

Mileage Influence on Conversion Efficiency of Catalytic Converter from In-Use Vehicles

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ABSTRACT

Although many works are published about the achieved advancements in the manufacturing of the catalytic converters (CC) system for vehicle engines and their testing under laboratory conditions, there is a lack in the published research about the mileages influence on their conversion efficiency (CE). Dependence of dual-brick CCs' CE in real-world driving conditions on vehicle mileage is studied for the first time. The CC tested are dismantled from the vehicles with mileage from 0 (new one) up to 150000 km. The studied CC are evaluated at the engine test bench containing a dynamometer coupled with a spark ignition engine suitable for this type of CC system. Measurements of CC efficiency are performed at four different engine operation regimes: two loaded regimes and two non-load regimes - low and high speed idling. It is found that the oxidation of CO and HC at all four tested regimes took place almost totally in the first CC. Under higher engine loads the conversion of NO_x also took place mainly in the first CC. The overall efficiency of conversion reaches values above 99% for most of the tested systems. No significant degradation of CE is found in the studied vehicle mileage range. CE of the CC system that has accumulated the highest mileage, of almost 150000 km, reaches values of 97-99% for CO, 86-99% for HC and 64-99% for NO_x at the loaded testing regimes. The smaller values are obtained for the low load regime when the CC temperature is decreased. Considering that the European legislation imposes a durability of 160000 km for the CCs, the results obtained in this work show that for the mileage of 150000 km CC keep a very high CE rate. The CC system that included an aftermarket non-genuine CC is the only one, where significant catalyst deactivation is observed. Registered values of the backpressure do not show any of the tested CC systems as being clogged.

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INTRODUCTION

In order to meet severe emission standards for gasoline fueled vehicles with spark ignition (SI) engines, thermally durable three-way catalyst (TWC) with enhanced activity has been developed. To achieve the goal of development of highly efficient TWC many efforts were spent and described in the numerous publications.

The implementation of the new regulations concerning the emission levels require fast catalyst light off and fast closed-loop control through high speed engine management. For this purpose the novel fast light off catalyst with perforated foil technology was developed, which showed superior emission light-off characteristic and robustness [1]. To satisfy the requirements concerning the durability at high exhaust gas temperatures (above 1000°C), an advanced metal substrate using newly developed stainless Fe-Cr-Al foil with more than 7.5 mass per cent of aluminum was created [2]. Substrates

featuring high cell density combined with ultra thin walls were developed. They offer significant improvement in catalytic efficiency, because of the increased geometric surface area and the reduced thermal mass [3, 4].

At the same time, the position of the catalytic converter has been moved closer to the engine [4]. To obtain high flexibility in converter design, various technologies were proposed [5, 6], e.g. modular block metallic substrate. The latter consists of pre-coated metallic foils, which are welded to a metallic frame and form a substrate block [6]. Another direction of TWC improvement was the increase in usage of palladium as catalyst [7,8,9]. Williamson et al.[8] show that incorporating the Pd-only technologies into close-coupled plus under floor systems, dual brick close-coupled converters, or into close-coupled Pd/Rh systems will be the more likely solutions for achieving optimal emissions, especially for high speed / hard accelerations as occur in the European EUDC or US06 driving cycle. Results of the study [9] indicate that dual

brick catalyst systems containing Pd-only catalysts followed by Pt/Rh three-way catalysts provide an effective strategy for managing Pt, Pd and Rh precious metal inventories while achieving LEV / ULEV emission standards.

However, the higher thermal loads exerted on CC system is the disadvantage arising from its placement near the engine. As a result of consistent further development of new washcoat formulations, temperatures of 1050°C now can be attained without impairment of the coating. The high temperature coating is capable of withstanding temperature up to 1050°C for 24 hours and still maintains very high conversion efficiency, thus allowing vehicle manufacturers to install the CC system closer to engine [10]. The idea of using thermally stable CeO_2 / ZrO_2 oxygen storage washcoat materials was published [11, 12]. In addition to their thermal stability, increase of the bulk oxygen mobility of the CeO_2 / ZrO_2 mixed oxides is of great interest to boost the conversion of the pollutants under transient modes and during the cold operations as well. In the forthcoming years advances are expected in nanofabrication techniques that should enable precise control over the shape, size and location of the catalyst to increase the reaction speed, yield and catalyst durability [13].

Although significant progress was achieved recently in the development of new TWC, their efficiency is reduced with aging. Therefore, comprehensive study is required on automotive catalysts deactivation as a function of vehicle mileage. It has been shown that there are many independent processes that collectively contribute to catalyst deactivation [14]. The most important of them are chemical and thermal mechanisms [15, 16]. Chemical deactivation mechanisms primarily consist of constituent poisoning and surface glazing (Zn, Ca and / or P containing phases). Thermal deactivation results in micro structural changes in the washcoat constituents and the precious metals. These thermally induced micro structural effects include sintering, alloying, particle size changes, phase transformations, and constituent interactions.

Arapatsakos and Sparis [17] showed that the CE of a TWC gradually deteriorates owing to thermal, chemical and mechanical effects. If the case of abrupt destruction as a result of extreme mechanical or thermal stresses is excluded, it is generally accepted that, under normal operating conditions, the deterioration in catalyst efficiency due to chemical deactivation originates from the entrance sections of the converter and gradually progresses towards the exit. Some of the chemical effects that cause catalyst efficiency reduction are reversible, such as HC and CO storage due to a temporary λ sensor malfunction or engine misfire. Other processes are considered to be more permanent, such as lead, sulfur and Zn poisoning. Thermal effects such Pt/Rh and Pd/Rh sintering are irreversible. Ball et al. [18] showed that phosphorus originating from the engine oil poisons the surface of automotive catalyst. In general it is believed that as engine oil is consumed, zinc-phosphorus compounds form a

diffusion barrier on the surface of the catalyst affecting its performance. It was found that non-combusted zinc-dialkyl-dithiophosphate (ZDP) in the exhaust can form a zinc-phosphate glaze over the catalyst, thus significantly reducing its activity. It is known that ZDP has been used for decades as an effective anti-wear, anti-oxidant ingredient in automotive engine oils. Due to the mentioned above reasons, in the last years the content of ZDP in engine oil has been reduced. Beck et al. [19] noted that calcium and magnesium sulfonates may also be present in the engine oil as detergents and their impact on catalyst performance has not been clearly identified. Some investigators have claimed a net advantage of these agents in preventing the deposition of phosphorous and zinc compounds [19].

Although many works were published about the continuing improvements of CC systems for SI engines and about the testing of those systems under laboratory conditions to estimate the CE as a function of the aging, no information is available about a dependence of CC conversion efficiency in real-world driving conditions on vehicle mileage. The aim of this study was to assess experimentally the CE of in-use CC system as a function of vehicle mileage and to compare these results with the CE of a new CC.

METHODOLOGY

For the purpose of this study, number of dual-brick CC systems have been dismantled from in-use passenger cars and tested at the laboratory experimental rig. Carrying out the study at the engine dynamometer test bench enables to reduce as much as possible the number of factors influencing measurement results and, therefore, improve the accuracy of CC evaluation. All the studied CC systems were of the same model. They were dismantled from the in-use vehicles of the same make and year of production - 2003. These vehicles were equipped with the same 1.6L 4 cylinder 4-stroke multipoint injection SI engine. No limitations have been put on vehicle's driving pattern, annual mileage, driving style etc. Only vehicles that are maintained in the authorized garage facilities were considered. Fifteen in-use cars and one new CC took a part in the study, with a mileage range from 0 to 149000 km as shown in [Table 1](#).

The 15 CC systems dismantled from the in-use vehicles were compared with a new CC (designated number 0 hereinafter). All those 16 CC systems were mounted and tested one after the other on the test bench as shown in [Figure 1](#). The test bench is composed of the Hoffman eddy current engine dynamometer and the Renault single point injection, 4 cylinders, 1.4L SI engine with a maximal power of 60 kW at 6000 rpm. As shown in [Figure 1](#), the exhaust system included dual brick CC and allowed the sampling of the exhaust gases from the three different points I, II, III. The 1st sampling point was at the exit of the engine, before the first CC. The 2nd sampling point was after the first CC. The 3rd sampling point was after the whole dual brick CC system.

Table 1. In-use vehicles served as a source of the tested catalytic converters.

No	Registration date	Make of the CC	Mileage Km
0	New	Genuine, OEM	0
1	30.05.03	Genuine, OEM	62011
2	27.05.03	Genuine, OEM	62299
3	26.06.03	Genuine, OEM	63602
4	06.02.04	Genuine, OEM	65012
5	19.11.02	Genuine, OEM	80694
6	29.10.03	Genuine, OEM	84241
7	24.03.04	Genuine, OEM	86251
8	20.07.03	Genuine, OEM	91712
9	19.06.03	Genuine, OEM	99212
10	26.08.03	Genuine, OEM	100323
11	28.05.02	Genuine, OEM	104401
12	11.12.03	Genuine, OEM	106326
13	24.09.03	Non-genuine	108250
14	22.03.04	Genuine, OEM	108518
15	14.08.02	Genuine, OEM	148750

Measurements of CO, HC, CO₂, O₂ concentrations and λ values have been performed by the Bosch non-dispersive infrared gas analyzer type BEA. Concentrations of NO_x in exhaust gases were measured by the Teledyne type 200 EHTM chemiluminescent gas analyzer. To avoid engine speed fluctuations and assure the possibility of engine operation under a steady-state regime, the electric motor of the radiator's cooling fan was powered from an external source and not from the engines alternator.

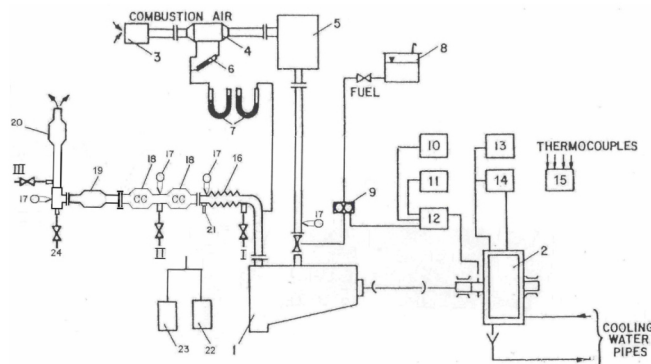


Figure 1. Layout of the engine dynamometer test bench.

1 - Engine; 2 - Dynamometer; 3 - Air filter; 4 - Air flowmeter; 5 - Plenum chamber; 6 - Inclined manometer; 7 - U-manometers; 8 - Fuel tank; 9 - Fuel flowmeter; 10 - Engine speed indicator; 11 - Fuel counter; 12 - Dual timer; 13 - Load indicator; 14 - Servo control module; 15 - Temperature indicator; 16 - Flexible tube; 17 - Thermocouples; 18 - Catalytic converters; 19 - Resonator; 20 - Muffler; 21 - Lambda sensor; 22, 23 - Gas analyzers; 24 - Water purge; I, II, III Exhaust gas sampling points.

Temperature of the engine's exhaust gas at the sampling points I, II and III, (Figure. 1), back-pressure in the exhaust system and the specific fuel consumption were measured in all experiments, as well. All measurements were performed at steady-state engine operation conditions.

The following four engine test regimes were chosen to measure the CE of in-use CC systems: 1st - power 8 kW @ 2000 rpm, 2nd - power 17 kW @ 3000 rpm, 3rd - high idle @ 2000 rpm and the 4th - low idle @ 950 rpm.

CE of CC was calculated by using the following expression:

$$E_i = \frac{(C_i^{before} - C_i^{after})}{C_i^{before}} \cdot 100\%$$

Where: E_i - CE of CC for the pollutant i ; C_i^{before} - concentration of pollutant i before the entrance of exhaust gas to CC; C_i^{after} - concentration of pollutant i at the exit of exhaust gas from CC. For a dual-brick CC system three different values of the CE may be calculated for the pollutants CO, HC and NO_x as follows: E1 is the efficiency of the first CC, E2 is the efficiency of the second CC and ET is the total efficiency of the whole CC system.

The fuel used in the experiments was a commercial gasoline 95 RON, with a sulfur content of 50ppm and a density of 0.738 g/cm³ at standard conditions. It should be mentioned that during the period between the vehicles' registration data until December 31 2004 the allowed content of sulfur in gasoline was 150ppm. From January 1 2005 until disassembling the CC systems from the vehicles, this limit was reduced to 50ppm. The allowed content of phosphorus in the Israeli engine oils has been decreased as well from 0.14% in the year 2003 to 0.08% in the year 2008.

TEST RESULTS

Based on the measurements of CO, HC and NO_x concentrations in exhaust gases, the appropriate CC conversion efficiencies were calculated for all of the considered pollutants at all engine test regimes. Figures 2,3,4 show the results of CC conversion efficiency assessment for CO, HC and NO_x, respectively. Backpressure values, as were measured at the point I (Figure 1), are given in Figure 5. Lubricant and average exhaust gas temperatures at the three sampling points I, II and III (Figure 1) are given in Table 2. Mean values of the engine-out pollutant concentrations, as were measured at all test regimes, are shown in Table 3. The mean values of the total CC conversion efficiency ET for the above-mentioned air pollutants at each one of the four test regimes were calculated. Using the Student t-distribution ($n=15$, $p<0.05$ level of significance) the "confidence interval for means" was calculated for the two loaded regimes. The results are shown in Table 4. The temperatures of the engine's lubricant at the four test regimes (Table 2) show that all the