

Performance Studies and Correlation between Vehicle- and Rapid- Aged Commercial Lean NOx Trap Catalysts

Jesus Emmanuel De Abreu Goes
 Volvo Car Corporation

Louise Olsson
 Chalmers University of Technology

Malin Berggrund, Annika Kristoffersson, Lars Gustafson, and Mikael Hicks
 Volvo Car Corporation

ABSTRACT

Even though substantial improvements have been made for the lean NOx trap (LNT) catalyst in recent years, the durability still remains problematic because of the sulfur poisoning and sintering of the precious metals at high operating temperatures. Hence, commercial LNT catalysts were aged and tested in order to investigate their performance and activity degradation compared to the fresh catalyst, and establish a proper correlation between the aging methods used. The target of this study is to provide useful information for regeneration strategies and optimize the catalyst management for better performance and durability. With this goal in mind, two different aging procedures were implemented in this investigation. A catalyst was vehicle-aged in the vehicle chassis dynamometer for 100000 km, thus exposed to real conditions. Whereas, an accelerated aging method was used by subjecting a fresh LNT catalyst at 800 °C for 24 hours in an oven under controlled conditions. Engine dynamometer studies were performed with a Volvo mid-sized diesel engine with the purpose of testing the NOx storage and reduction performance, as well as the THC and CO conversion activity of the catalysts under controlled conditions. The aged catalysts activity was shown to be significantly degraded, mainly at low working temperatures compared to the fresh LNT, and one reason for this could be limited NO oxidation. In addition, the oven-aged sample was found to be well correlated to the vehicle-aged catalyst. On top of that, several vehicle emission cycles were carried out in the vehicle chassis dynamometer with a 2.0 l Volvo XC90 diesel vehicle in order to study the catalysts performance under real driving conditions and monitor the gradual deterioration of the vehicle-aged catalyst during the vehicle aging testing.

CITATION: De Abreu Goes, J., Olsson, L., Berggrund, M., Kristoffersson, A. et al., "Performance Studies and Correlation between Vehicle- and Rapid- Aged Commercial Lean NOx Trap Catalysts," *SAE Int. J. Engines* 10(4):2017, doi:10.4271/2017-01-0940.

INTRODUCTION

Carbon dioxide (CO₂) is an important greenhouse gas emitted by natural processes and human activities. After power generation, burning fossil fuels to transport goods and people is the second largest contributor to global CO₂ emissions. Therefore, as a countermeasure to global warming, low-carbon dioxide emission vehicles have been investigated by promoting lean-burn engines and high combustion efficiencies. Nevertheless, the main constraint for this approach is related to NOx emission control. Thermal NOx is formed in the combustion process when nitrogen reacts in an environment of high concentration of oxygen and elevated temperatures. Hence, emission standards have been established to ensure air quality standards and protect the human health by setting quantitative limits on the permissible amount of specific air pollutants. The evolution of emission standards leads to more and more stringent emission limits, which requires the development of efficient NOx abatement materials, technologies and strategies for lean-burn vehicles.

Selective catalytic reduction (SCR) and lean NOx traps (LNTs) are currently the most popular NOx reduction technologies implemented by car manufacturers. High NOx conversion efficiencies can be achieved with the SCR system, however it requires that the temperature at the urea dosing position is above 180 °C, limiting the effectiveness of the system at low engine operating temperatures. This technology also has some cost and space requirements, such as storage tank, urea injection and control system, which limits its implementation in small vehicles. On the contrary, LNTs are a low cost and simple technology that do not require any additional devices and it has a better low-temperature NOx reduction performance compared to SCR system [1]. LNTs store NOx emissions during the lean-burning phase. Subsequently, before NOx slip becomes significant, the nitrous oxides are released and reduced to N₂ over the precious metal during a rich combustion phase. The engine control unit is able to manage the lean/rich transitions by changing engine parameters such as fuel injection quantity and timing.

An efficient LNT is formulated with a NO_x storage component, alkali or alkaline earth metals, and precious metals impregnated on a high surface area support. Particularly, the first generation of LNT was composed by noble metals, barium and alumina [2]. Subsequently, several studies have been focused on the development of more efficient NO_x abatement materials. It is well known that modern commercial LNT formulations generally contain noble metals, Ba, Ce, Zr, Al and many high temperature stabilizers [3, 4, 5, 6, 7, 8]. Platinum, palladium, and rhodium are the most common noble metals used and they are responsible for the catalytic oxidation and reduction of the exhaust emission species. Moreover, ceria is widely known as an oxygen storage support, however it can also contribute in the NO_x storage-reduction process as a supplement to the Ba NO_x storage component [9]. Furthermore, ceria enhances the LNT sulfur tolerance due to its ability of trapping sulfur species, thus reducing their accumulation on the Ba NO_x storage component [9]. Lastly, the addition of zirconium to ceria is reported to inhibit the sintering of ceria and enhance the thermal durability of the catalyst [10].

Although lean NO_x traps have been studied extensively, sulfur poisoning still remains one of the major challenges for this technology. Even with the improved sulfur tolerance and lower fuel sulfur levels, sulfur poisoning still leads to a significant reduction of NO_x storage capacity and conversion efficiency of the LNT. As a consequence, LNTs have to perform periodic desulfurization strategies, in which the catalyst temperature exceeds 650 °C in order to recover its storage capacity [11]. The high temperatures required increase the sintering of precious metals, and storage and support materials. In addition, the interactions between barium and γ -Al₂O₃ support will decrease to form less efficient storage media [11, 12]. However, new formulations show significant improvements in terms of thermal stability to tolerate the desulfation conditions. In addition, desulfation strategies have been enhanced to achieve fast and efficient sulfur removal under real driving conditions [13, 14].

Moreover, the deactivation mechanisms of a particular catalyst depends on the operating conditions which it has been exposed to [15]. For vehicles running mainly in urban environments, the catalyst might be subjected to several interrupted desulfation events due to short transients and low temperature working conditions. Thus, the poisons can accumulate and form chemical compounds with the active catalytic materials, reducing the catalyst effectiveness. On the contrary, for vehicles running in extra-urban driving conditions, the catalysts can be exposed to high temperatures for extended periods of time, thus high thermal degradation could be the primary cause of catalyst deactivation in this case [15]. Both extreme working modes are considered by car manufacturers for the development of the catalysts in order to guarantee the emission performance in the projected life of the vehicle. Thus, long and expensive durability tests have to be performed to assess the catalyst operation after the aging process. Hence, the implementation of alternative methods are being studied by car manufacturers and legislators to reduce durability testing time and cost.

In fact, different accelerated aging procedures have been developed to replicate the catalyst deterioration under real-world operating conditions, achieving an equivalent emission performance in a reduced time. The processes can be performed on a road, vehicle chassis dynamometer, engine rig or in an oven to thermally stress the

catalyst. Since the thermal stress procedures do not include all the effects of the normal real use (abnormal deposition of ash from engine-oil for instance [16]), they need to be properly correlated with on-road aged catalysts in order to have a meaningful demonstration of catalyst durability and fulfil the performance requirements. However, because of the dominant effect of the thermal aging, the most common durability evaluations are based on high temperatures aging and thermal stress methods. There is one study where Benramdhane et al. [4] examined thermal and accelerated vehicle aging on LNTs and observed similar impact on their functionalities. Ottinger et al. [11] studied the thermal aging of fully-formulated LNTs in the flow reactor at different aging temperatures and found different degradation mechanisms depending on the aging temperature. Moreover, Ruetten et al. [17] presented an alternative method of accelerating the catalyst aging by increasing the aging temperatures through modified burner technique.

However, to our knowledge, there are no investigations that focus on the deterioration of a 100000 km vehicle-aged LNT catalyst and studied its correlation with accelerated aging methods. Hence, this study describes Volvo Cars's continuing efforts to explore the deactivation mechanisms affecting the performance and durability of commercial lean NO_x traps through engine bench and vehicle chassis dynamometer experiments. Moreover, this investigation intends to establish a proper correlation between vehicle-aged and rapid-aged LNT catalysts, which is critical for cost effectiveness when evaluating new catalyst formulations.

EXPERIMENTAL

Catalysts

This study has been performed with three commercial LNT catalysts with the same formulation. The catalysts are supported on 1.5 l standard honeycomb metallic substrates with a cell density of 300 cpsi (cells per square inch). The washcoat is deposited on the substrate channels, composed by a modern commercial LNT formulation with 119 g/ft³ of precious metal loading (Pt:Pd:Rh = 95:19:5, see also Table 1).

Table 1. Overview of the catalysts tested

Samples	Fresh catalyst
	Vehicle-aged catalyst
	Oven-aged catalyst
Washcoat composition	Modern commercial LNT formulation
Precious metal loading	119 g/ft ³ (Pt:Pd:Rh = 95:19:5)
Substrate	Metallic
Dimension	124 x 124 x 128 mm (V = 1.546 l)

Aging Methods

Throughout this investigation, the vehicle aging and oven aging methods are evaluated and compared between them. The vehicle aging method provides realistic conditions, however the process requires long durability testing time. Thus, the oven aging approach has been used as an accelerated aging method with the purpose of reducing the total duration of the test by thermally stressing the catalyst in a high temperature environment.

Vehicle Aging

A LNT catalyst was aged for 100000 km in a vehicle chassis dynamometer exposed to real conditions in order to mimic the effect of sulfur and thermal exposure under real driving conditions. The aging was performed in a 2 liter Volvo XC90 diesel vehicle, using standard fuel with 10 ppm of sulfur content. The method consisted of firstly driving a sequence of Standard Road Cycles (SRC) [18] up to a total distance of 60000 km. This cycle can be used by car manufacturers in order to demonstrate the durability of the pollution control devices as it is established in the US and European emission legislations [18]. However, this cycle might not replicate the real driver behavior as the Common Artemis Driving Cycle (CADC), being developed based on a statistical analysis of European real world driving patterns [19]. There are some differences between SRC and CADC, such as the CADC cycle is shifted to lower operating temperatures compared to SRC, which might lead to a reduced thermal deterioration of the catalyst. Moreover, CADC incorporates more transient operating modes than the SRC which might lead to several interrupted desulfation events, which affect the chemical poisoning. In addition, real driving patterns from Volvo Cars users were analyzed, suggesting that a modified Artemis cycle mimic more precisely the real driving behavior. Therefore, the last 40000 km were driven following a modified Artemis cycle, which consisted of four driving schedules: two times the urban cycle, one rural road cycle and one motorway cycle. In addition, vehicle emission cycles were performed along the vehicle aging testing in order to follow the catalyst performance and degradation.

Oven Aging

The oven-aged catalyst underwent an accelerated aging procedure corresponding to 160000 km by subjecting the catalyst to 800 °C during 24 hours in a furnace under a flow of air. The suitable temperature, gas exposure time and gas composition were obtained from the internal database of Volvo Cars.

Engine Bench Testing



Figure 1. Representation of the thermocouples position. T1 and T12 measure the inlet and outlet gas temperatures respectively. The substrate temperatures are measured with the thermocouples T3, T8 and T10 mounted along the axis of the catalyst.

In this investigation, fresh, vehicle-aged and oven-aged catalysts were evaluated in the engine bench by carrying out several performance tests. The systems were tested in close-couple position in a 2-liter Volvo diesel engine attached to an AVL dynamic dynamometer. The emission species were measured before and after the LNT brick by means of a Horiba MEXA-7500DEGR system. A quantum-cascade laser (QCL) was also used to detect ammonia emissions and other species after the lean NOx traps catalyst. The

exhaust gases and substrate temperatures were measured along the catalyst axis to monitor the temperature patterns during the regeneration and NOx storage events, as it is illustrated in Figure 1.

The LNT temperature was calculated as the average substrate temperature measured by the thermocouples disposed along the LNT brick (see Equation 1).

$$T_{LNT} = \frac{T_3 + T_8 + T_{10}}{3} \quad (1)$$

Prior to testing, the fresh LNT sample was first degreened in the engine bench by performing several soot and sulfur regeneration events until the activity of the catalyst has been stabilized. This procedure was also implemented on the vehicle- and oven-aged samples before carrying out the performance tests. It was performed for the vehicle-aged catalyst to ensure the sulfur trapped removal, while it was carried out for the oven-aged to re-activate the catalyst after 24 hours in an oxidant environment. In this way, the variability of the final state of the samples is minimized after the different aging procedures.

Firstly, the catalyst performance has been evaluated in terms of NOx storage at different working conditions. The NOx storage test consisted of a DeNOx or NOx purge event followed by a lean period until the NOx conversion has decreased below 50 % of efficiency. The DeNOx event was composed by a sequence of rich periods of 15 seconds ($\lambda = 0.94$) up to two lambda breakthrough were reached. The lambda breakthrough refers to the point in which the downstream air-to-fuel ratio intercepts the upstream air-to-fuel ratio of the catalyst. The engine operating points were chosen based on representative situations of real driving behavior. They include different inlet exhaust gas temperatures ranging from 180 °C to 450 °C and space velocities between 35000 h⁻¹ and 125000 h⁻¹. The composition of the exhaust gases depends on the fuel injected and the gas mass flow required in order to reach the desired working condition. Figure 2 depicts the engine-out emissions and the LNT substrate temperature for four different space velocities. The water and oxygen concentrations are assumed to be similar over the different space velocities. THC and CO engine-out emissions decrease by increasing the operating temperature. However, NOx emissions rises as the LNT temperature increases, although the NO₂ / NOx ratio is reduced. Additionally, note that the engine-out gas composition vary in a limited range by keeping the LNT substrate temperature constant, hence it is assumed comparable among different space velocities.

Secondly, some representative working points were selected in order to evaluate the NOx purge capabilities of the LNT at different engine operating conditions. The test involved a series of cycles of rich and lean periods until the NOx conversion rate is stable as it is shown in Figure 3. Since the regenerated NOx quantity cannot be measured directly, it is assumed that the NOx stored amount is equal to the NOx purged quantity when the steady conversion rate is reached. Thus, the regenerated NOx amount is computed by the difference between NOx LNT-in and LNT-out during a full rich-lean cycle. In contrast to the previous test, the lambda value and the duration of rich periods vary and the lean periods were determined based on fixed periods of time.

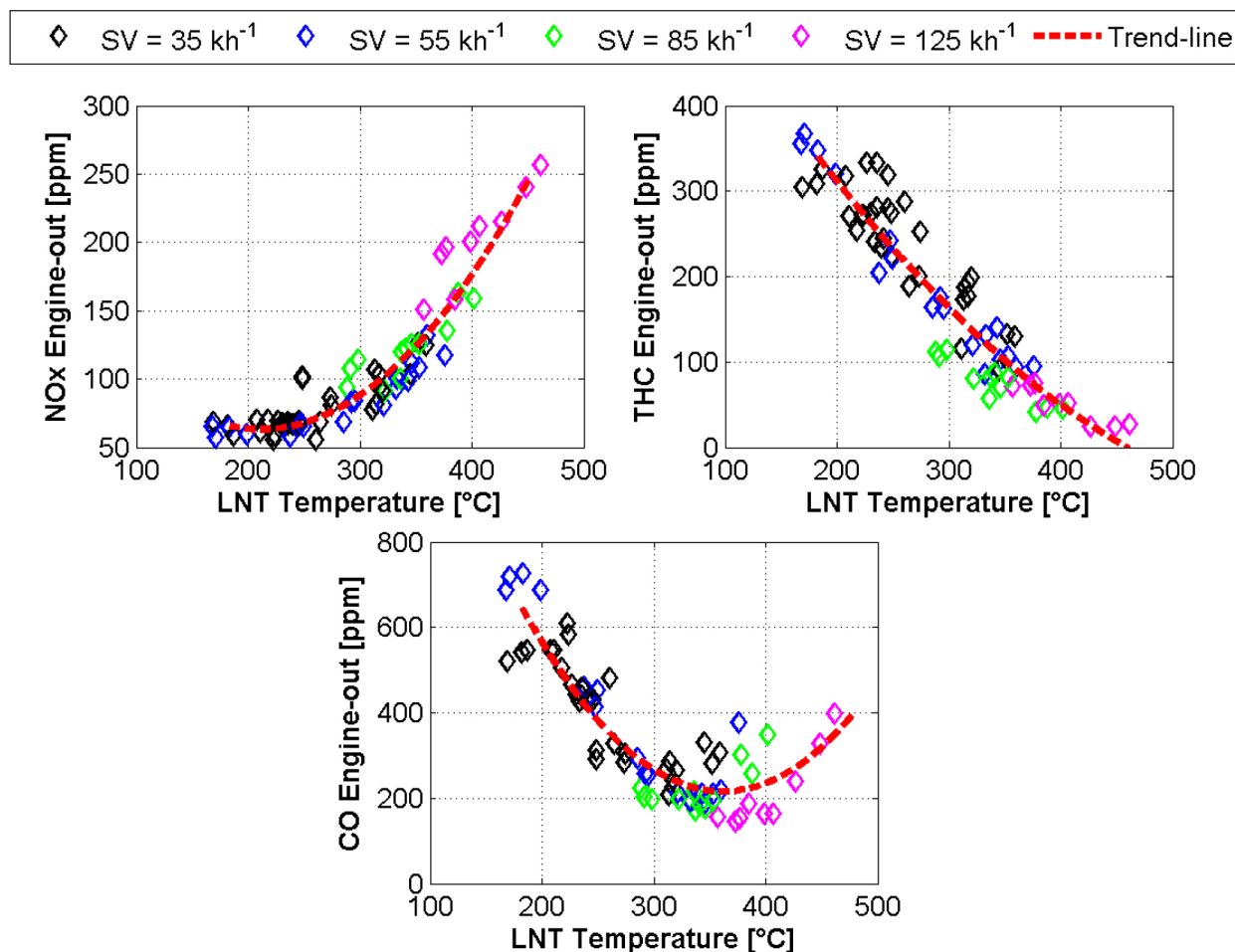


Figure 2. Engine-out emissions as a function of the LNT temperature and space velocity for the LNT NO_x storage test.

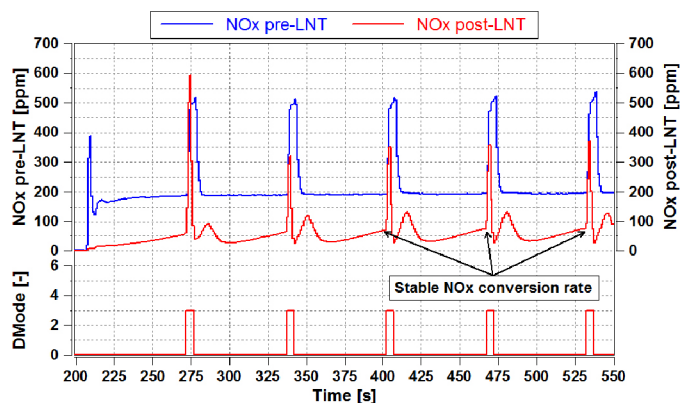


Figure 3. NO_x purge capabilities test representation. DMode means the engine operating mode used: DMode 0 - normal operating mode and DMode 3 - DeNO_x event.

It is observed that during rich periods hydrocarbons (THC) and carbon monoxide (CO) slips through the LNT. Particularly, for instance during cold start periods when the catalyst is less effective due to the relatively low temperature operation. Therefore, THC/CO light-off is important to investigate, especially its performance

degradation with aging under different engine operating conditions. Note that THC/CO light-off represents the temperature at which the catalyst reaches 50 % of THC and CO conversion respectively. The test consisted of executing three different engine operating points with two fuel injection ramps of 15 minutes from 100 % to 0 % of THC and CO conversion efficiencies and vice-versa, as it is illustrated in Figure 4.

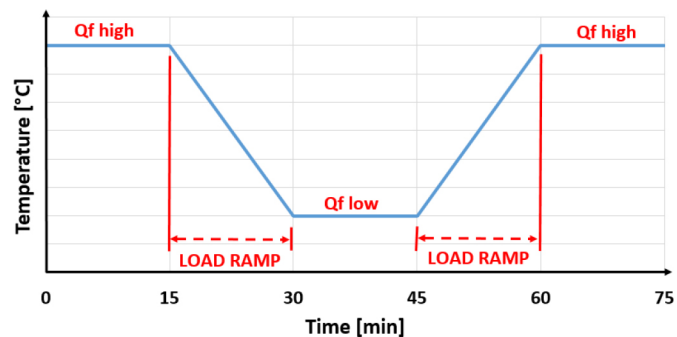


Figure 4. THC/CO light-off test description. Q_f high and Q_f low represent the fuel quantities needed to achieve the proper exhaust gas temperatures able to reach 100 % and 0 % of THC/CO conversion efficiency respectively.

Vehicle Emissions Testing

The performance of the catalysts were also investigated in a vehicle chassis dynamometer by running some vehicle emission cycles, such as New European Driving Cycle (NEDC), Worldwide harmonized Light duty driving Test Cycle (WLTC) and Common Artemis Driving Cycle (CADC). They were conducted in a 2-liter Volvo XC90 diesel vehicle following the procedures and requirements established by the European legislation. The pre-conditioning consists of running the same driving cycle which was successively used for the emission tests. Before the emission tests were carried out, the vehicle remained between 8 to 24 hours in the soak area in order to cool down the engine and reach stable conditions.

In terms of emissions, the engine-out and post-catalyst pollutants were continuously measured with a Horiba MEXA-7100D system. The tailpipe diluted emissions were correspondingly collected in bags and analyzed after the cycle was finalized. Note that a Selective Catalytic Reduction (SCR) system was placed in underfloor position downstream of the LNT since the complete exhaust system was mounted in the vehicle for this test, therefore the tailpipe bag emissions were affected by the SCR performance as well. However, in this study the results are focused on the LNT.

RESULTS AND DISCUSSION

Durability Testing - Vehicle-Aged Catalyst

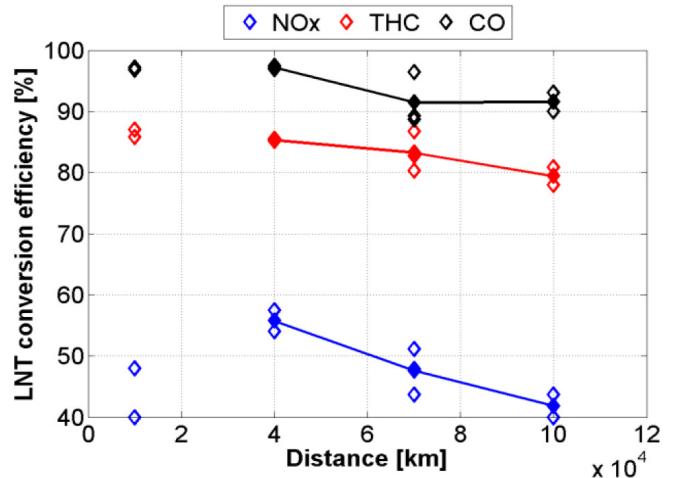


Figure 5. LNT conversion efficiency as a function of the driving distance for the vehicle-aged catalyst. The emission measurements were obtained from WLTC cycles performed each 30000 km.

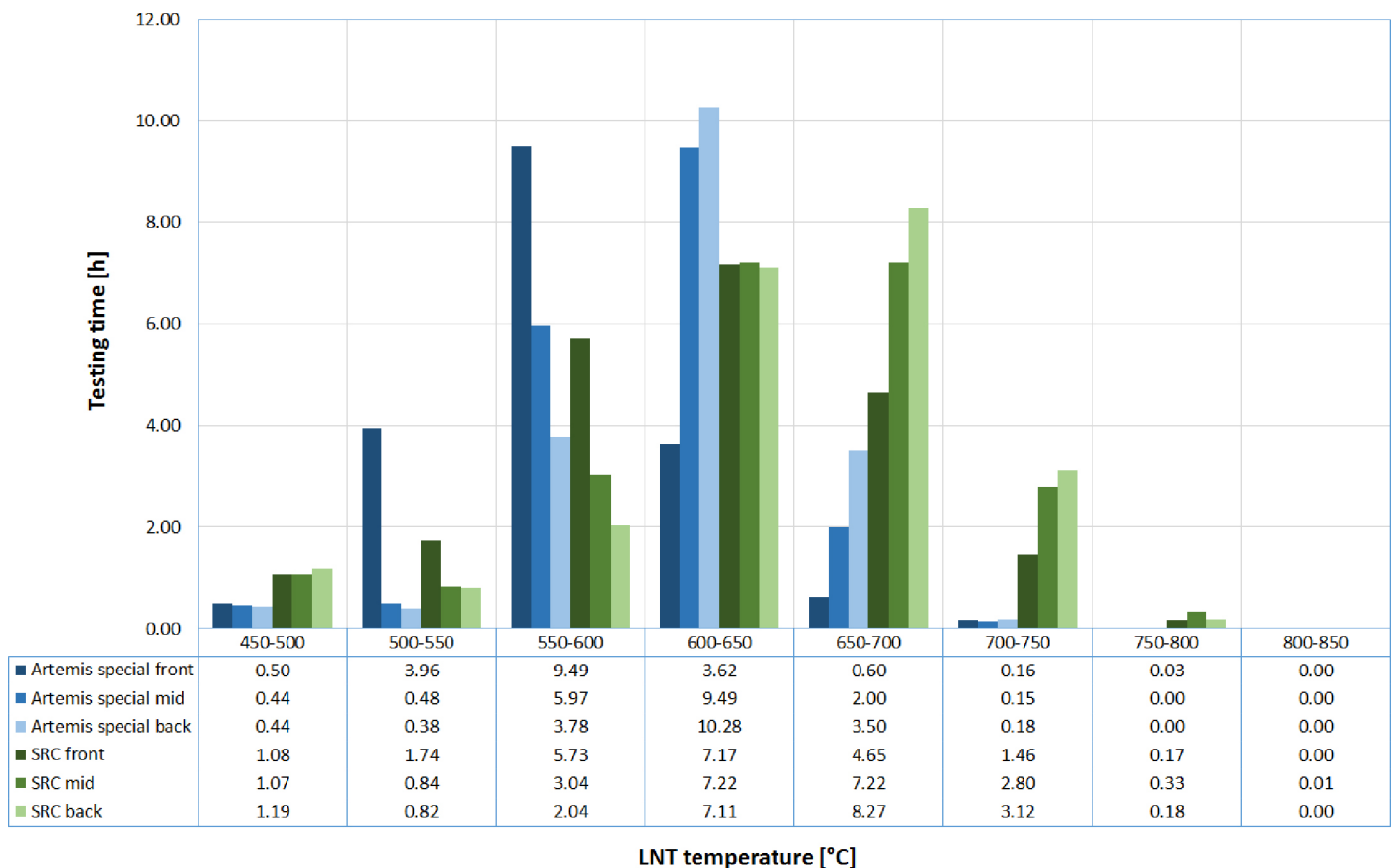


Figure 6. Aging time of the vehicle-aged catalyst exposed to high operating temperatures (above 450 °C).