Report

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Three-way catalyst performance using natural gas with two different sulphur levels

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Three-way catalyst performance using natural gas with two different sulphur levels

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ABSTRACT

Stoichiometric engines running on natural gas rely on three-way catalysts to meet limits e.g. Euro 6 regarding emissions of hydrocarbons (including methane), carbon monoxide and oxides of nitrogen. As is well known from decades of industry experience with three-way catalysts for petrol applications, sulphur naturally present in the fuel can, following combustion in the engine, cause poisoning of the aftertreatment system. Through complex mechanisms including steric effects, sulphur blocks active sites and prevents the metals in the washcoat from performing their task of facilitating the simultaneous oxidation and reduction of harmful components in the exhaust gas. Through related mechanisms, the presence of sulphur reduces the washcoat's oxygen storage capacity, which severely limits the catalyst's ability to oxidise hydrocarbons and carbon monoxide under rich conditions. However, desulphation processes can occur during normal driving, which might lead to partial (or even full) recovery of the catalyst's performance. Little work has been done recently to understand the effect of sulphur and especially on the catalyst systems of modern natural gas vehicles.

KEYWORDS

Natural gas, CNG, sulphur, three-way catalyst (TWC), sulphur poisoning

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SUMMARY

An ageing programme was conducted on both light and heavy duty natural gas-specific three-way catalysts (TWC). One TWC unit of each type was aged on high sulphur (equivalent to 30ppm) natural gas, while the other unit was aged on low sulphur (10ppm) natural gas. The light duty catalysts were tested by mounting the unit on a passenger car running on a chassis dynamometer after ageing on a light duty engine dyno. The heavy duty TWC's were tested by being mounted to an engine on a heavy-duty engine dyno after ageing on the engine dyno. The results revealed complex responses that were not linear in every case although a negative impact of the high sulphur in the fuel on the catalysts' overall reduction of regulated pollutants was clear, the rate of deterioration depended on the pollutant measured. The deterioration of NOx conversion was low compared to the deterioration of methane conversion in both light duty and heavy duty vehicles over the ageing period used. The rate of deterioration when running on low sulphur natural gas was overall much slower and the test units proved to be more durable when running on that fuel compared to the higher sulphur fuel.

1. INTRODUCTION

Three-way catalysts (TWCs) are deployed in all new vehicles featuring spark-ignition engines sold in major markets (including the European Union) in order to reduce regulated tailpipe emissions of hydrocarbons (HC), carbon monoxide (CO) and oxides of nitrogen (NO_x). The technology has a history stretching back decades, though continuous improvements have been made to both the structure and the chemical makeup of such systems in order to improve their performance, increase durability and reduce the associated costs.

Such systems are called "three-way catalysts" stems from the fact that they can simultaneously oxidise exhaust gas components deriving from incomplete combustion (HC, CO) to water and carbon dioxide while also reducing oxidised nitrogen (NO and NO_2; NO_x) to harmless elemental nitrogen (N_2). These simultaneous oxidising and reducing reactions can only occur to a satisfactory extent when the ratio of air to fuel is in a very narrow range centred on perfect stoichiometry with regards to oxygen (λ=1). Such a requirement does have certain disadvantages, not least for fuel consumption [6], but the effectiveness of TWCs operating under stoichiometric conditions is sufficiently high as to make their application universal in virtually all markets.

Spark ignition engines can run on a variety of fuel types (or even mixtures thereof); however, where the stoichiometric combustion strategy is employed, TWCs remain the main (and in most cases only) solution to reducing tailpipe emissions from spark ignition engines, regardless of the fuel type. Vehicles designed to run on natural gas therefore feature TWCs to control tailpipe emissions. In the case of natural gas, the gas flow emanating from the cylinders features a much higher concentration of methane (CH_4) than when petrol is used as the fuel. (Although natural gas is not pure methane, methane is by far the most abundant component and the other most prevalent components are all small, light hydrocarbons) (see Appendix 1). Being a small, stable molecule, CH_4 is somewhat harder to oxidise (i.e. has a higher activation energy) than other hydrocarbons; this difference in hydrocarbon speciation can sometimes necessitate the use of TWCs which feature higher Platinum Group Metals (PGM) loading and are sometimes physically larger compared to their petrol-specific counterparts. A further complication is the broader chemistry of the exhaust gas, being significantly richer in water vapour than the combustion products of petrol. Water vapour can impede methane oxidation reactions [1] and such effects must be borne in mind when designing natural gas-specific exhaust gas aftertreatment systems.

As is well known from decades of industry experience with three-way catalysts for petrol applications, sulphur naturally present in the fuel can, following combustion in the engine, cause poisoning of the aftertreatment system. Through complex mechanisms including steric effects sulphur blocks active sites and prevents the metals in the washcoat from performing their task of facilitating the simultaneous oxidation and reduction of harmful components in the exhaust gas. Through related mechanisms, the presence of sulphur reduces the washcoat's oxygen storage capacity, which severely limits the catalyst's ability to oxidise hydrocarbons and carbon monoxide under rich conditions. However, desulphation processes can occur during normal driving under high speed and load conditions, which might lead to partial (or even full) recovery of the catalyst's performance

Sulphur was one of the properties which was studied in the European Programme on Engine Technologies and Fuels (EPEFE) (Auto-oil) programme in the late 1990's [2} and that programme was the basis for the gasoline (EN228) specifications [3] which are in place now (10 ppm sulphur) to ensure the integrity of the aftertreatment systems that were available at that time. Since then little work has been done looking at the sulphur sensitivity of modern three-way catalyst systems. A. Gremminer et al. studied SO_2 deactivation and regeneration ability at different temperatures and varying SO_2 concentration (2.5 ppm or 5 ppm) [4] and enhanced the understanding of the mechanism of formation of sulphur compounds on the catalyst. This study indicated that even low concentrations of sulphur can cause poisoning of the catalyst. Other researchers have looked at the relationship between sulphur poisoning and water [5] in lean burn automotive catalyst systems and concluded that the sulphur poisoned catalyst seems to be more sensitive to water inhibition which mentioned above inhibits the low temperature methane oxidation ability.

In light of the Euro 6 regulations which were put in place starting from 2014 for type approval, natural gas is considered a promising alternative fuel to help meet the new regulations and has been compared favourably with gasoline (particularly for CO_2 and particulates reduction) in light duty applications [6], [7] using the NEDC and the new WLTP test cycle. Two different CNG technologies but both with three way catalyst have also been compared with diesel in a heavy duty study [8] over a range of stationary and transient HD cycles and the results were found to be variable depending on the technology although in general NO_2 was lower for the CNG vehicles. In a study of a range of different technologies installed in heavy duty and tested on the chassis dynamometer a stoichiometric CNG bus fitted with TWC was shown to have very low NOx emissions as well as very low particulate and low CO_2 over a range of urban cycles [9]. The current automotive European specification for natural gas is EN 16723-2 developed by CEN [10] and in particular the sulphur specification was the subject of discussion although there is little data available to demonstrate the effect of ageing using fuels of different sulphur levels. It was decided to run the current programme to develop some more data in this area and to include both a light duty vehicle and a heavy duty engine equipped with different three-way catalyst systems.

2. INVESTIGATION AND THREE-WAY CATALYTIC CONVERTERS USED

Two TWC types fitted to commercially available European vehicles type approved to run on natural gas were tested for emissions performance following ageing on natural gas with two different sulphur levels.

The light duty TWC was the emissions aftertreatment device used as the original equipment in a small passenger car equipped with a bi-fuel petrol/CNG engine. This vehicle runs for approximately the first 20 seconds on gasoline and then switches to CNG and was chosen as it is a common technology and vehicle found in Europe. This TWC was tested in the vehicle for which it was intended, with the test vehicle running on a chassis dynamometer. The heavy duty TWC was the emissions aftertreatment device installed as the original equipment in an engine used in a variety of applications, including large delivery vans. This TWC was tested on the engine for which it was intended, with the engine installed on an engine dynamometer. The latter engine ran solely on CNG.

Selected characteristics of the four TWCs types used for testing are presented in **Table 1**.

Table 1 Selected characteristics of TWCs used in testing

Aspect / Appellation	TWC LOW S	TWC HIGH S	TWC LOW S	TWC HIGH S
Intended use	Light duty (passenger car)		Heavy duty (delivery vehicle)	
Ageing carried out on	Engine dyno (light duty engine)		Engine dyno (heavy duty engine)	
Ageing fuel	Low-sulphur CNG	High-sulphur CNG	Low-sulphur CNG	High-sulphur CNG
Emissions testing carried out on	Chassis dyno (light duty vehicle, various test cycles)		Engine dyno (heavy duty engine, various test cycles)	
Emissions testing fuel	Reference CNG		Low-sulphur CNG	
Stabilisation before testing/ageing commenced	12 repetitions of the EUDC run on a chassis dynamometer with the TWC installed on the test vehicle		Degreened during engine operation on the engine dyno (in-house cycle) (5 hours)	
Pre-cat PGM ratio (Pt/Pd/Rh)	Not present		0/24/1	
Pre-cat PGM loading (Pt/Pd/Rh)			0/8.476/0.3531 g/dm^3	
Pre-cat volume			0.65 dm^3	
Main cat PGM ratio (Pt/Pd/Rh)	0/192/8		0/14/1	
Main cat PGM loading (Pt/Pd/Rh)	0/6.78/0.283 g/dm^3		0/2.3072/0.1648 g/dm^3	
Main cat volume	1.0296 dm^3		2.3 dm^3	

As outlined in **Table 1,** two separate units of both types of TWC (light duty and heavy duty) were tested. Testing was conducted on all four unaged TWCs and thereafter periodically during the ageing programme. Ageing was carried out by fitting the TWC in question to the engine for which it was designed, running on natural gas with two different sulphur levels. The TWC aged using natural gas of Low sulphur content was called 'the Low S TWC', while the TWC aged on natural gas of High sulphur content was called 'the High S TWC'. Since both light duty and heavy duty TWCs were tested, this means there was a total of four TWCs used in the programme.

2.1. AGEING OF LIGHT AND HEAVY DUTY TWCS INCLUDING DESCRIPTION OF FUELS

Both the light duty and heavy duty TWCs were aged by mounting them to the engine for which they were specified by original equipment manufacturer and running on an engine dyno. The ageing cycle used was an automotive industry cycle used for accelerated ageing of aftertreatment systems. The cycle is dynamic and features fluctuating load points – the majority of the speed-load points run by the engine are high speed and load, corresponding to high velocity motorway driving. Some analyses of the cycle run on the LD engine suggests that the temperature was above 600°C for some 26% of the cycle, the temperature was above 700°C for some 8% of the cycle and the temperature was above 800°C for some 4% of the cycle. The *mean* temperature for the latter half of the cycle was typically 590-605°C and the *mean* temperature for the final portion of the cycle was typically 650-660°C.

This procedure contained a fair amount of TWC exposure to high exhaust gas temperatures and is thought to be reasonably representative of a situation where highway driving might contribute to desulphating the catalyst periodically during driving.

The cycle is normalised to the engine's full load power curve, such that the load factor was comparable for the light duty engine and the heavy duty engine. The heavy duty engine completed more ageing cycles of longer duration, in line with typical operating patterns for this engine type: for the light duty engine, each cycle lasts 1.4 hours (250 cycles = 350 hours); for the heavy duty engine, each cycle lasts 1.8 hours (500 cycles = 900 hours). The correlation factor between the dyno and on-road km is thought to be 1.6 for both LD and HD so the final equivalent number of kilometres for LD would be 82,000 for LD and 172,000 for HD. For ageing of each TWC, CNG fuel was used.

It was planned that the low S TWC be aged using CNG of sulphur level approximately 10 ppm; the high S TWC was planned to be aged using CNG of sulphur level approximately 30 ppm. Natural gas was sourced from the local (Polish) gas network and was subjected to period chemical analyses for a range of parameters, including sulphur and methane content. The total sulphur content of the natural gas had a mean level of 8.51 mg/Nm^3 (close to 6ppm mass) with a coefficient of variance of 16.6%; the methane content was approximately 94%v/v with a low coefficient of variance (0.8%); content of higher hydrocarbons was always < 5%v/v. The "as found" natural was used as the Low S CNG fuel. THT was added to this natural gas to create the High S CNG, at a nominal level of 30 ppm S. **Figures 1** and **2** show the sulphur analysis for the various batches of gases used for low sulphur and high sulphur ageing.

Figure 1 Sulphur analysis for light duty a) low sulphur and b) high sulphur gases

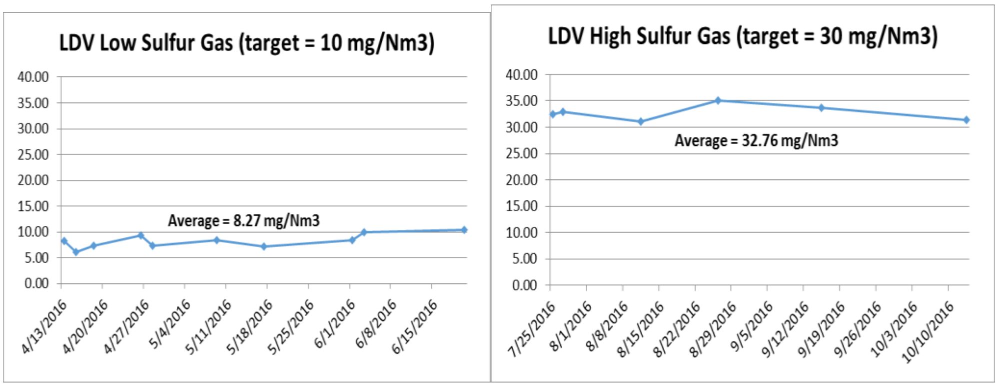
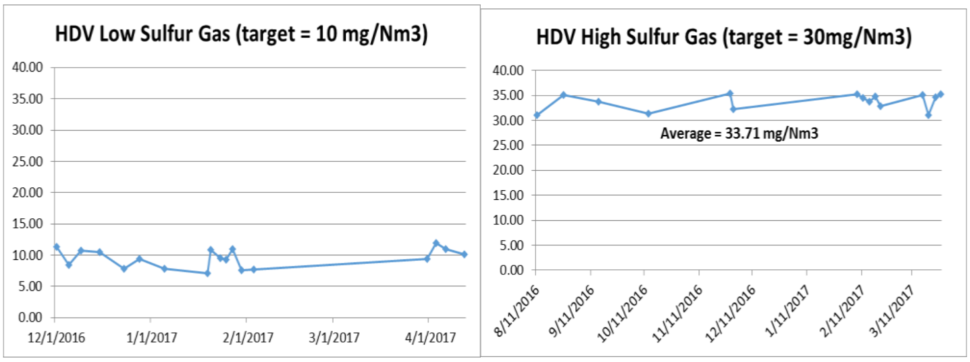


Figure 2 Sulphur analysis for heavy duty a) low sulphur and b) high sulphur gases



Ageing was carried out continuously, with the exception of breaks for emissions testing. Emissions tests were performed periodically (as detailed in the following sections). The engines used for ageing were of the original specification, had been broken in, were in sound working order and used lubricating oil of the type specified by the engine manufacturer. In both cases the engine oil type met the ACEA C3 standard, which requires an oil sulphur level ≤ 0.3%. During ageing the engines operated in stoichiometric mode, with limited lambda excursions. At periods of high load, lambda values >1 were encountered, as maximum engine power output occurs at a lambda value of approximately 1.1 for turbocharged spark ignited engines running on CNG.

2.2. EMISSIONS TESTING OF LIGHT DUTY TWCS

Tests were performed at 0 cycles (before start of ageing), after 50 cycles, after 100 cycles, after 175 cycles and after 250 cycles. Both light duty TWCs were tested in a light duty vehicle on a chassis dynamometer.

Three driving cycles were employed: the well-known NEDC and WLTC and a constant speed cycle (80 km/h). All three drive cycles were used for testing at 0 and 250 cycles; for all other points (50, 100, 175 cycles), only the WLTC was used. The test vehicle was the vehicle for which the light duty TWCs were designed: a European bi-fuel CNG passenger car, with the characteristics given in **Table 2.**

Table 2 Details of passenger car used in testing

Vehicle type	Passenger car, M category
Engine type, combustion strategy	Turbocharged, indirect injection 2-cylinder engine, stoichiometric with spark ignition
Engine displacement [dm^3]	0.875
Engine rated power [kW] @ engine speed [rpm]	59.7 @ 5500
Supported fuel types	CNG, petrol
Aftertreatment system	Single three-way catalyst (close coupled to the engine)
Emissions standard	Euro 6
Vehicle mass in running order [kg]	1090
Power to weight ratio [W/kg]	54.8
Mileage at start of testing [km]	1933

The vehicle used for emissions testing used lubricating oil of the type specified by the engine manufacturer, which met the ACEA C3 standard (oil sulphur level ≤ 0.3%).

Prior to using the test vehicle to test the two light duty TWCs, the test vehicle was run in on the chassis dyno (with the factory original TWC fitted) and periodic cold start NEDC tests performed, to establish compliance with the Euro 6 standard. In the periodic tests performed, all regulated emissions were below the applicable Euro 6 limits and the test vehicle's fuel consumption and CO_2 emissions were stable from test to test. Thus, while the test vehicle's mileage was less than 3000 km, it was concluded that it was in a suitable state to perform testing of the two test TWCs.

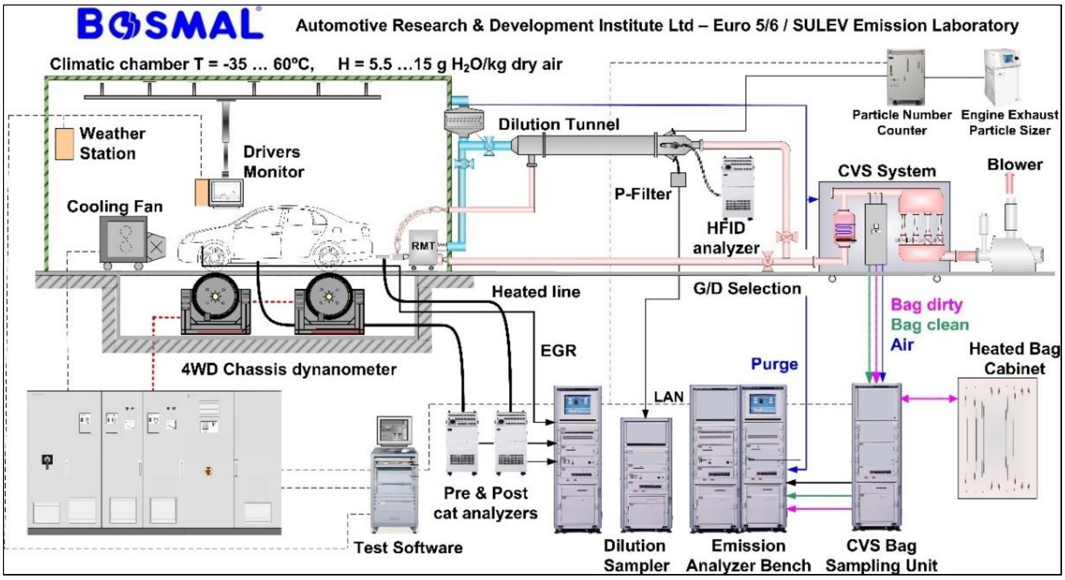
Both catalysts (the Low S TWC and the High S TWC) were subjected to emissions tests before any ageing was carried out (0 cycles; start of testing). However, before the aforementioned tests were performed, the TWCs were preconditioned by performing 12 repetitions of the EUDC cycle (the industry standard approach for preparing a completely fresh aftertreatment system for emissions testing). This involved covering a distance of approximately 84 km at a mean speed of 62.6 km/h, with a deceleration to 0 km/h and some idling every 7 km.

2.3. EMISSIONS LABORATORY AND TEST SETUP

Emissions test laboratory no. 2 at BOSMAL Automotive Research and Development Institute Ltd (Bielsko-Biala, Poland) was used to perform all chassis dyno testing. The laboratory consists of a climatic chamber housing a four-wheel drive chassis dyno, with associated emissions sampling and measuring equipment for performing both legislative and R&D automotive emissions testing. A scheme of the laboratory is shown in **Figure 2.** This cell was used for execution of the three test cycles used (NEDC, WLTC and constant speed - 80 km/h in 5^{th} gear).

WLTC testing was carried out in accordance with UNECE Global Technical Regulation (GTR) No. 15 [11]; NEDC testing was carried out in accordance with UNECE Regulation NO. 83 [12]; the constant speed test was carried out broadly in accordance with GTR 15, with the necessary modifications - all in line with good emissions testing practice. The test vehicle was fueled with G20 reference fuel (CNG) as defined in UNECE Regulation No. 83. As the vehicle always starts on petrol, the petrol tank was filled to 60% capacity with reference petrol (the E5 reference fuel type defined in UNECE Regulation No. 83) and this fuel type was used for all emissions tests. The vehicle's fuel selector was always in CNG mode; the decision when to switch over from petrol to CNG was made by the engine control unit and was not influenced by the driver.

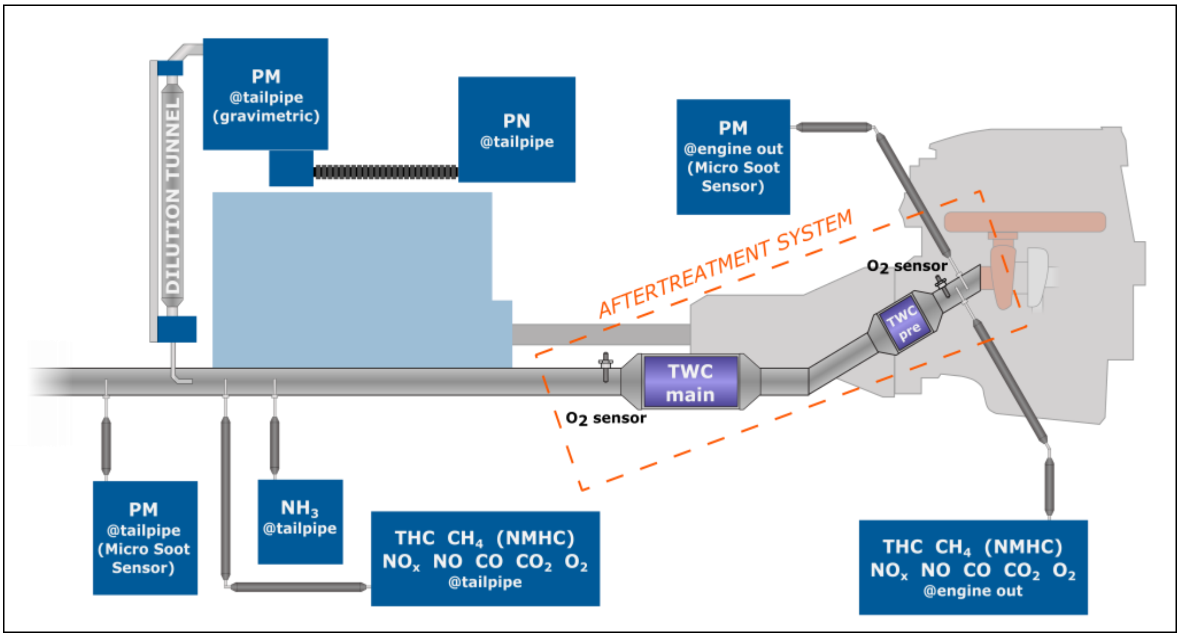
Figure 2 Schematic of dynamometer test set-up



2.4. EMISSIONS TESTING OF HEAVY DUTY TWCS

The HD aftertreatment system was mounted to the HD engine running on an engine dynamometer. A range of measurements were carried out at various points to measure gaseous and solid pollutants, as shown below in **Figure 3**.

Figure 3 Schematic of heavy duty engine test set-up



This setup was used for both engine dyno test cycles performed in this study: Worldwide Harmonized Test Cycle (WHTC) and Worldwide Harmonized Stationary Cycle (WHSC).

The heavy duty TWCs were tested on the engine for which they were designed. This engine is a medium/heavy duty engine typically fitted to large vans. The engine was in its original configuration and was lubricated by engine oil of the type specified by the engine manufacturer, which met the ACEA C3 standard (oil sulphur level ≤ 0.3%). The engine details are shown in **Table 3** (below).

Both test catalyst systems (the Low S TWC and the High S TWC) were subjected to emissions tests before any ageing was carried out (0 cycles; start of testing). However, before the aforementioned tests were performed, the TWCs were preconditioned on the engine dyno (identical procedure for both TWCs).

Table 3 Details of HD engine used for testing

Engine type	Road engine for commercial vehicles
Engine type, combustion strategy	Turbocharged, indirect injection 4-cylinder engine, stoichiometric with spark ignition
Engine displacement [dm^3]	3.0
Engine rated power [kW] @ engine speed [rpm]	100 @ 3500
Supported fuel types	CNG, petrol
Aftertreatment system	Two three-way catalysts: pre cat and main cat (packaged in two separate cans)
Emissions standard	Euro 6
Operating time at start of testing [hours]	<20

3. RESULTS AND DISCUSSION

3.1. LIGHTY DUTY (CHASSIS DYNO) EMISSIONS RESULTS

Ageing of both TWCs was successfully carried out. The TWCs were mounted on the test vehicle and emissions tests were performed at 0 cycles and at 250 cycles (full test range) as well as at 50, 100, 175 cycles (WLTC only).

In terms of general observations during emissions testing of the light duty vehicle with the High S and Low S TWCs, it was noticed that emissions behaviour was relatively stable and repeatable. Regulated emissions were at low levels for the Low S TWC all the way up to 250 ageing cycles; the High S TWC saw a progressive and rapid decrease in its overall efficiency from 100 ageing cycles onwards. Following 100 ageing cycles, when the High TWC was mounted to the test vehicle the vehicle's MIL illuminated and the ECU returned an error relating to catalyst efficiency. Since oxygen storage capacity is commonly used to monitor catalyst efficiency for OBD purposes, the presence of such an error suggests significant deteriorations in exhaust emission levels from 100 ageing cycles onwards – this was, generally speaking, the trend observed.

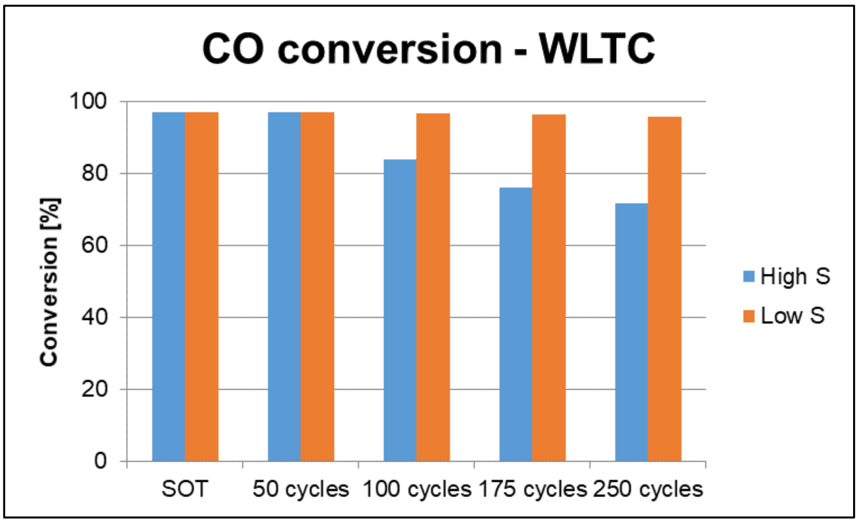
Despite not being regulated for this engine type, particulate emissions were successfully measured. However, the very low level of particulate emissions and the limited sooting propensity of the fuel type (CNG) meant that the gravimetric (PM filter) method was of limited sensitivity and that results from the AVL Microsoot Sensor were at a very low level after the engine had been running for 20-30 seconds. For that reason, only solid particle number (PN) particulate results are presented and discussed here, as PM and Microsoot mass-based particulate results were too low and showed too much variation to be considered meaningful. Charts showing the absolute emissions results are given in Appendix 1.

3.1.1. Carbon Monoxide emissions

Carbon monoxide emissions from the test vehicle fitted with the Low S TWC were low over all three test cycles, even following 250 ageing cycles. While CO results at 175 and 250 cycles were marginally higher than at 0 and 50 cycles, there was no evidence of a significant deterioration in the CO elimination efficiency of the Low S TWC. The High S TWC showed identical behaviour up to 50 cycles, but thereafter suffered a monotonic decrease in its CO elimination efficiency, such that CO emissions at 250 cycles were approaching 10 times Higher than at 0 cycles. No significant differences were observed in terms of the two TWCs' CO performance over the three different test cycles.

The calculated CO conversion efficiency in **Figure 4** shows the negligible decrease in CO elimination efficiency for the Low S TWC, even following 250 ageing cycles; the rapid deterioration for the High S cat at some point between 50 and 100 cycles is also clearly visible.

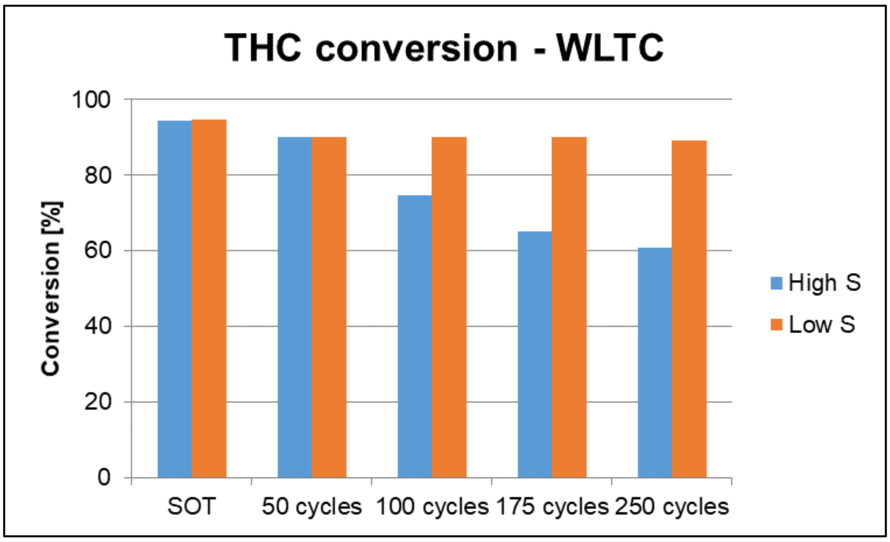
Figure 4 CO conversion efficiency

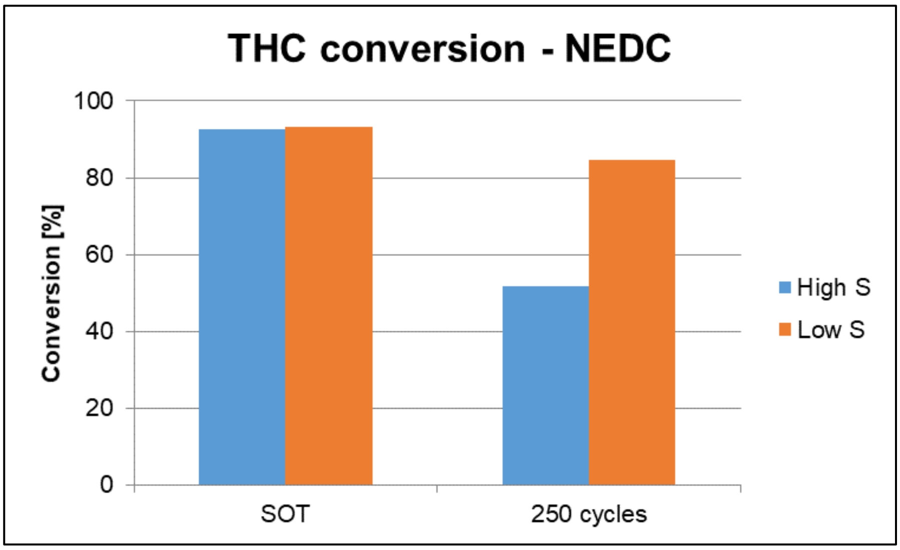


3.1.2. Total hydrocarbon emissions

For THC emissions, the behaviour was somewhat different from that of CO, as shown in the graphs in Appendix 1. The THC emissions with both TWCs fitted increased as ageing was carried out – however, the rate of deterioration was massively higher in the case of the High S TWC. Notwithstanding the lower number of measurement points, behaviour over the NEDC and the constant speed cycle was very similar to that observed over the WLTC – at 250 cycles the THC elimination efficiency of both samples was compromised to the extent that the Euro 6 limit was exceeded even with the Low S TWC mounted. Over the WLTC THC emissions were numerically lower, meaning that the Euro 6 limit was not exceeded with the Low S TWC mounted, even following 250 cycles. The higher distance covered by the WLTC (23.2 km) compared to the NEDC (11 km) means that the cold start event and warmup period are diluted by a higher number of kilometres. A change in the TWC's light off behaviour regarding the elimination of hydrocarbons (reaching light off at a higher temperature – i.e. later in the cycle) therefore has a greater impact over the NEDC than the WLTC, as evidenced by the THC results. During the constant speed test, the entire engine and all its components (including the TWC) are fully warmed up and so the THC emissions are simply a result of the TWC's ability to reduce the emissions – the trend observed regarding THC was very similar to that observed for CO.

Figure 5 THC conversion efficiency



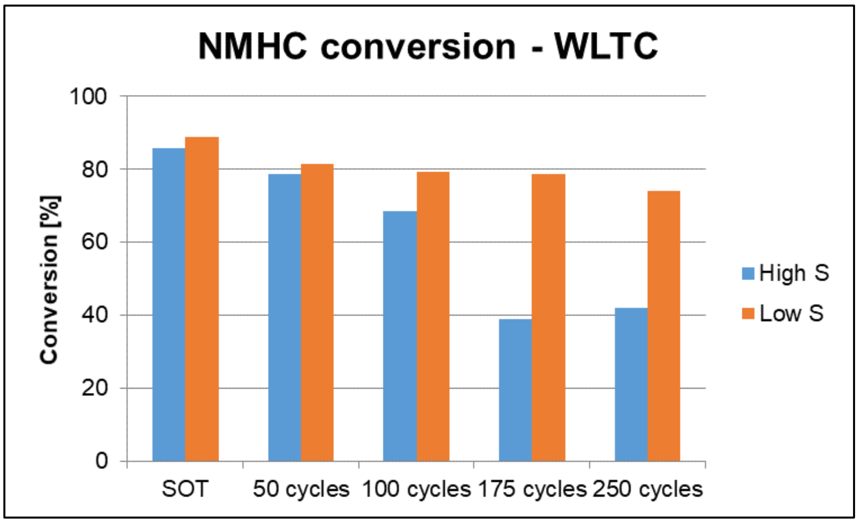


3.1.3. Non-methane hydrocarbon emissions

For an engine running on CNG over a typical driving cycle, NMHC emissions are typically roughly half the magnitude of THC results. The CNG fuel used for testing consisted of over 99% CH_4 by mass and thus NMHC deriving from fuel itself can be considered negligible. The test vehicle starts on petrol and switches over to CNG after a few seconds and so petrol is a significant contributor to NMHC emissions over cold start test cycles (WLTC, NEDC). A further source of NMHC emissions is the emission of unburned (or partially burned) lubricating oil. At 0 cycles emissions were approximately 20 mg/km over the WLTC. The Low S TWC suffered a gradual decrease in its NMHC elimination performance as ageing progressed; the greatest deterioration per cycle occurred between 0 and 50 cycles, with further ageing causing relatively limited changes. In contrast, the High S TWC suffered marked deteriorations following every ageing stage, such that following 250 cycles the emissions were at the Euro 6 limit over the WLTC and well over the limit when running on the NEDC. (See the above discussion of the impact of cycle distance on the emissions results.)

Over the constant speed cycle, no petrol at all is consumed and the fuel and oil are the only sources of hydrocarbons. Under such conditions, emissions were very low, but there was a distinct increase for both TWCs following 250 ageing cycles, with the deterioration for the High S TWC approximately 4 times greater than for the Low S TWC.

Figure 6 NMHC conversion efficiency



3.1.4. Methane emissions

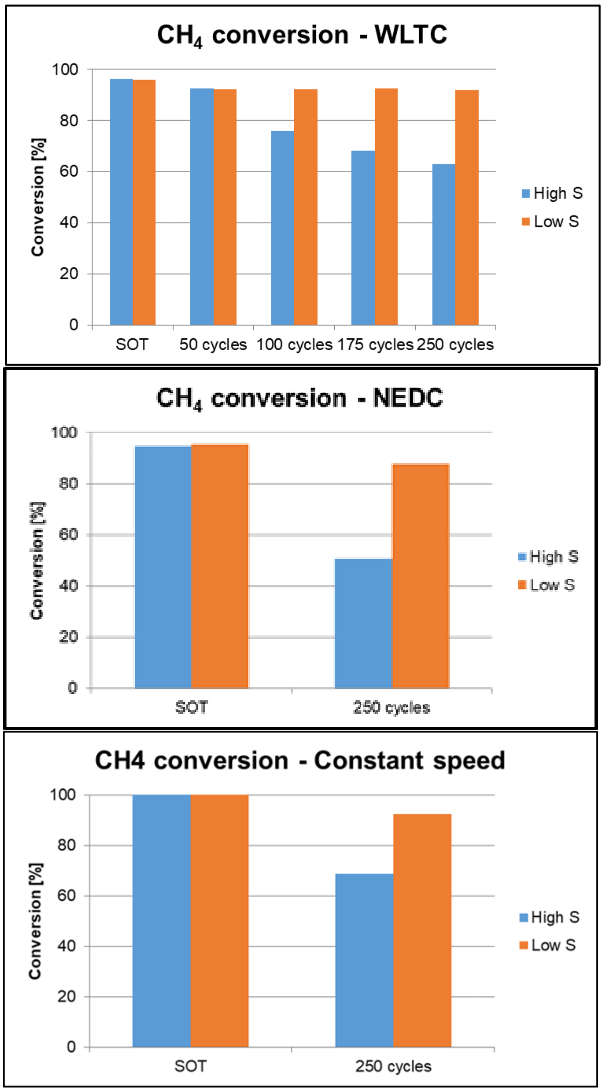
Emissions of CH4 are not directly regulated in the EU, but based on the THC and NMHC limits, an equivalent Euro 6 limit of 32 mg/km would result. It should be noted that since the light duty vehicle starts on gasoline for the first 20 seconds, there would be a small contribution from the gasoline at the beginning of each test. The modal emissions data could be used to determine the amount although this was not expected to significantly alter the results so has not been studied to date. Methane emissions were generally high over the WLTC; at 0 cycles the emissions with either TWC mounted were approaching 30 mg/km. Following ageing, emissions were much higher, such that the Euro 6 equivalent limit of 32 mg/km was exceeded for both TWCs after 50 cycles. Further ageing caused very small deteriorations in CH4 elimination efficiency for the Low S TWC, but the High S TWC continued to deteriorate, such that after 250 cycles emissions were almost 9 times higher than the Euro 6-equivalent limit.

Over the NEDC, the trend observed was the same, but at 250 cycles the emissions were even higher - almost 12 times higher than the Euro 6-equivalent limit. Focusing on the 250 cycle condition, the higher CH4 results over the NEDC compared to the WLTC may have been due to the aforementioned cycle distance dilution effect. That being said, for the fully hot running conditions encountered during the content speed test (where there is no cold start), the situation was in fact similar.

At 0 cycles emissions of CH4 over the constant speed cycle were effectively zero while at 250 cycles emissions with the Low S TWC mounted approached those measured over the cold start WLTC at 0 cycles, while CH4 emissions with the High S TWC mounted approached 80 mg/km (cf. the Euro 6 total hydrocarbon limit of 100 mg/km).

The CH_4 conversion efficiency of the Low S TWC never fell below 90%, even following 250 cycles, while the High S TWC's efficiency fell below 80% at 100 cycles and continued to fall thereafter, reaching a low of 63%. Over the NEDC the efficiencies of both TWCs following 250 cycles were lower, than over the WLTC, most likely due to the extra 10 minute's hot operation of the latter test cycle. When fully warmed up (i.e. during the constant speed test) the effectiveness of both TWCs was 100% at 0 cycles; at 250 cycles the High S TWC was able to remove some 69% of the CH4 in the exhaust gas.

Figure 7 Methane conversion for a) WLTC, b) NEDC and c) constant



3.1.5. NOx emissions

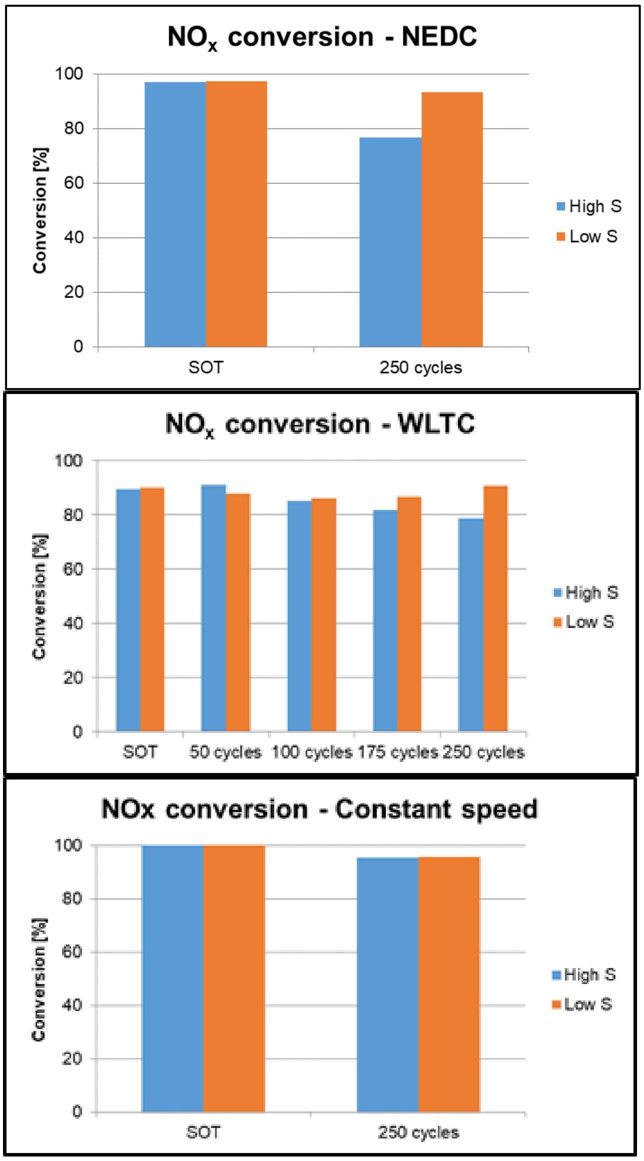
Emissions of NOx differ from hydrocarbons and CO, both in terms of the origin and process of formation of the pollutant and in terms of the means by which they can be eliminated in a TWC.

Over the WLTC NOx emissions were high with both TWCs fitted – emissions exceeded the Euro 6 limit, even at 0 cycles.

However, over the NEDC the emissions at 0 cycles were below the Euro 6 limit and thus the test cycle was the underlying reason for this behaviour. The extended idling, limited acceleration and overall load conditions of the NEDC are not particularly conducive to high NO_x formation. When running the WLTC, the higher load and the non-legislative nature of the driving cycle appear to have caused the elevated NO_x emissions. The WLTC also calls for vehicle inertia to be calculated in a different manner, such that when running the WLTC the simulated inertia was 22 kg (some 2%) higher than over the NEDC, increasing the load on the engine and thereby NO_x formation rates.

The High S TWC in fact showed improvement in NO_x elimination following 50 ageing cycles; thereafter its performance decreased rather rapidly, such that following 250 ageing cycles emissions over the WLTC were over five times the Euro 6 limit. The Low S TWC also suffered a deterioration, with the highest emissions occurring following 100 cycles, but following further ageing its performance recovered, such that following 250 ageing cycles NOx emissions over the WLTC were virtually identical to those at 0 cycles. However, over the NEDC this was not the case – following 250 cycles NO_x emissions with the low S TWC mounted were almost three times higher than at 0 cycles. Over the constant speed test, both TWCs performed perfectly (100% elimination) at 0 cycles and rather poorly following 250 cycles. Interestingly, NO_x conversion performance of the Low S TWC following 250 cycles was virtually identical to that of the High S TWC.

Figure 8 Conversion efficiency of a) WLTC b) NEDC and c) Constant speed



Thus, for both TWCs 50 ageing cycles appeared to complete the degreening process of the TWC regarding elimination of NOx – performance was better than that point than at 0 cycles. Thereafter, the High S TWC's performance deteriorated monotonically. The Low S TWC appeared to undergo at least two counteracting processes, which caused fluctuations in its efficiency over the WLTC at with better performance following 250 cycles than following 100 or 175.

The NEDC is a ramped modal test cycle primarily composed of straight lines, with idling accounting for 22.6% of the test and extended periods of non-zero constant speed (6.3 km, or 57% of the cycle's 11 km distance is driven at zero acceleration). By definition, the constant speed cycle also has zero acceleration for its entire duration. This is in marked contrast to the WLTC, which features a fluctuating speed trace with virtually no driving at constant speed, as well as frequent gear changes. Gear changes are important regarding the emission of NO_x, as the surge of oxygen that results from the use of the clutch and the unloading of the engine creates conditions highly conducive to the reduction of NO and NO_2 to N_2. Such differences in the demands places on the engine and the chemistry of the exhaust gas may explain the difference in behaviour over the WLTC and the other two cycles, but the reasons behind the chaotic behaviour of the Low S WLTC remain unclear. It is hypothesised that as the TWC matured through ageing, different types of chemical reactions came to dominate, with some effects being stronger than others at different points, such that the ability of the TWC to reduce NO_x was neither constant nor monotonically decreasing as ageing cycles were performed.

3.1.6. Carbon dioxide and Fuel Consumption

Carbon dioxide emissions are mainly derived from the combustion of fuel, but are also a product of the oxidising reactions occurring in the TWC. Thus, if the TWC's effectiveness at oxidising CO, THC, NMHC or CH_4 (or – more realistically – all of those compounds simultaneously), the exhaust emissions of CO_2 should logically decrease. However, such a situation emphatically does not equate to a reduction in fuel consumption; in a full carbon balance fuel consumption consideration, CO and unburned fuel (i.e. THC) are taken into consideration along with CO_2. Fuel consumption measured at the pre-cat and post-cat sampling points, as well as from the sampling bags, remained constant during the test programme. Differences between the start of testing (0 cycles) and end of testing (250 cycles) were of a similar order of magnitude to test-to-test variations. Both fuel consumption and CO_2 emissions are heavily influenced by the resistance to motion simulated by the chassis dyno. The dyno's road load simulation settings used were not altered during the course of the testing and coast down verifications revealed that the measured force did not differ from the targeted force by more than 3% at any speed (a commonly-used limit for chassis dyno testing is a difference of 5% for most speeds and 10% at Low speed). Data obtained from the ECU via the OBD port also showed that the engine's reported fuel consumption varied very little from test to test and showed no significant correlation with the TWC installed or the mileage of the vehicle.

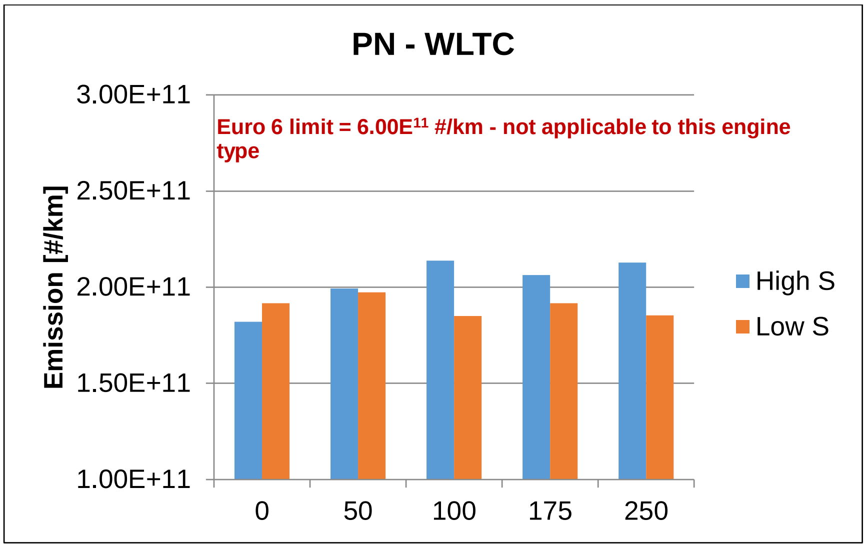
3.1.7. Particulate matter and number

As mentioned previously, the engine and fuel type used in the testing show a limited propensity for particulate formation and there are no specified Euro 6 limits for this engine type. Gravimetric (PM) results were below 2 mg/km in all tests and any variations from test-to-test showed no evident correlation with the number of ageing cycles. (For comparison, the Euro 6 limit for direct injection spark ignited engines and Diesel engines is 4.5 mg/km.)

The Microsoot sensors used at the pre-cat and post-cat sampling locations measured the startup event (cold engine, initial operation on petrol) successfully, but after the engine had been running for approximately 30 seconds, the measured particulate level was virtually indistinguishable from the level measured when the engine was not running. For that reason, results from the MSS are not presented and discussed here.

Particle number proved a reliable metric for testing this vehicle-fuel combination. It should be noted that in line with EU legislative requirements, the PN counter measures only solid particles of diameter 23 nm or greater and it bears repeating that in the EU vehicles with the indirect injection spark ignition engine type are not subject to legal limits for particulate emissions.

Figure 9 PN emissions of WLTC



PN emissions with the Low S TWC mounted showed no overall tendency, with slight fluctuations in the results occurring as ageing progressed from 0 to 250 cycles. The High S TWC did appear to show a tendency for PN to increase, although the increase was not strictly monotonic. Results from the 100, 175 and 250 cycle stages were all greater than $2E^{11}$ #/km, while results at 0 cycles were well below $2E^{11}$ #/km. Taking into consideration the variation in the three tests performed at each ageing stage, it appears that ageing caused increases in PN emissions for the High S TWC only, but that the strength of the effect was weak. It should be noted that in line with the EU legislative test method and standard industry practice, PN was measured from a sampling point on the dilution tunnel. The potential for hydrocarbons and sulphur-based compounds emitted from the vehicle's tailpipe in the gaseous (or even liquid) form to transform into solid particles in the dilution tunnel in the presence of cool, oxygen rich dilution air of limited humidity should not be discounted. In other words, PN measured in the tunnel may have been to some extent dependent on the availability of hydrocarbons, etc. in the exhaust gas leaving the TWC. This hypothesis, while not confirmable from the data collected in this study, might explain why PN emissions were higher at the Higher ageing stages, but only for the High S TWC (recall the Low THC elimination efficiency of the High S TWC from 100 ageing cycles onwards).

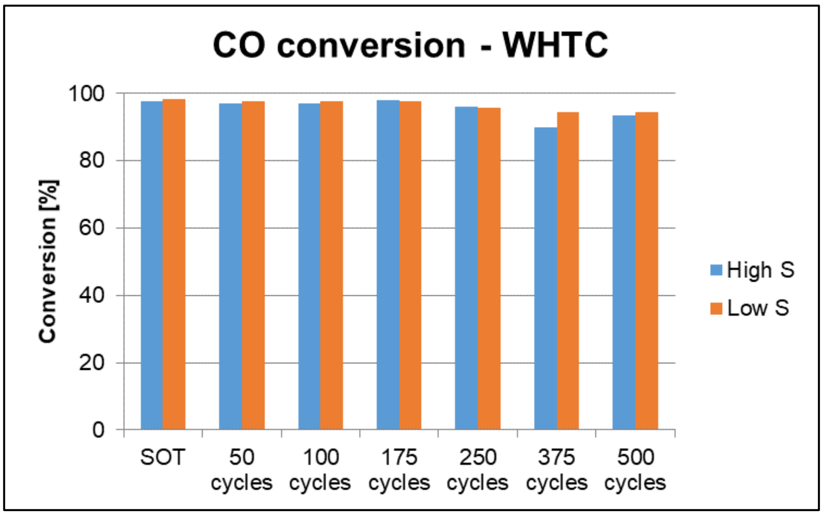
3.2. HEAVY DUTY (ENGINE DYNO) EMISSIONS RESULTS

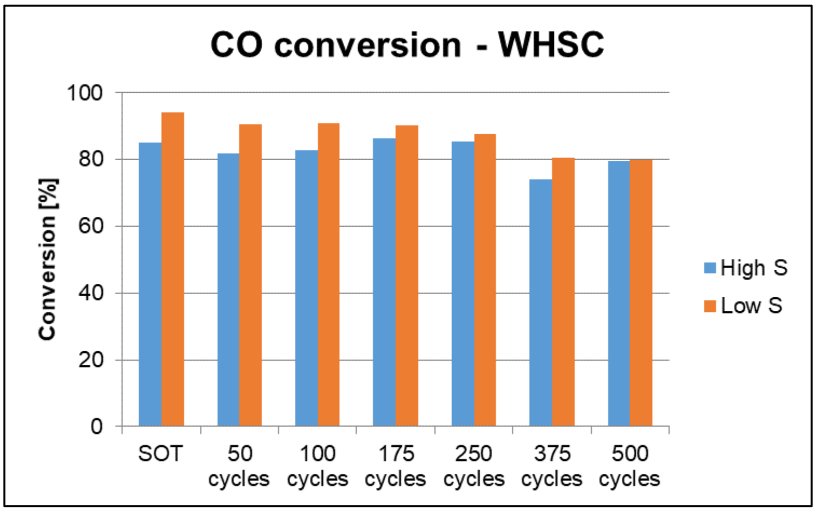
Ageing of both TWCs was successfully carried out. Emissions tests were performed at 0 cycles and at intermediate points during the ageing process, as well as following the ageing (after 500 cycles) – in total seven test points. Charts with the absolute heavy duty testing results are shown in Appendix 2.

3.2.1. Carbon monoxide emissions

Emissions of CO were reasonably low over the WHTC, only exceeding 3 g/kWh at one point (375 cycles; recall that the Euro 6 limit for engines of this type is 4 g/kWh). Both the post-cat emissions and the calculated conversion efficiency showed a complex relationship with the number of ageing cycles performed on the TWC under test. For the High S TWC, the highest emissions and the lowest conversion performance occurred at 375 cycles (over both test cycles), and not at 500 cycles. For the Low S TWC the behaviour was somewhat more in line with the expected trend, but the differences between 50 and 175 cycles (WHTC) and 100 and 175 cycles (WHSC) were surpassingly small. The highest CO emissions over the WHTC were measured following 375 cycles (and not 500); over the WHSC emissions and CO elimination were virtually identical at 375 cycles and at 500 cycles.

Figure 10 CO conversion efficiency from a) WHTC and b) WHSC





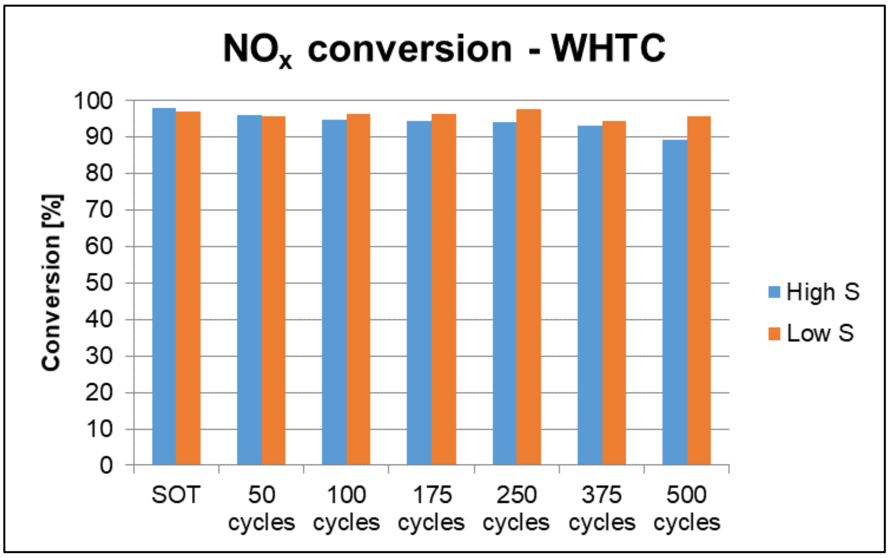
3.2.2. NOx emissions

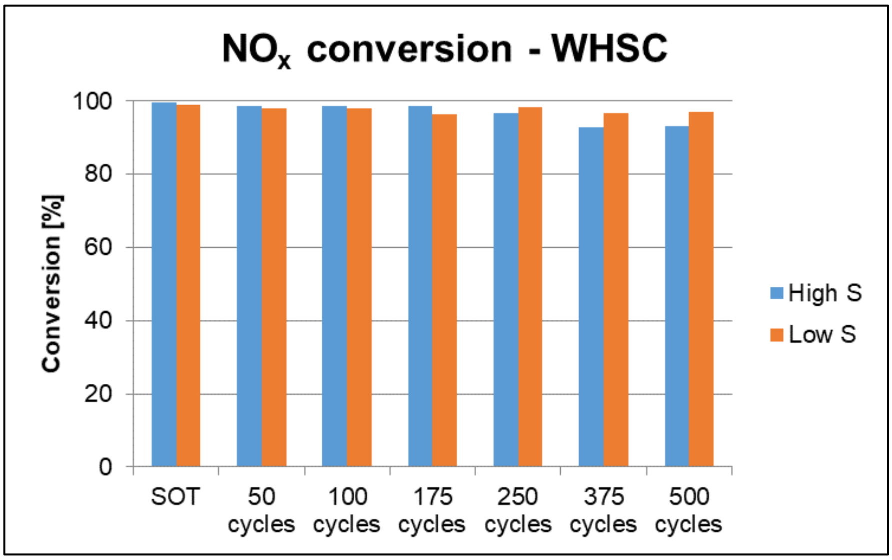
Emissions of NOx were low at the start of testing (approximately half the Euro 6 limit), but increased thereafter. For emissions measured over the WHTC, The first 50 cycles caused an identical deterioration on the NOx elimination performance for both TWCs. From 100 cycles onwards the behaviour of the two test units diverged: the Low S TWC recovered its performance and emissions following 250 cycles were lower than at 0 cycles. The High S TWC suffered a near-monotonic decrease in its performance with the highest emissions (by far) occurring at 500 cycles.

For emissions measured over the WHSC, the deterioration in the performance of the High S TWC was near-monotonic. The highest emissions were measured following 350 cycles and the increase in emissions moving from 0 cycles to 375-500 cycles was over an order of magnitude. The Low S TWC appeared to suffer at least two counteracting effects in response to ageing, whereby emissions were unexpectedly low at 250 cycles. The highest emissions of all were measured at 175 cycles; at 375-500 cycles emissions were close to three times higher than at 0 cycles.

Despite these observations, the conversion efficiencies of the TWC when aged on the low and high sulphur fuels were still high at above 90% for both test cycles after 500 cycles.

Figure 11 NOx conversion efficiency from a) WHTC and b) WHSC



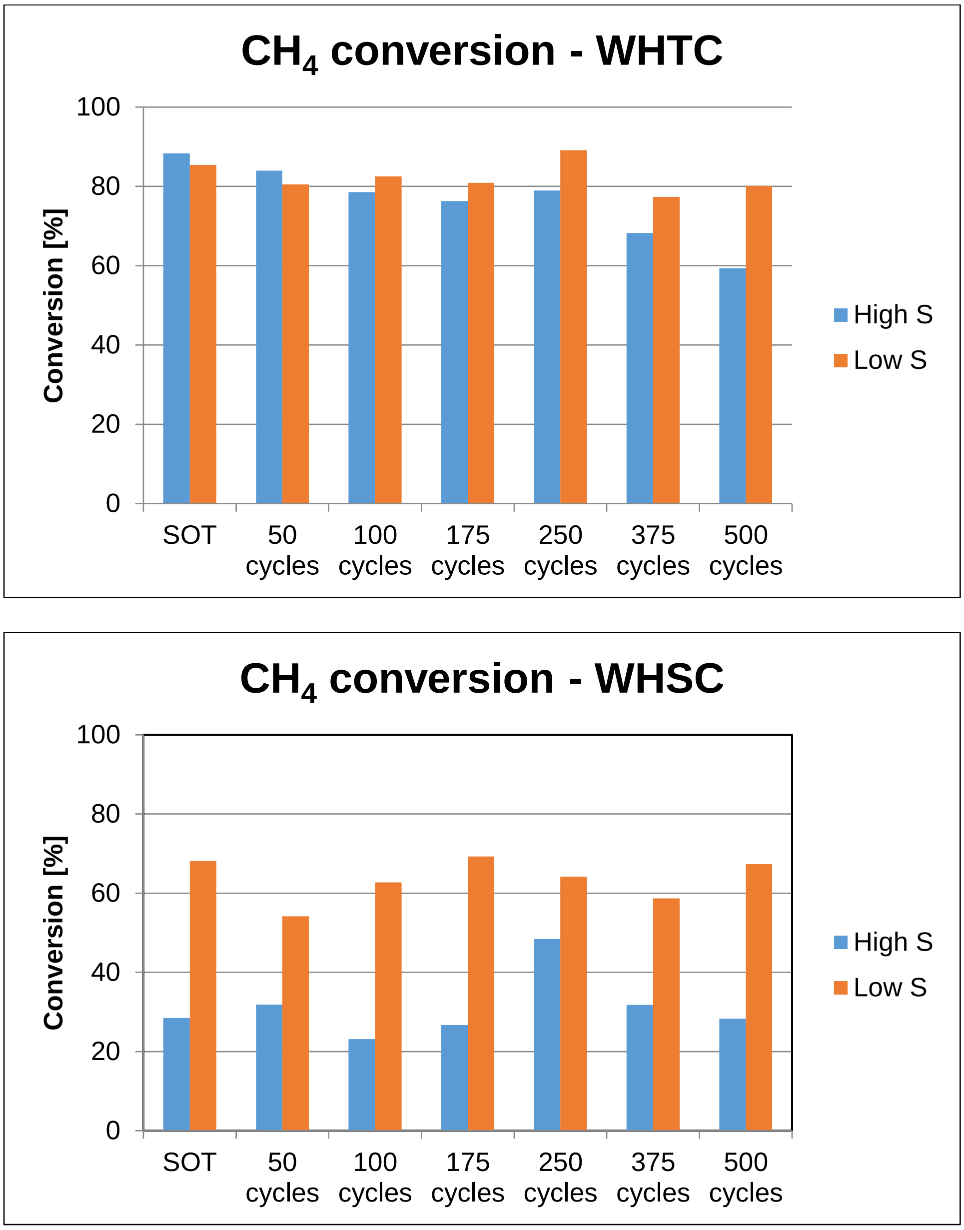


3.2.3. Methane emissions

Emissions of CH_4 also showed complex behaviour. Emissions increased following the first 50 ageing cycles, for both TWCs. The next 50 cycles (i.e. up to 100 cycles) caused a substantial increase in emissions with the High S TWC mounted, causing the Euro 6 limit to be exceed; emissions with the Low S TWC mounted actually decreased over this interval. Emissions with both TWCs mounted were unexpectedly low at 250 cycles, but the increase in ageing to 375-500 cycles caused increases for both TWCs, such that for both TWCs the Euro 6 limit was exceeded from 375 cycles onwards. Despite this the conversion efficiencies did not show much deterioration until after 250 cycles and the trends were as expected.

Over the WHSC the behaviour was more unexpected – emissions from both TWCs fluctuated as the ageing cycles were carried out. For the High S TWC the trend in emissions was strongly non-monotonic, but the highest emissions were measured following 500 cycles. For the Low S TWC, the highest emissions occurred at 375 cycles, but emissions at 500 cycles were at virtually the same level as at the start of testing. The methane conversion efficiencies for the WHSC did not follow the same trends as the WHTC.

Figure 12 Methane conversion efficiency of a) WHTC and b) WHS



3.2.4. Particulate matter and number

Particulate emissions were measured using three techniques: legislative PM, legislative PN and Microsoot sensor. Overall, particulate emissions were low, with repeatability suffering as a result of the low emissions. PM and PN emissions were well below the applicable Euro 6 limits at all ageing point - often an order of magnitude below. PM results from the Microsoot appeared to show an overall trend for emissions measured using that device to *decrease* with ageing (however, the trend was noisy and non-monotonic). The only conclusion which could be drawn is that ageing with both fuel types up to 500cycles did not cause any significant increases in PM emissions compared to the emissions measured at start of testing.

4. CONCLUSIONS

Comparison between results after ageing with high and low sulphur fuels gave the following conclusions:

For Light Duty

- Some emissions were at low levels for the Low S TWC all the way up to 250 ageing cycles especially for CO and NOx
  - Other emissions showed a gradual deterioration with the Low S TWC for example THC, NMHC and CH_4
- The High S TWC saw a progressive and rapid decrease in its overall efficiency from 100 ageing cycles onwards and with some emissions even earlier e.g. CO, NMHC, CH_4, NOx, THC.
- PN emissions with the Low S TWC mounted showed no overall tendency to change, with only slight fluctuations in the results occurring as ageing progressed from 0 to 250 cycles. The High S TWC did appear to show a tendency for PN to increase to a small degree.
- Data obtained from the ECU via the OBD port also showed that the engine's reported fuel consumption varied very little from test to test and showed no significant correlation with the TWC installed or the mileage of the vehicle.

For Heavy Duty

- The first 50 cycles caused an identical deterioration on the NOx reduction performance for both TWCs. From 100 cycles onwards the behaviour of the two test units diverged: the Low S TWC recovered its performance and emissions following 250 cycles were lower than at 0 cycles. The High S TWC suffered a near-monotonic decrease in its performance with the highest emissions (by far) occurring at 500 cycles.
- Methane emissions increased following the first 50 ageing cycles, for both TWCs. The next 50 cycles (i.e. up to 100 cycles) caused a substantial increase in emissions with the High S TWC mounted, causing the Euro 6 limit to be exceed; emissions with the Low S TWC mounted actually decreased over this interval. Emissions with both TWCs mounted were unexpectedly low at 250 cycles.
- Ageing with both fuels up to 500 cycles did not cause any significant increases in PM emissions compared to the emissions measured at start of testing.

Tables in Appendix 3 summarize the results of the conversion efficiencies for key emissions in LD and HD tests for high sulphur (HS) and low sulphur (LS) fuels.

Conversion Efficiencies:

- The results revealed complex responses that were not linear in every case.
- The negative impact of the higher sulphur in the fuel on the catalysts' overall conversion of regulated pollutants was clear.
- The rate of deterioration when running on low sulphur natural gas was overall much slower and the test units proved durable when running on that fuel type.

- In the LD case the NOx emissions were least affected by the use of the higher sulphur fuel with a reduction in conversion of 11% compared with the start of test to around 79% after 250 cycles. The greatest degradation was seen for NMHC removal of around 44% to 41% after 250 cycles.

- In the HD case the NOx emissions conversion decreased by around 9% to 89% from start of test after 500 cycles for the WHTC and by around 7% to 93% for WHSC. The methane conversion showed the most degradation with the higher sulphur fuel of 29% to around 60% after 500 cycles for WHTC. For the WHSC, the methane conversion was low for both the low sulphur and high sulphur fuels but didn't change much with ageing.

Comparison with limit values:

- In terms of the Euro 6 limits the passenger car was over the NOx limit at the start of test under WLTC cycle. With the higher sulphur fuel the THC were pushed over the limit after 100 cycles and the methane was over the limit for both high and sulphur fuels after 100 cycles.
- The HD vehicle was under the Euro VI limit for all regulated emissions at the beginning of test although the NOx limit was reached for the low sulphur fuel at 375 cycles and for the high sulphur fuel at 175 cycles although 250 cycles was on the limit. For methane the low sulphur fuel also went over the limit at 375 cycles and 100 cycles and over for the high sulphur fuel.

5. GLOSSARY

ACEA	European Automobile Manufacturer's Association
CH_4	Methane
CNG	Compressed Natural Gas
CO	Carbon monoxide
CO_2	Carbon dioxide
EPEFE	European Programme on Engine Technologies and Fuels
ECU	Engine control unit
EU	European Union
EUDC	European Urban Driving Cycle
GTR	Global Technical Regulation
HD	Heavy duty
NEDC	New European Driving Cycle
NMHC	Non-methane hydrocarbons
N_2	Nitrogen
NO	Nitrogen oxide
NO_2	Nitrogen dioxide
NOx	Oxides of nitrogen
OBD	On-board diagnostics
PGM	Platinum group metals
PM	Particulate matter
PN	Particulate number
THC	Total hydrocarbons
THT	Tetra hydro thiophene
TWC	Three way catalyst
UNECE	United Nations Economic commission for Europe
WHSC	Worldwide Harmonized Stationary Cycle
WHTC	Worldwide Harmonized Test Cycle
WLTC	Worldwide harmonized Light duty Test Cycle

6. ACKNOWLEDGEMENTS

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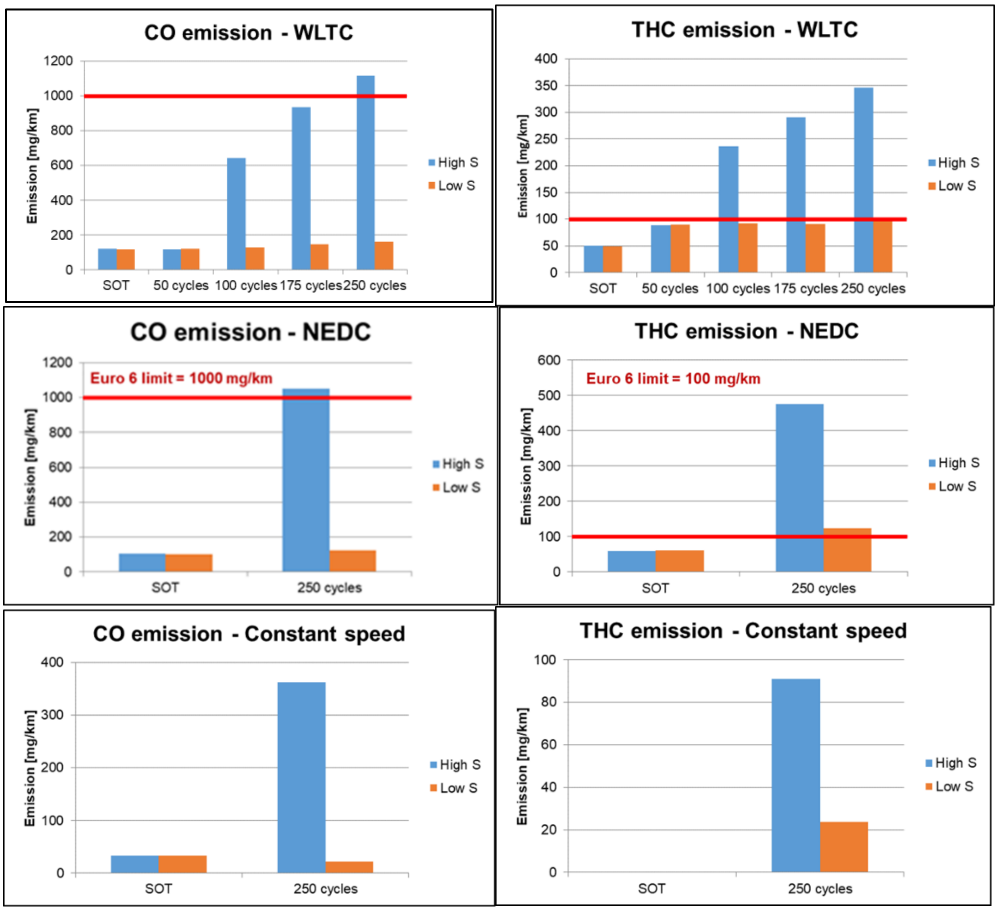
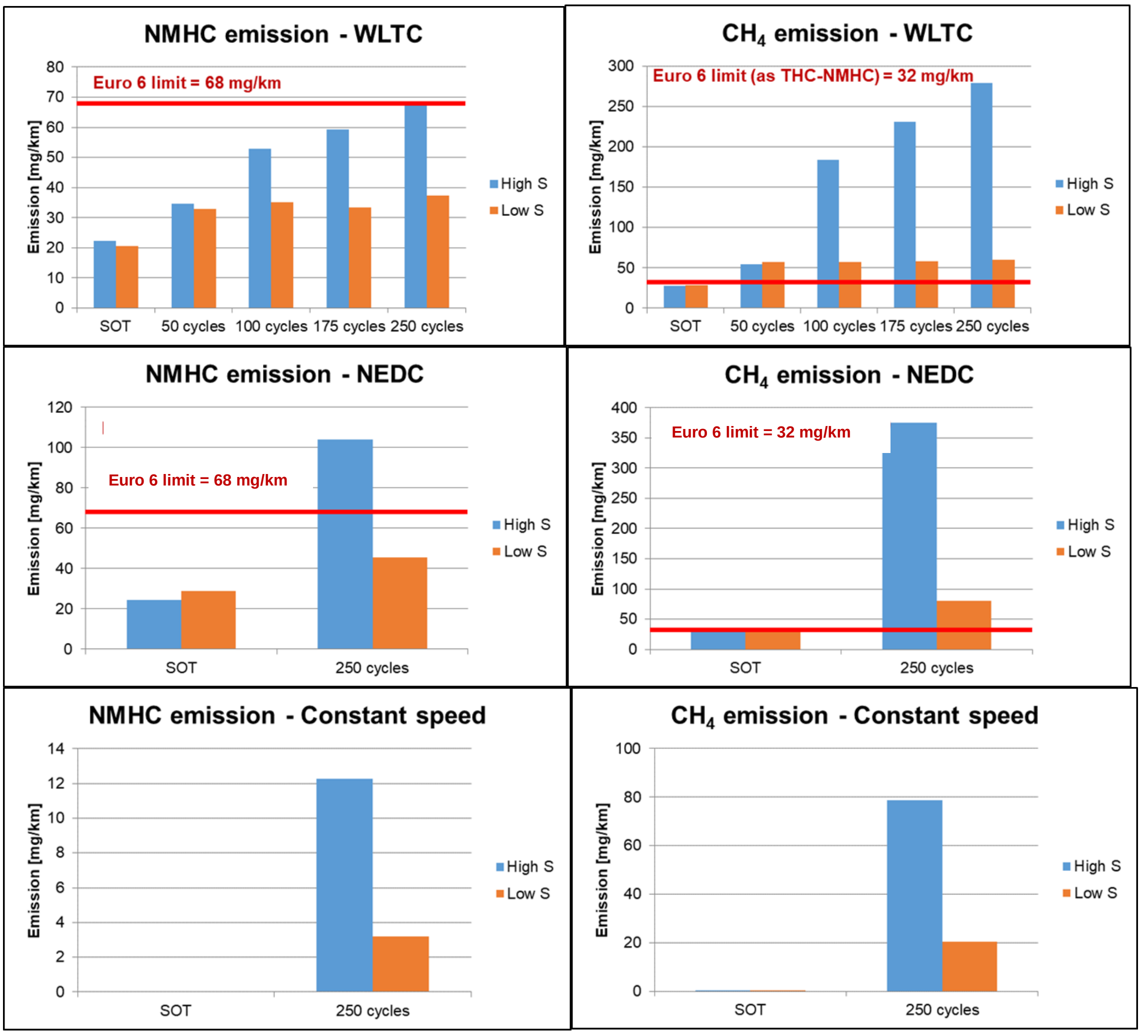
8. APPENDICES

APPENDIX 1 – LIGHT DUTY EMISSIONS RESULTS

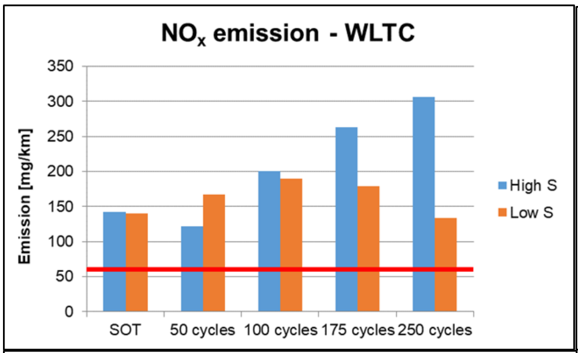
CO and THC

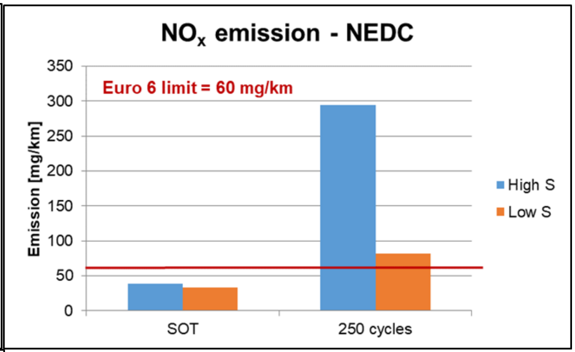


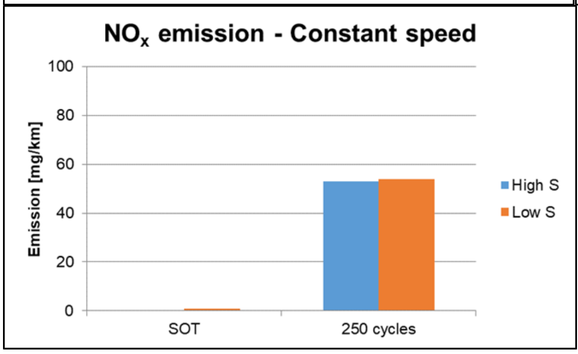
NMHC and CH_4


NMHC emission - WLTC
Euro 6 limit = 68 mg/km
Emission [mg/km]
SOT
50 cycles
100 cycles
175 cycles
250 cycles
High S
Low S
CH4 emission - WLTC
Euro 6 limit (as THC-NMHC) = 32 mg/km
NMHC emission - NEDC
Euro 6 limit = 68 mg/km
CH4 emission - NEDC
Euro 6 limit = 32 mg/km
NMHC emission - Constant speed
CH4 emission - Constant speed

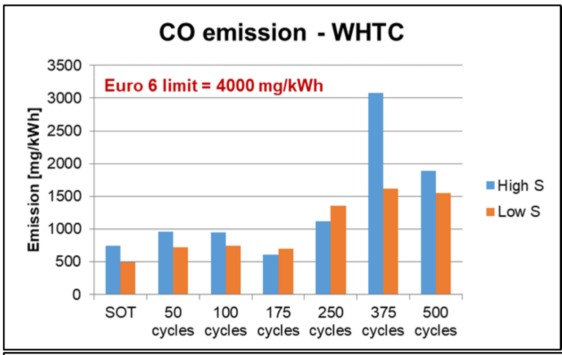
NO$_x$

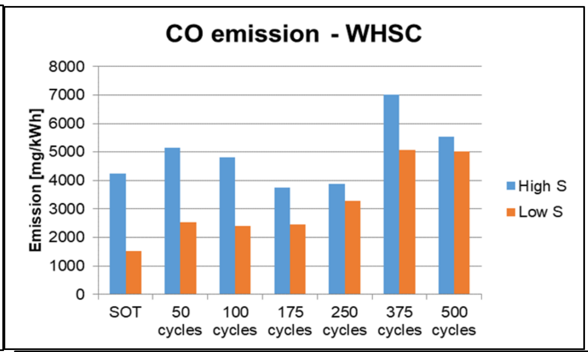

NOx emission - WLTC
Emission [mg/km]
350
300
250
200
150
100
50
0
SOT
50 cycles
100 cycles
175 cycles
250 cycles
High S
Low S

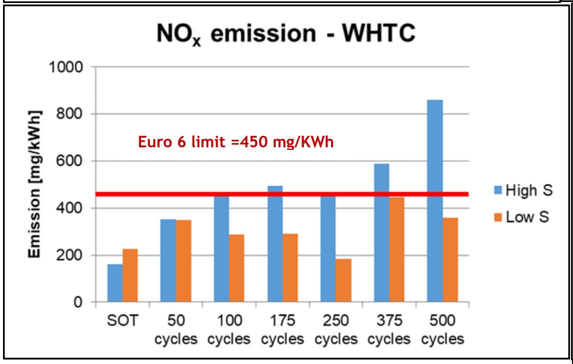

NOx emission - NEDC
Euro 6 limit = 60 mg/km
Emission [mg/km]
350
300
250
200
150
100
50
0
SOT
250 cycles
High S
Low S

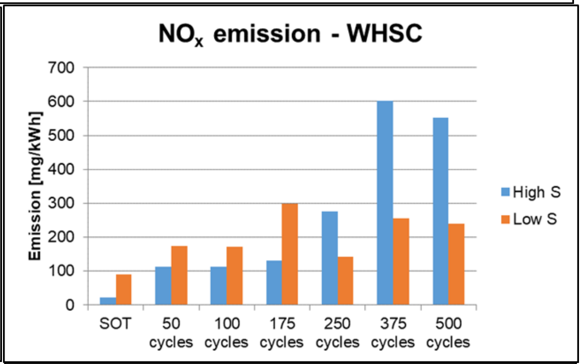

NOx emission - Constant speed
Emission [mg/km]
100
80
60
40
20
0
SOT
250 cycles
High S
Low S

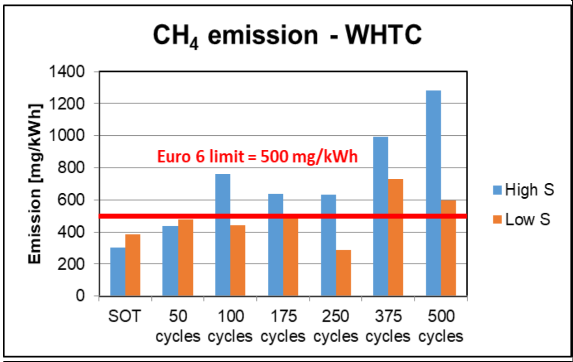
APPENDIX 2 – HEAVY DUTY EMISSIONS RESULTS

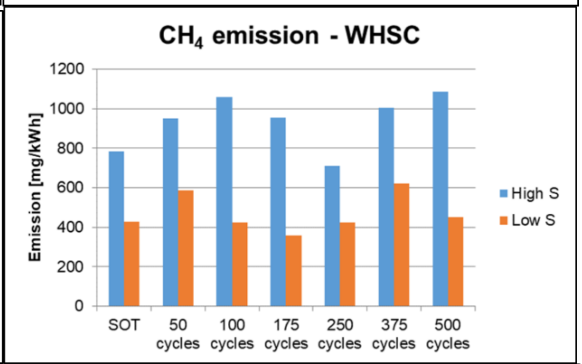


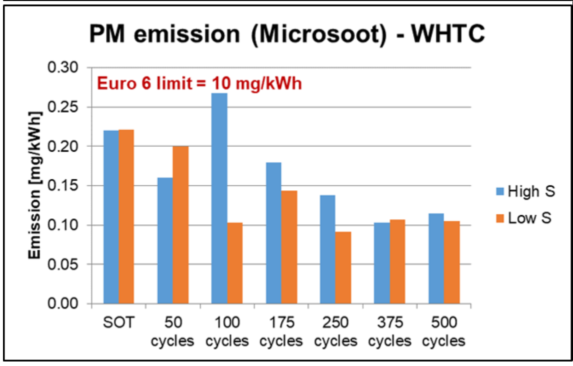


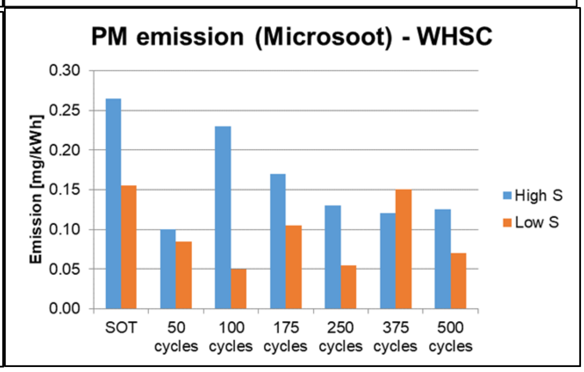












APPENDIX 3

Conversion efficiencies for selected emissions from LD vehicle (WLTC)

					WLTC					
	NOx (%)		CO (%)		CH4 (%)		THC (%)		NMHC (%)	
	LS	HS	LS	HS	LS	HS	LS	HS	LS	HS
SOT	90.12	89.38	97.12	96.96	96.06	96.31	94.69	94.49	88.94	85.88
50 cycles	88.09	91.14	96.96	97	92.33	92.47	90.27	90.02	81.38	78.73
100 cycles	86.28	85.21	96.86	84	92.37	76.05	90.02	74.71	79.43	68.54
175 cycles	86.68	81.8	96.42	76.17	92.5	68.16	90.23	65.01	78.71	39.07
250 cycles	90.62	78.87	95.9	71.62	92.07	63.12	89.31	60.7	73.92	41.97

Conversion efficiencies for selected emissions from HD vehicle (WHTC & WHSC)

			WHTC			
	NOx (%)		CO (%)		CH4 (%)	
	LS	HS	LS	HS	LS	HS
SOT	97.15	98.11	98.31	97.71	85.45	88.31
50 cycles	95.83	95.15	97.58	97.97	80.49	83.95
100 cycles	96.44	94.79	97.52	97.02	82.48	78.53
175 cycles	96.48	94.57	97.67	98	80.89	76.32
250 cycles	97.71	94.26	95.71	96.18	89.16	78.98
375 cycles	94.57	93.25	94.37	89.89	77.32	68.27
500 cycles	95.62	89.35	94.56	93.56	80.08	59.4

			WHSC			
	NOx (%)		CO (%)		CH4 (%)	
	LS	HS	LS	HS	LS	HS
SOT	98.9	99.72	94.1	85.18	68.16	28.43
50 cycles	97.92	98.73	90.45	81.84	54.16	31.9
100 cycles	97.88	98.69	90.71	82.85	62.71	23.09
175 cycles	96.32	98.56	90.3	86.27	69.25	26.72
250 cycles	98.2	96.81	87.51	85.35	64.16	48.88
375 cycles	96.79	92.9	80.48	74.03	58.69	31.8
500 cycles	96.93	93.11	80.02	79.42	67.32	28.32

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