AFR...). However, it is generally accepted that the working principle follows the simplified steps depicted in Figure 2, shown exemplarily for a Pt/Rh/Ba catalyst:

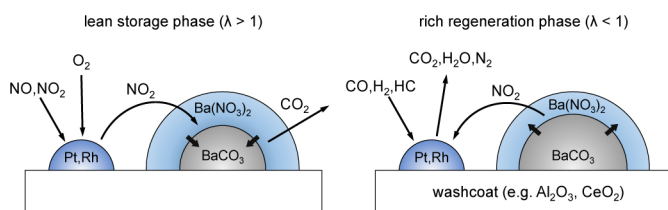


Figure 2. Simplified reaction scheme during the storage and regeneration phases for a Ba-based NO_x storage and reduction catalyst

During the lean storage phase (adsorption), NO is oxidised to NO_2 on the precious metal sites, which then reacts with the alkali/alkaline earth metal sites to form nitrates and nitrites (NO_x storage). In the case of barium-based catalysts, BaCO_3 is the stable carbonate form of the adsorbing material present when the storage site is not saturated. During NO_x adsorption, the carbonate decomposes while releasing CO_2 , giving way to the formation of the stable NO_x -containing compounds $\text{Ba}(\text{NO}_3)_2/\text{Ba}(\text{NO}_2)_2$. During the much shorter rich regeneration phase (purge), NO_2 is released from the nitrate or nitrite sites and reduced to N_2 at the catalytic elements by reducing agents CO, H_2 and HC, products of the impartial combustion inside the combustion chamber. During the purge, H_2 proves to be the most effective reductant at low temperatures, while CO and HC require higher temperatures to effectively regenerate the catalyst surface [3].

Different catalytic materials are reported to have different functions during the phases of storage and regeneration: Platinum seems to be necessary for NO_x oxidation and consequently a high NO_x storage performance during the adsorption phase, whereas rhodium is needed for the NO_x reduction capability to N_2 during the purge [4, 5].

The maximum NO_x storage capacity and conversion efficiency of commonly used NO_x storage-reduction catalysts is reached at temperatures of around 250 - 450 °C [1, 2, 5, 6, 7, 8, 9], depending on noble metal loading, washcoat formulation, exhaust gas composition and catalyst ageing condition. A high storage capacity is desirable as it allows either decreasing the catalyst's dimensions and, thereby, the amount of precious metals (reduced costs), or lengthening the adsorption phase, thus reducing fuel penalty caused by the cyclic purge.

In comparison to transient automotive application, operation of small stationary gas engines shows several benefits that make the use of a NSC particularly suitable:

- Constant engine speed and load (n , IMEP = const.)
- Quite constant ambient and fuel conditions (AFR , p_{amb} , $T_{\text{amb}} \approx \text{const.}$)
- Quite constant exhaust mass flow (space velocity $\text{SV} \approx \text{const.}$)
- Quite constant exhaust gas composition ($\text{NO}_x \approx \text{const.}$)
- Low sulphur content of natural gas

While a vast amount of literature can be found on NO_x storage with lean-burn diesel and petrol combustion, only very little to no work has been published on natural gas or compressed natural gas (CNG) engines. Parks et al. conducted experiments on NO_x aftertreatment using a NSC system on a large-bore 6-cylinder Cummins 8.3-liter lean-burn natural gas engine (see summary of their research activities in [10, 11]). Their setup allowed reducing mean NO_x emissions by over 90 % from the levels emitted by the engine, with fuel penalties ranging between 1.4 and 3.8 %, depending on engine load. To obtain the rich conditions required for regeneration, they injected natural gas into the exhaust system upstream of the NSC (Pt/Ba/K/ Al_2O_3 , 100 g/ft³ Pt $\approx$ 3.53 g/l), which was then partially oxidised by an oxidation catalyst and reformed by a reformer catalyst before entering the NSC. This allowed increasing the fraction of reductants CO and specially H_2 , required for an effective NSC regeneration. The approach of injecting fuel after the combustion chamber was chosen as switching from lean to rich combustion would have supposed difficulties in power control. The exhaust system employed comprised two parallel streams, one containing all catalysts, one being a simple pipe, both controlled by an exhaust brake valve. This allowed reducing the exhaust gas flow, i.e. space velocity, through the catalysts during the cyclic NSC regeneration, thereby reducing fuel penalty. Experiments conducted on a bench reactor for NSC inlet temperatures from 400 to 550 °C (similar to those produced by the engine at 10, 25 and 50 % load) showed that NO_x storage capacity was highest at 400 °C (about 2 g/l NO_2 , $\text{SV} = 30,000$ 1/h), rapidly decreasing with rising temperatures. Lower temperatures were, however, not investigated, probably because of the worsened methane oxidation efficiency of the oxidation catalyst.

The authors of the present paper chose the conventional approach to provide the reductants needed for catalyst regeneration, i.e. by means of a rich impartial combustion. Nevertheless, utilising highly stable methane (main constituent of natural gas) as a reducing agent may present a major challenge, particularly at low exhaust gas temperatures.

SYSTEM DEVELOPMENT AND EXPERIMENTAL SETUP

Modification of the CHP/Gas Engine Test Bed

The NSC exhaust gas aftertreatment systems presented in this paper was developed for a naturally aspirated SenerTec Dachs G5.5 cogeneration engine running on low-pressure natural gas (see technical specifications in [Table 1](#)).

Table 1. Test bed engine specifications

Engine type	SenerTec Dachs G5.5 / swirl port
Nominal speed	2450 rev/min
Rated electric power	5.5 kW
Nominal IMEP	6.1 bar
Compression ratio (geom.)	13.2:1
Stroke/Bore	91 mm / 90 mm
Displacement volume	578 cm ³
Number of valves	2
Ignition system	prechamber spark plug

The series version comprises a fixed Venturi-based gas/air mixer positioned right behind the air filter to create a very lean main air-fuel mixture. An additional electronically controlled enriching valve with a high-resolution stepper motor is allocated about 1500 mm downstream and 500 mm before the intake port to control engine power depending on actual ambient conditions and the fuel's heating value. A prechamber spark plug with constant spark timing in used to induce combustion of the still lean mixture (around $\lambda = 1.5 - 1.6$) inside a heron shape combustion chamber with flat cylinder head and piston bowl. After exhaust valve opening, the hot residual gases are fed to an oxidation catalyst (OC) for reducing both HC and CO emissions and then led through an exhaust gas heat exchanger in order to recover waste heat energy for heating or process heat purposes. Finally, the gas stream flows through a muffler to damp the pressure waves and reduce the emitted noise before exiting the unit. In order to reduce thermal losses to the ambient and increase the thermal efficiency of the installation, the whole unit is surrounded by an insulated casing, leading to an evenly distributed casing temperature of about 80 °C during stationary operation.

For investigating the potential of NSC aftertreatment on this specific engine, the series exhaust system had to be replaced completely (see [Figure 3](#), coloured components): The oxidation catalyst (orange), usually mounted inside the exhaust gas heat exchanger's body, had to be placed outside and canned in order to analyse its effect on the NSC's operation behaviour. After the OC, the exhaust gas stream is split into a double-flow, the top pipe containing a conventional EGR cooler, the

bottom one being a straight pipe with constant diameter. The purpose of this setup is to adjust and control NSC inlet temperature in a window of 200 °C - 360 °C by varying the flow ratio between the cooled and uncooled flow path using adjustable normally-open exhaust-gas flaps in each stream. Cross section of all flow paths was designed so that the influence of flap position on exhaust gas pressure is minimal. The NSC (red) is positioned after the two paths are joined again. After the NSC, the still hot exhaust gas is routed back to the series exhaust gas heat exchanger and cooled down to approximately 120 - 150 °C before leaving the unit. The muffler needed to be removed for packaging reasons. All ducts and catalysts were thermally insulated using high temperature mineral wool.

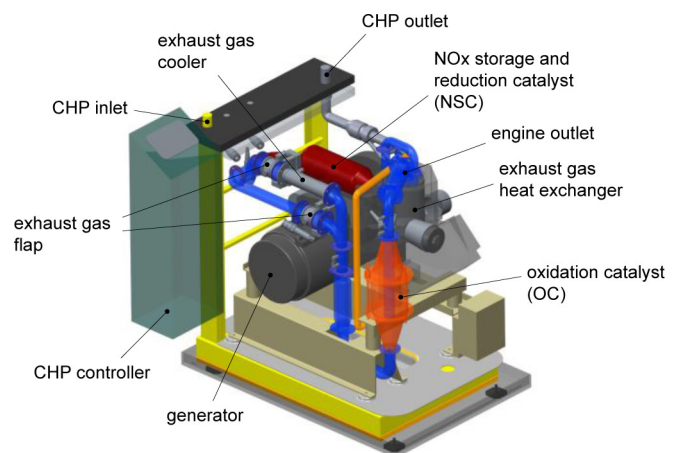


Figure 3. SenerTec Dachs G5.5 test bed with NSC aftertreatment system

Thy cyclic alternation of storage and regeneration phases when operating a NSC system requires an air-fuel-mixing system capable of adjusting the air-fuel ratio (AFR) in a wide band from very rich ($\lambda \approx 0.72$) to very lean ($\lambda \approx 1.7$). Since the series configuration does not provide the high NG mass flows required during the purge, an electronic needle valve with larger cross section was mounted before the Venturi gas/air mixer. The design constraint of the coupled generator with a maximum electric power of 5.5 kW limits IMEP to about 6.1 bar. To avoid an increase of engine power during NSC regeneration, the air mass flow needs to be throttled. For this purpose, the enriching valve was replaced by a throttle valve, also actuated by a stepper motor. In addition, spark timing needs to be adjusted so as to avoid too advanced or too retarded combustion phasing. Therefore, an electronic spark timing adjustment system with a resolution of 0.1 °CA was implemented.

In summary, setup for engine trials, shown in detail in [Figure 21](#) of the [Appendix](#), differs significantly from series configuration:

- Additional proportional NG valve
- Additional throttle valve
- Electronic spark timing adjustment
- Oxidation catalyst positioned outside the heat exchanger
- Considerably longer exhaust gas line
- Removed muffler

A commercial BaO type NSC from a 2010 Mercedes-Benz M276 6-cylinder 3.5 l DI petrol engine that runs in stratified-charge operation [12] was used. The catalyst has a precious metal loading of 100 g/cft (3.53 g/l) [6]. The series oxidation catalyst that was used is optimised for the reduction of methane at rather low exhaust gas temperatures and contains palladium (Pd) as a catalytic element. Specific information on precious metal ratio or the washcoat composition of both catalysts are proprietary information to the catalyst manufacturers, and were not available. Selected technical data are shown in Table 2:

Table 2. Technical data of employed NO_x storage reduction catalyst (NSC) and oxidation catalyst (OC)

	NO _x storage-reduction catalyst (NSC)	Oxidation catalyst (OC)
Precious metal	Pt/Rh	Pd
Precious metal loading	100 g/cft (3.53 g/l)	unknown
Volume [l]	1.9	1.81
Space velocity [1/h]	17,500 (STP)	18,400 (STP)

Especially for a single-cylinder engine, is inevitable that changes in the exhaust gas path would affect the gas exchange inside the combustion chamber. Figure 4 shows the influence of different configurations on the pumping loop. While exhaust pressure is nearly constant during the whole exhaust stroke for series configuration, pressure wave reflection inside the oxidation catalyst lead to the characteristic shape depicted for both configurations with OC. On the one hand, these gas dynamic effects lead to a reduction of the gas exchange work, on the other hand, however, to a negative pressure during valve overlap. This is expected to cause scavenging effects, leading to small amounts of fresh mixture being pushed directly into the exhaust port. In comparison to series configuration, this is reflected in a slightly increased fuel consumption and higher engine-out HC emissions. A positive effect of the lower pressure at gas exchange TDC is the reduction of the residual gas fraction in the cylinder, allowing for lower combustion temperatures and NO_x emissions.

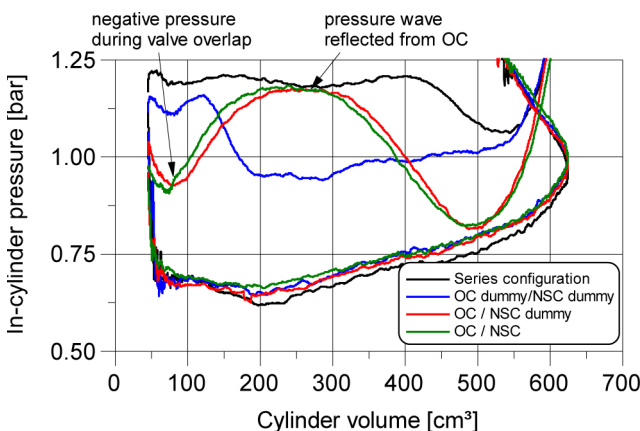


Figure 4. Pumping loop for different exhaust system configurations at WOT, $n = 2450$ 1/min and IMEP = 6.1 bar

The experiments for analysing the interaction of OC and NSC were in part conducted using an OC dummy in form of a straight pipe. The altered gas dynamics lead to an increase of the mean exhaust gas pressure before OC by about 20 mbar, thereby worsening fuel consumption slightly.

Employed Metrology

A Kistler 6125C11 pressure transducer and a 5018A charge amplifier as well as a DEWE-800-CA combustion analyser were used for recording the in-cylinder pressure against crank angle. Combustion attributes such as the mass fraction burnt profile, including combustion phasing in terms of 50 % mass fraction burnt (CA50), were calculated using the fast net heat-release method with a constant polytropic exponent. Fuel consumption was monitored using a Bronkhorst F-103-low Δp thermal mass flow meter for natural gas. Air mass flow was measured using a calibrated hot wire mass airflow sensor (MAF) from Bosch (HFM 5/4.7). Relative air-fuel ratio λ was monitored after the NSC using an ETAS ES635 lambda meter and a Bosch LSU4.9 wideband λ sensor. All gas temperatures were measured using 1.5 mm K-type thermocouples, positioned in the centre of the stream.

As a standard equipment for measuring exhaust gas emissions an ABB AO2020 6-component exhaust gas analyser with heated sample lines was used. Wet total hydrocarbons (THC) are measured as C₃H₈ with a flame ionisation detector (Multi FID 14) and converted to THC (ppmC). Wet NO and NO₂ (NO_x) are measured using a photometer after the DUV-RAS/NDUV (Differential Ultra Violet Resonance Absorption Spectroscopy / Non Dispersive Ultra Violet) principle (Limas 11 HW). Dry CO and CO₂ are measured with an IR photometer (Uras14). Dry O₂ concentration is measured using a Magnos 206 based on the paramagnetic properties of O₂. The analyser is not suited to monitor very fast-changing processes as the ones occurring during the NSC regeneration phase, mainly due to a low sample rate of 1 Hz and long sample lines. For this reason, some trials were conducted using an FTIR (Fourier Transform Infrared Spectroscopy) MKS MultiGas Analyzer 2030 HS with shorter heated sample lines and an increased sample rate of 5 Hz. The device continuously measures the absorbance spectra of the sampled gas stream and is capable of calculating the wet concentration of a wide range of gaseous species under the premise that the molecule has a dipole moment, i.e. it absorbs IR radiation. Hence, chemical compounds such as O₂, H₂, noble gases and homodimers are excluded in general. Emission concentrations such as NO_x, CO and THC were determined online using the proprietary software MG2000 and a proprietary method for natural gas engines (NG Engines HS 5Hz R3).

The results of both analysers were compared beforehand over a wide range of operating points and showed only marginal differences in the level of detected NO_x, CO and THC. Thanks to the heated sample lines in both analysers, both NO and NO₂ were measured on a wet basis. Since NO₂ is highly soluble in water [13], this avoids NO₂ absorption in the condensate of the chiller if measured on a dry basis, therefore allowing accurate NO_x measurements. During NSC

regeneration, CO concentration exceeds the calibrated measuring range ($>1\%$ for MKS and $>0.5\%$ for ABB) and values were therefore extrapolated.

Operation Strategy

The series engine operates with rather late spark timing, mainly to reduce combustion temperatures and the NO_x output. In this work, the chosen approach is to set spark timing to maximum break torque (MBT) at optimal engine efficiency i.e. fuel consumption. This results in significantly higher engine-out NO_x emissions, a disadvantage that is addressed by the use of the NSC, whose function is to store the additional NO_x during the adsorption phase. Since advancing spark timing not only results in better fuel economy but also in higher engine power, the AFR needs to be increased simultaneously. In the case of naturally aspirated homogeneous lean-burn engines, this means leaning the mixture by reducing the injected mass of fuel. Figure 5 shows the effect of spark timing on CA50, the required relative air-fuel ratio λ , engine-out NO_x emissions and absolute fuel consumption m_{fuel} at a constant IMEP of 6.1 bar and wide-open throttle (WOT). Fuel consumption shows a minimum at CA50 = 8 °CA ATDC and was therefore used as standard combustion phasing for all subsequent trials.

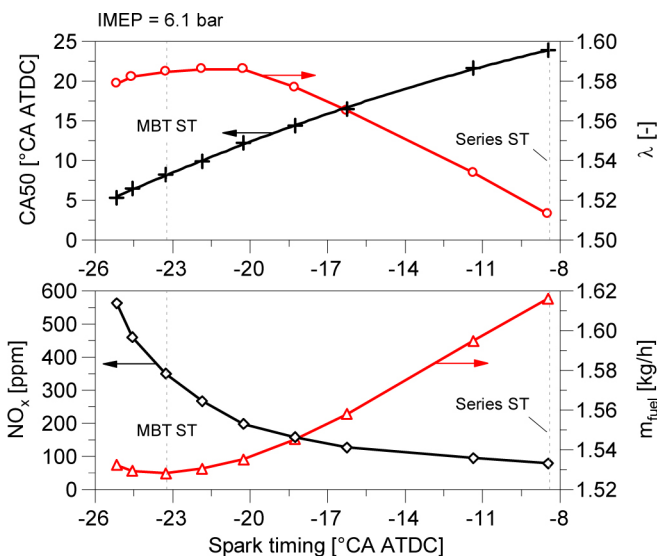


Figure 5. Spark timing sweep for reference configuration with oxidation catalyst (OC) and NSC dummy ($p_{\text{amb}} = 1006.7 \text{ mbar}$, $T_{\text{amb}} = 28.9^\circ\text{C}$)

While operation during the adsorption phase is straight forward (MBT spark timing, constant IMEP, WOT), a strategy that allows enriching the mixture ($\lambda < 1$) for regenerating the NSC once its storage capacity is reached and avoiding leaps in engine power at the same time needed to be developed. Figure 6 shows the timed adjustment of throttle valve, gas valve and spark timing for a purge time of 15 s of the implemented NSC regeneration strategy exemplarily. It accounts for the long pipe length between gas mixer and the inlet port as well as for mixing effects provoked by gas dynamic effects. Both gas valve and spark timing are adjusted in function of the throttle opening grade using a polynomial approach of second order. The required parameters were determined beforehand in steady-state trials.

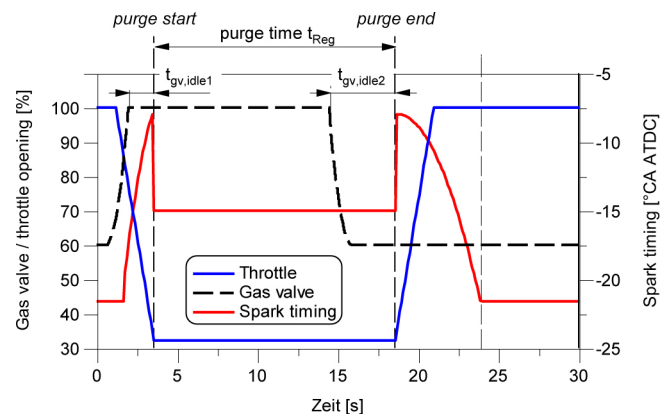


Figure 6. Adjustment of gas and throttle valve opening as well as spark timing over time for a 15 s NSC regeneration

The throttle stepper motor allows adjusting the valve's opening grade at a speed of around $30\%/s$. Starting from WOT, thus it takes 2.4 s to reach the throttle position required for regeneration. As the mixture is created upstream, the idle time between the AFR is adjusted and the richer mixture reaches the cylinder ($t_{\text{gv, idle1}}$) is 2 s. To avoid a drop in engine power, the gas valve needs to be opened before actuating the throttle. As for spark timing, the adjustment starts slightly after since intake port pressure is only marginally reduced during the first few degrees of throttle closing. As λ approaches 1, spark timing needs to be retarded for keeping CA50 at MBT as a result of the increased flame propagation speed. Below $\lambda = 1$ combustion slows down again, counteracted by a sudden advance of spark timing. Subsequently, the actual regeneration begins (purge start) at about $\lambda = 0.72$ (value that was reached at 100 % gas valve opening). The partial oxidation products of the natural gas combustion (mainly CO, H_2 and methane HC) are used to purge the NSC by desorbing the stored NO_2 and reducing it to N_2 . Ending the purging process is slightly more challenging: Due to the reduced mass flow during regeneration, the idle time between setting back the gas valve and reaching lean-burn conditions inside the combustion chamber ($t_{\text{gv, idle2}}$) is increased significantly. Furthermore, the large gas column between gas mixer and throttle valve is still filled with under-stoichiometric mixture at higher pressure that first needs to be consumed. The gas exchange of the engine leads to pronounced pulsations and pressure wave reflections over the whole intake duct. This results in mixing effects that hinder mixture stratification of the aspirated air-fuel mixture, thus only allowing a gradual leaning of the mixture despite rapidly closing the gas valve. This requires a slower spark timing adjustment for returning to the parameters used for the adsorption phase. Purging ends once overstoichiometric conditions are met and both throttle and spark timing begin to set back (purge end). The regeneration phase, on the other hand, is only fully completed once all parameters are set back.

EXPERIMENTAL RESULTS

In this section, experimental results that were obtained using the aforementioned regeneration strategy are presented. Besides analysing the phenomena taking place during the catalyst regeneration phase, the effect of purge time and NSC inlet temperature on storage efficiency, NO_x emissions and fuel consumption as well as the interaction of oxidation catalyst and NSC were of special interest.