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# Evaluation of catalytic converter aging for vehicle operation with ethanol

Poliana Rodrigues de Almeida [a, 1], Akira Luiz Nakamura [a, 2], José Ricardo Sodré [b, *]

[a] FIAT Chrysler Latin America, Laboratory of Emissions, Rodovia Fernão Dias, BR 381, km 429, 32530-970 Betim, MG, Brazil
[b] Pontifical Catholic University of Minas Gerais, Department of Mechanical Engineering, Av. Dom José Gaspar, 500, 30535-901 Belo Horizonte, MG, Brazil

## HIGHLIGHTS

- Temperature is the most influent parameter in catalytic converter aging.
- High temperature increases catalytic converter degradation and reduces efficiency.
- Fuel influence on catalytic converter aging was only noticed in the first 20,000 km.

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## ABSTRACT

As the automotive catalytic converter must perform its function independent of the fuel used in flexible fuel vehicles, this paper aims to analyze how operation with ethanol influence catalytic converter performance. To conduct the study, three catalytic converters were aged in a vehicle operating on a chassis dynamometer by 30,000 km. During aging of the first catalytic converter the vehicle was fueled with gasoline containing 22% v/v of anhydrous ethanol, while the second and third catalytic converters were aged using hydrous ethanol (4.9% v/v of water) as fuel, but with different operating temperatures of the catalytic converters. Different tests were performed for each catalytic converter: determination of the degradation factor, surface area analysis by the Brunauer Emmett Teller method (BET), evaluation of oxygen storage capacity (OSC), and determination of conversion efficiency using synthetic gas. The results revealed that the operating temperature is the primary parameter to influence catalytic converter aging.



## 1. Introduction

Catalytic converter deactivation occurs with aging by either chemical or thermal reason, or, to a lesser extent, by mechanical reason. The chemical deactivation of a catalytic converter causes incrustation in the washcoat surface, pore obstruction, modified aluminum oxide ($Al_2O_3$) structure by aluminum phosphate ($AlPO_4$) formation, reduced rates of oxidizing and reducing reactions and loss of conversion efficiency due to chemisorption of impurities in the active phase [1,13]. Chemical compounds present in fuels and lubricating oils, such as lead (Pb), sulfur (S), phosphorus (P), zinc (Zn), calcium (Ca) and magnesium (Mg) are known to cause chemical deactivation of catalytic converters [2]. Catalytic converter poisoning by P, Pb and S is one of the main aging and deactivation mechanisms [8]. Increased P concentration causes obstruction, incrustation of palladium (Pd) particles, deactivation of components and decreased surface area [13].

Thermal deactivation is the main deactivation mechanism of a catalytic converter [1], causing loss of specific surface area, pore obstruction and Pd dispersion, preventing the precious metals to interact with the exhaust gas [3,4,12,13]. In addition, high operating temperature can promote the interaction between the precious metals and the $Al_2O_3$ support, thus reducing conversion efficiency and oxygen storage capacity (OSC) [12]. Catalytic converters aged in an oven at 900 °C showed $Al_2O_3$ segregation and no phase

* Corresponding author. Tel.: +55 31 3319 4911; fax: +55 31 3319 4910.
*E-mail addresses:* poliana.almeida@fiat.com.br (P. Rodrigues de Almeida), akira.luiz@fiat.com.br (A.L. Nakamura), ricardo@pucminas.br, jrsodre@pq.cnpq.br (J.R. Sodré).
[1] Tel.: +55 31 9719 1847; fax: +55 31 2123 5074.
[2] Tel.: +55 31 2123 5324; fax: +55 31 2123 5074.

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alteration of the mixed oxides of cerium (Ce) and zirconium (Zr), but, for aging at 1200 °C, it was observed segregation of all phases and drastic loss of surface area [11].

Deactivation of automotive catalytic converters due to high operating temperatures and inorganic contamination from gasoline and the lubricating oil has been demonstrated [10]. Chemical and mechanical deactivation occurred with catalytic converter contamination by sulfur and pore obstruction by soot. Large texture variation, sintering and loss of surface area showed that the $Al_2O_3$ film is unstable at high temperatures. Zirconium oxide ($ZrO_2$) and ceria ($CeO_2$) have good thermal stability and OSC, but they are not resistant to $Al_2O_3$ sintering [7]. In this case the precious metals dispersed in the washcoat can lose their conversion capacity from the permanent isolation of their particles when the catalytic converter operates at temperatures over 1050 °C.

The primary consequence from thermal deactivation is increased light-off temperature [6,9], increasing tailpipe pollutant emissions during the engine cold start and warm-up period. Increased light-off temperature for carbon monoxide (CO) and propane ($C_3H_8$) conversion has observed for palladium/rhodium (Pd/Rh) catalytic converters aged at 900 °C in a gas flow reactor and at 1200 °C in an oven [4]. An aged catalytic converter can still maintain an adequate CO conversion rate, but there is a loss of efficiency for $C_3H_8$ conversion [6]. Thermal aging was noticed to improve oxides of nitrogen ($NO_x$) reduction and reduce CO and hydrocarbons (HC) oxidation [13].

The light-off for nitric oxide (NO) conversion is less affected for a platinum/palladium/cerium (Pt/Rh/Ce) type catalytic converter than for a Pd type one, as this one shows lower surface area than the former when submitted to the same degradation conditions [9]. NO preferably participates in a reduction reaction with hydrogen ($H_2$) at any temperature; at 350 °C it preferably reacts with CO instead of $C_3H_8$, but, at 400 °C, this trend is the opposite. A Pt/Pd catalytic converter with substitution of rhodium (Rh) by lanthanum (La), Ce, barium (Ba) and Mg compounds does not cause loss of $NO_x$ conversion efficiency, making it adequately perform as a three-way catalytic converter [5]. A Pd–CeZr–LaAl catalytic converter aged at 1200 °C could still convert CO, $C_3H_8$ and $NO_x$, indicating that Pd in mixed oxides of Ce and Zr added by lanthanum-doped aluminum (LaAl) improves the catalytic converter efficiency and thermal stability [11].

The use of ethanol has recently gained importance as an alternative fuel or antiknock additive to gasoline [14]. In Brazil, for instance, ethanol fueled automobiles account for over 92% of total production. In comparison with fossil fuels, ethanol can reduce carbon dioxide ($CO_2$) and most pollutant emissions. To date there is no report on the effects of ethanol on aged catalytic converter performance. Thus, this paper has as an objective to verify the performance of catalytic converters aged for over 30,000 km of vehicle operation over a chassis dynamometer, fueled by hydrous ethanol (E100) and gasoline-ethanol blend (E22). The aged catalytic converters have been submitted to analysis of degradation, specific surface area by the (Brunauer, Emmett and Teller) (BET) method, OSC and synthesis gas conversion.

## 2. Experiments

Catalytic converter aging and emission tests were carried out in a compact passenger vehicle powered by a four-cylinder, eight-valve, 1.0-L spark ignition engine, of 12.15 compression ratio, 93.1 Nm rated torque at 3850 rev/min and 64.4 kW rated power at 6250 rev/min when fueled by gasoline (E22). The engine was fueled by gasoline with 22% v/v of anhydrous ethanol (E22) and hydrous ethanol (E100), which contains 4.9% v/v of water. The vehicle was operated over a single-roll eddy-current chassis dynamometer manufactured by Schenck, of 150 kW rated power and 220 km/h rated speed. To guarantee the correct execution of the tests a driver robot with pedals and gear shift controllers was used.

**Table 1**
Characteristics of the catalytic converters.

| Parameter | Type or value |
|---|---|
| Shape | Cylindrical |
| Diameter | 118.4 mm |
| Height | 127.0 mm |
| Number of cells | 93 cel/cm$^2$ |
| Wall thickness | 0.11 mm |
| Volume | $1.398 \times 10^{-3}$ m$^3$ |
| Pd | 1.82706 g |
| Rh | 0.14814 g |

Table 1 describes the characteristics of the catalytic converters used in this work. Two K-type thermocouples, of 1.5 mm diameter, reading range from 0 °C to 1200 °C and uncertainty of ±2 °C were used to measure the catalytic converter temperature. The thermocouples were installed at 2.50 cm after the beginning of the ceramic monolith and 2.50 cm before the end of the monolith of the catalytic converter. The temperature at both locations was monitored throughout the tests.

The catalytic converter aging tests were performed according to the FIAT standard (Fig. 1) [15]. The vehicle was submitted to this cycle 150 times, totalizing 30,000 km. In this cycle the section ABC was repeated 33 times, the section DEF was repeated 3 times, and the section GHI was repeated 11 times, making a total of 200 km per cycle. Before initiating the tests and at each 50 cycles, corresponding to 10,000 km, the vehicle emission levels, engine setting and air/fuel ratio employed were verified and maintenance was executed if necessary.

The preliminary results obtained revealed the necessity to perform aging tests with a third catalytic converter to verify the individual effects of fuel and operating temperature. That was because the second catalytic converter, operated with E100, presented lower operating temperature than the first catalytic converter, operated with E22. An attempt was made to approach the operating temperature of the third catalytic converter, operated with E100, to that of the first catalytic converter. This was done by new settings of the ignition and injection system electronic control unit (ECU). When the vehicle was operated with the third catalytic converter the ignition timing was retarded. Thus, the combustion

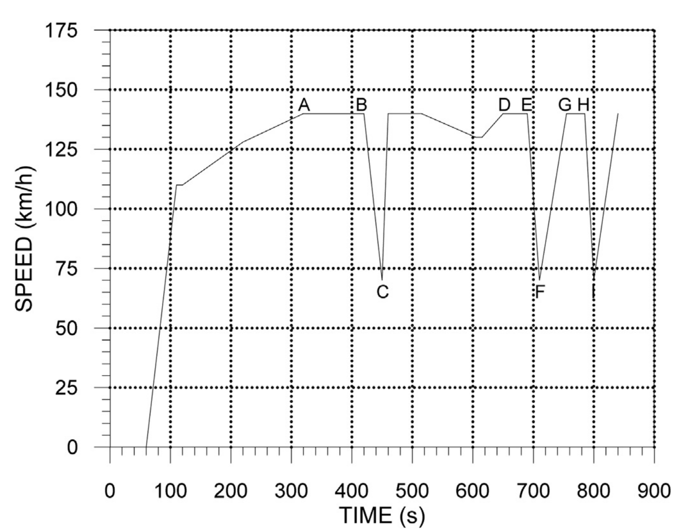


**Fig. 1.** Catalytic converter aging test driving cycle [15].

process finished later in the cycle and higher exhaust gas temperature was produced, approaching that of the first catalytic converter. This way the temperature effect could be eliminated when comparing the results of the first and the third catalytic converters. The complete aging test consumed about 3150 L of E22 and 4150 L of E100.

Before initiating the emission tests the vehicle was preconditioned in an ambient with controlled temperature between 20 °C and 30 °C during a period between 12 h and 36 h. During the cycle execution the exhaust gas sample was collected by a flexible tube connected to the exhaust pipe, diluted in ambient air and stored in adequate recipients. After execution of the cycle the stored gas sample was analyzed to quantify the concentrations of CO, total HC, non-methane HC (NMHC) and $NO_x$. The deterioration factor (DF) of the catalytic converters for HC, CO and $NO_x$ conversion was calculated by the ratio of the concentration of those components at the different aging periods and their concentrations before aging, for a new catalytic converter:

$$DF = \frac{\text{Emission concentration after aging}}{\text{Emission concentration before aging}} \quad (1)$$

The emissions tests were performed according to 1975 U.S. Federal Test Procedure (FTP-75) [16]. The vehicle was initially operated using E22 as fuel, with the default setting of the ignition and injection system ECU. After 30,000 km the catalytic converter was changed by a new one and the vehicle was again operated, this time fueled by E100. Stoichiometric air/fuel ratio was adopted for both fuels. A constant volume sampling (CVS) system was used in the tests. CO and $CO_2$ were measured by non-dispersive infrared (NDIR) analyzers model ABB URAS 14EGA, with 1 ppm and 0.1% resolution, respectively. $NO_x$ was measured by a chemiluminescent detector (CLD) analyzer model AVL CLD i60 LH, with 1 ppm resolution. Methane ($CH_4$) and total HC were determined by a flame ionization detector (FID) analyzer model AVL Cutter FID i60 LDH, with 1 ppm resolution.

After the emission tests the catalytic converters were submitted to an OSC analysis. The OSC is determined by simple observation of the output signals from two oxygen ($O_2$) sensors, located in the catalytic convert inlet and outlet. For new catalytic converter the outlet $O_2$ sensor shows a delayed signal with regard to the inlet $O_2$ sensor. This delay is given as a function of oxidizing and reducing reactions of ceria that involves oxygen retention or release in the catalytic converter surface. If the response time of the outlet $O_2$ sensor is reduced in relation with the inlet $O_2$ sensor, it can be concluded that the catalytic converter is losing oxygen storage capacity due to aging. A catalytic converter is defined to be degraded when the delay is nearly zero, meaning that the catalytic converter lost its oxygen storage capacity. The OSC measurement was made at steady state condition, with the vehicle positioned on the chassis dynamometer. Cooling water temperature and lubricating oil temperature were both kept at 90 °C. The OSC calculation was done by a computer program developed in MATLAB® language.

The tests to determine the catalytic converter efficiency to convert a synthetic gas were carried out according to FIAT 9.02165/02 standard [17]. The aged catalytic converters were submitted to a thermal stabilization treatment at 400 °C ± 5 °C during 30 min. Then, under this same temperature, a synthetic gas was forced to flow through the samples with a constant flow. The synthetic gas composition in nitrogen ($N_2$) balance at the inlet of the catalytic converter is shown by Table 2. The synthetic gas composition at the outlet of the catalytic converter was analyzed by a reactor with an NDIR CO detector of 0.1% resolution, a FID HC detector of 1 ppm resolution and a CLD $NO_x$ detector of 1 ppm resolution. The catalytic converter efficiency was determined according to:

**Table 2**
Synthetic gas composition.

| Component | Concentration |
|---|---|
| $O_2$ (%) | 0.76 ± 0.02 |
| CO (%) | 1.00 ± 0.02 |
| $C_3H_8$ (ppm) | 835 ± 40 |
| $NO_x$ (ppm) | 600 ± 20 |
| $H_2$ (%) | 0.32 ± 0.02 |

$$\text{Efficiency} = 1 - \frac{\text{Outlet concentration}}{\text{Inlet concentration}} \quad (2)$$

After the previous tests the catalytic converters were submitted to an analysis to determine the loss of specific surface area. Each catalytic converter was divided into four parts along its length (Fig. 2). A small sample of each part, of approximately 0.1 g, was analyzed according to the BET method. The BET method is based on the mathematical Theory of Multimolecular Adsorption, which describes the physical adsorption of nitrogen ($N_2$) gas molecules over a solid surface. The equipment used for the BET analysis has an accuracy of ±0.073% within the range of pressure measurement from 0 mmHg to 950 mmHg (0 bar–1.27 bar).

## 3. Results and discussion

Fig. 3 shows the average operating temperature of the catalytic converters during the aging tests. The catalytic converter operated with gasoline and standard engine setting presented average operating temperature of 810 °C. The catalytic converter operated with ethanol and standard engine setting showed average operating temperature of 746 °C. The catalytic converter operated with ethanol and modified ignition and injection system setting showed operating temperature of 844 °C.

The temperature difference between the first and second catalytic converter is due to the fact that, with the standard setting, the engine operates with more advanced ignition timing when operating E100 in comparison with E22 [14]. That is done to avoid engine knocking when operating with E22, once ethanol has better antiknock properties in comparison with gasoline [18]. As combustion starts earlier with ethanol operation and ethanol flame speed is faster than that of gasoline, the combustion products reaches a lower value when released through the exhaust pipe. The application of retarded ignition timing when operating the third catalytic converter, modifying the original setting, produced higher exhaust gas temperature even using ethanol as fuel.

In order to obtain a more detailed analysis of the operating temperature of the catalytic converters, the temperature histograms are shown in Figs. 4–6. The catalytic converter operated with gasoline remained approximately 98% of the whole operation at temperatures between 725 °C and 875 °C (Fig. 4). Using ethanol as fuel and standard engine setting the catalytic converter was operated 95% at temperatures between 675 °C and 825 °C (Fig. 5). With ethanol as fuel and retarded ignition timing the catalytic converter experienced temperatures between 775 °C and 875 °C 93% of the time of operation (Fig. 6). From Fig. 3 and the temperature histograms it is noticed that, ethanol as fuel and retarded ignition timing, the catalytic converter was operated at a higher average temperature and remained 80% of the aging period at 850 °C (Fig. 6). The catalytic converter operated with gasoline was exposed to this temperature level only 19% of the aging period, 67% of which was at a temperature close to 800 °C (Fig. 4). The catalytic converter operated with ethanol as fuel and standard engine setting showed the lowest average temperature (Fig. 3) and stayed 60% of the aging period at a temperature close to 750 °C (Fig. 5).

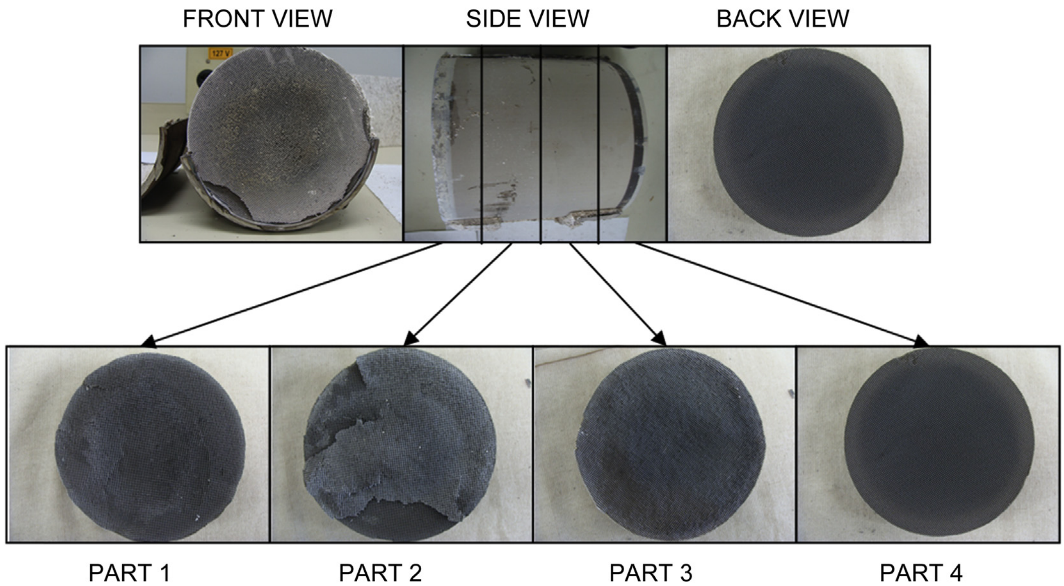


**Fig. 2.** Catalytic converter fractions for BET analysis.

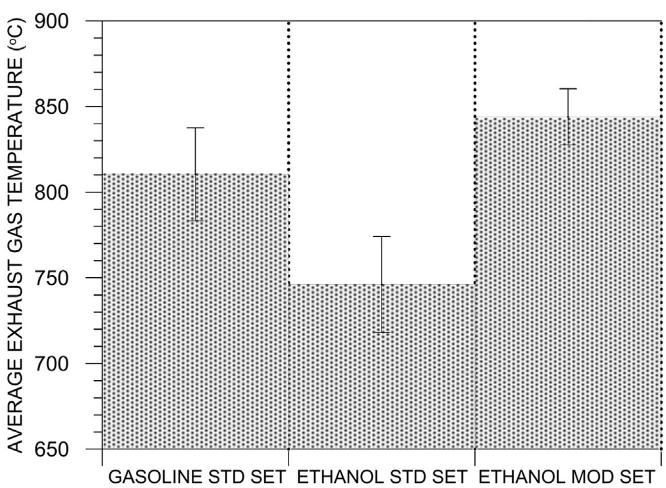


**Fig. 3.** Average operating temperature of the catalytic converters.

The degradation factor growth indicates that tailpipe emission levels were gradually higher after each 10,000 km operation during the aging period for all catalytic converters (Figs. 7–9). Overall the catalytic converter operated with ethanol and standard engine setting presented the lowest degradation factor for all pollutant components throughout the whole aging period. This catalytic converter operated at the lowest exhaust gas temperatures (Figs. 3 and 5). The catalytic converter operated with ethanol and elevated temperature due do modified engine setting presented degradation factors slight higher than the catalytic converter operated with gasoline at the end of the total aging period for all pollutant components (Figs. 7–9). However, up to 20,000 km of operation, the catalytic converter operated with gasoline presented higher degradation factor for CO and $NO_x$ emissions than the catalytic converter operated with ethanol and modified engine setting, even though this one operated at slightly higher temperature (Figs. 3, 4 and 6). For NMHC the catalytic converter operated with ethanol and modified ECU setting, with higher exhaust gas temperature than

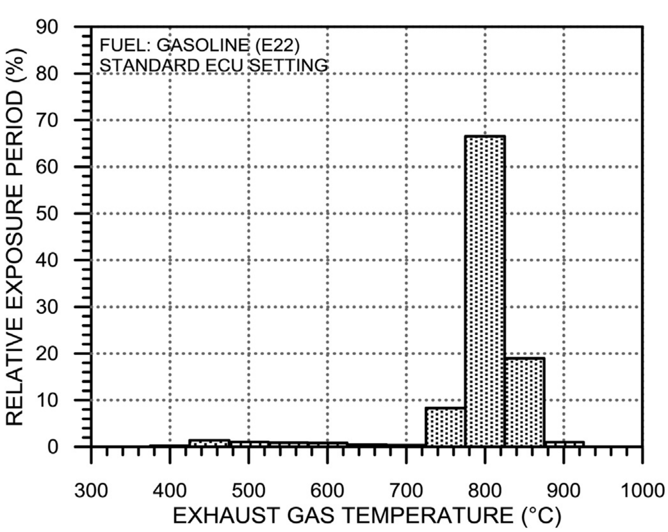


**Fig. 4.** Temperature histogram of the catalytic converter operating with gasoline combustion products and standard engine control setting.

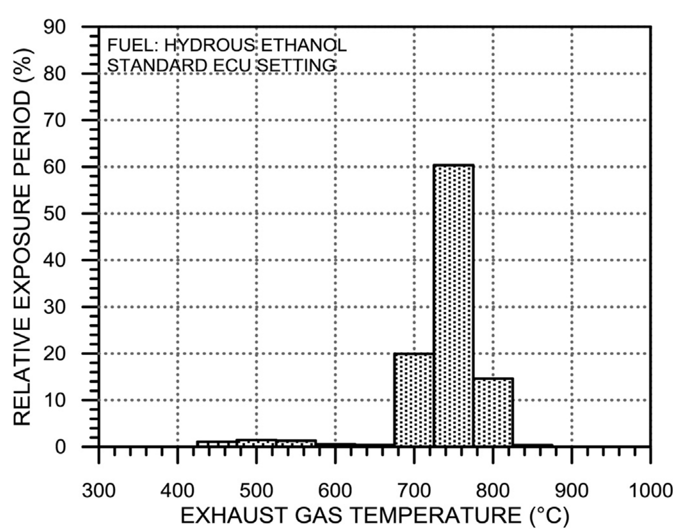


**Fig. 5.** Temperature histogram of the catalytic converter operating with ethanol combustion products and standard engine control setting.

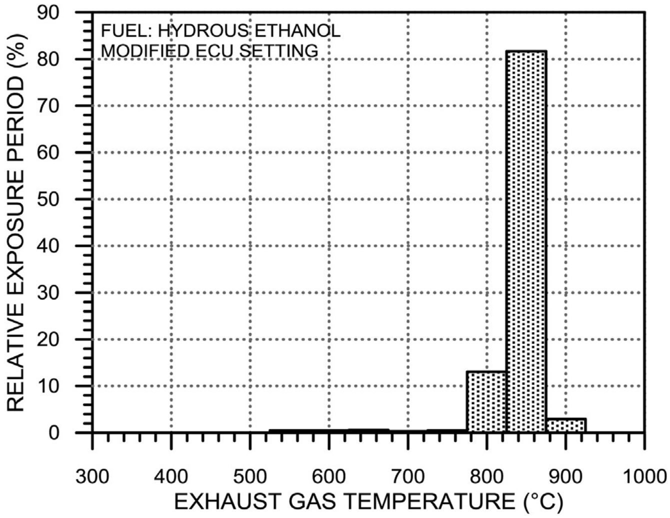


**Fig. 6.** Temperature histogram of the catalytic converter operating with ethanol combustion products and modified engine control setting.

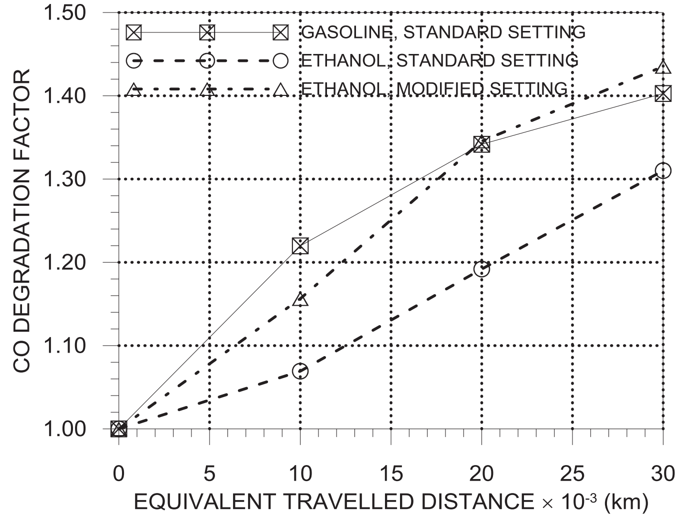


**Fig. 8.** Catalytic converter degradation factor for exhaust carbon monoxide conversion.

the catalytic converter operated with gasoline, showed higher DF throughout the entire aging period.

These results indicate that exhaust gas temperature is the main parameter to affect the catalytic converter degradation with aging. As higher is the temperature of operation of the catalytic converter, as faster is its degradation with aging, making it less efficient to convert the exhaust gas pollutant components. The exhaust gas composition, which varies according to the fuel type burned in the combustion chamber, may also have a significant effect on the conversion of CO and $NO_x$ up to 20,000 km of operation. The conversion of NMHC does not seem to be significantly affected by fuel type even in this aging range, but only by temperature.

The catalytic converter aged with gasoline combustion products showed lower OSC and BET specific surface area than the catalytic converter operated with ethanol and standard setting (Fig. 10). However, the catalytic converter operated with gasoline also showed higher OSC and BET specific surface area than the catalytic converter operated with ethanol and modified setting. This is the opposite trend shown by the average catalytic converter operating temperatures (Fig. 3). These results demonstrate that, as higher is the catalytic converter operating temperature, as lower are OSC and BET specific surface area. A similar relationship between OSC and catalytic converter operating temperature has been pointed out by Nakamura et al. [12]. Fuel type is not noticed to influence these parameters.

The OSC parameter is a technique used to verify the aging level of automotive catalytic converters. As the catalytic converter is aged its OSC tends to be reduced. If the OSC reaches very low levels it means that the catalytic converter lost its capacity to retain oxygen and, thus, can be considered degraded as it no longer can efficiently perform the oxidation and reduction reactions [12]. Therefore, the OSC analysis indicates that the catalytic converter operated with ethanol and modified ECU setting was the most degraded (Fig. 10). Also, the catalytic converter operated with ethanol and standard setting was the least degraded, being the gasoline operated catalytic converter at an intermediary position. This result is in agreement with those shown by Figs. 7–9, as the ethanol operated catalytic converter with modified setting presented the highest degradation factor and the ethanol operated

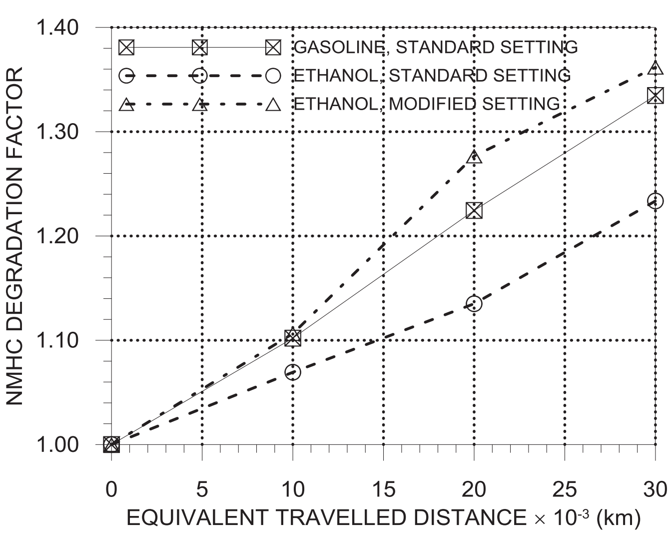


**Fig. 7.** Catalytic converter degradation factor for exhaust non-methane hydrocarbons conversion.

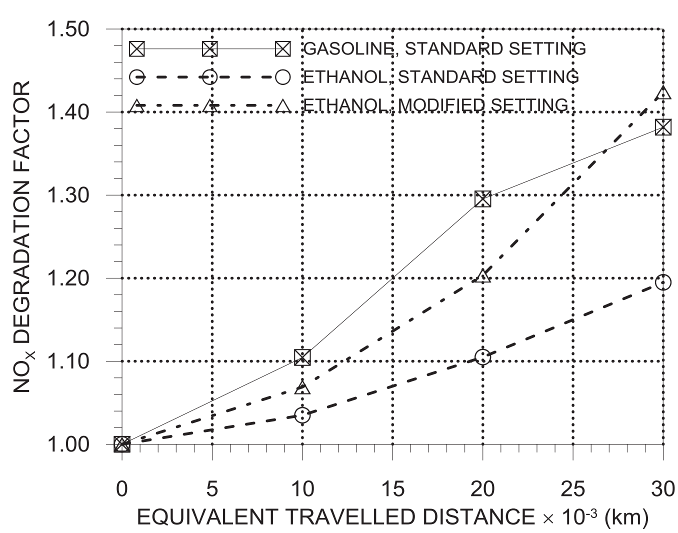


**Fig. 9.** Catalytic converter degradation factor for exhaust oxides of nitrogen conversion.

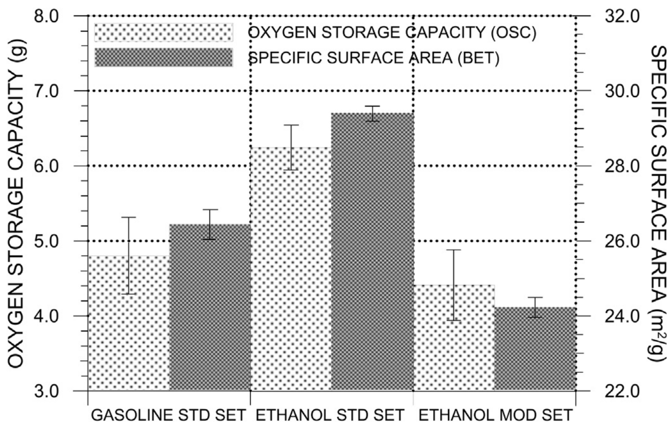


**Fig. 10.** Catalytic converter oxygen storage capacity (OSC) and specific surface area (BET).

catalytic converter with standard setting showed the lowest DF at the end of the aging period.

According to Lassi [1], the loss of surface area by a catalytic converter is mainly due to its submission to high operating temperatures. This agrees with the results here obtained, as the catalytic converter operated at the highest temperatures, with ethanol as fuel and modified engine setting, presented the lowest specific surface area (Fig. 10). In addition, the catalytic converter operated at the lowest temperatures, with ethanol as fuel and standard ECU setting, showed the highest specific surface area determined by the BET method. Generally speaking, the BET analysis associates the specific surface area to the conversion efficiency of a catalytic converter [1]. As higher is the specific surface area, as higher is the catalytic converter efficiency. This is in agreement with the results here obtained, as the catalytic converter with the highest specific surface area also showed the highest conversion efficiency, expressed as the lowest degradation factor (Figs. 7–10). Additionally, the catalytic converter that showed the lowest surface area also presented the lowest conversion efficiency, or highest degradation factor.

A confirmation of the previous results is given by the analysis of the catalytic conversion efficiency using a synthetic gas (Fig. 11). Overall the conversion efficiency of total hydrocarbons (THC), CO and $NO_x$ was very high. That was because the sample length used for these tests was more than double than that indicated by the standard method [17]. The standard recommends the sample length of 50.8 mm, while in this work the total length of the catalytic converter was used, of 127 mm. This is justified because the samples presented cracks that could result in fractures during the cutting process. As the adopted sample length was longer, the catalytic efficiency was considerably elevated for all gas components. Nevertheless, for comparative purpose the results here obtained are adequate.

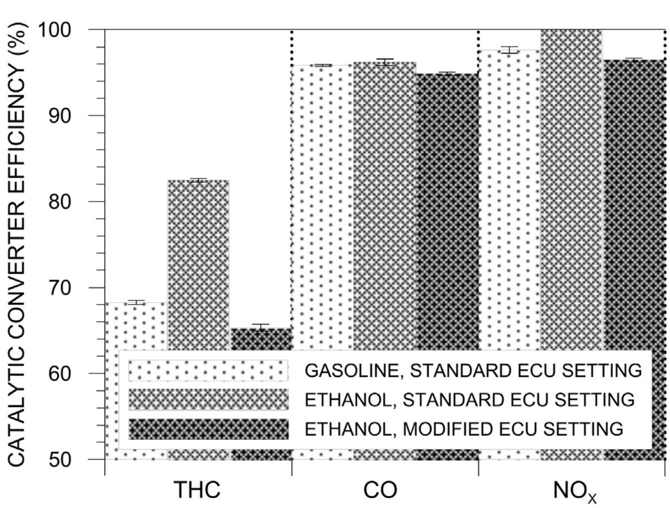


**Fig. 11.** Catalytic converter efficiency for conversion of synthetic gas components.

The catalytic converter operated with ethanol and standard setting presented the highest conversion efficiency for all synthetic gas components of interest (Fig. 11). The catalytic converter operated with ethanol and modified setting showed the lowest conversion efficiency, while the catalytic converter operated with gasoline presented intermediate values. These results are in agreement with the results presented by the FD, OSC and BET analyses, also expressing that increasing catalytic converter temperature decreases fuel conversion efficiency. As it occurred with the OSC and BET analyses, fuel type effects on the results are not identified.

## 4. Conclusions

Different analytical methods applied to analyze catalytic converter aging, using vehicles operated for 30,000 km over chassis dynamometer, fueled by gasoline with 22% of anhydrous ethanol (E22) and hydrous ethanol (E100), demonstrated that the catalytic converter temperature is the most influent parameter. Increasing operating temperature causes increased catalytic converter degradation, decreased specific surface area, decreased oxygen storage capacity and decreased conversion efficiency. The fuel type did not influence the results obtained at the end of the catalytic converter aging period. Nevertheless, up to 20,000 km of vehicle operation, there is an indication that the differences in gasoline and ethanol combustion products composition may affect the conversion of CO and $NO_x$, with no effect on NMHC. The ECU setting to adequate engine operation with the different fuels has an indirect effect on catalytic converter aging, as it determines the exhaust gas temperature and, consequently, the catalytic converter operating temperature. For a flexible fuel engine operating with E100 the ignition timing is commonly more advanced than that for operation with E22, making combustion to finish earlier in the cycle and producing lower exhaust gas temperature.

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## References

[1] U. Lassi, Deactivation Correlations of Pd/Rh Three-way Catalysts Designed for Euro IV Emissions Limits: Effect of Ageing Atmosphere, Temperature and Time, Ph.D. Thesis, University of Oulu, Finland, 2003.
[2] T.N. Angelidis, V.G. Papadakis, Partial regeneration of an aged commercial automotive catalyst, Appl. Catal. B Environ. 12 (1997) 193–206.
[3] R.M. Heck, R.J. Farrauto, Catalytic Air Pollution Control, Commercial Technology, New York, 2002.
[4] D.M. Fernandes, C.F. Scofield, A.A. Neto, M.J.B. Cardoso, F.M. Zotin, The influence of temperature on the deactivation of commercial Pd/Rh automotive catalysts, Process Saf. Environ. Prot. 87 (2009) 315–322.
[5] S. Li, C.C. Wu, H. Li, B. Li, The high-temperature durability of Rh-free three way catalysts used for automobile emission control, React. Kinet. Catal. Lett. 65 (1998) 293–300.
[6] J.R.G. Velasco, M.A.G. Ortiz, J.L. Marc, J.A. Botas, M.P.G. Marcos, G. Blanchard, Catalytic activity study of ceria-zirconia mixed oxides submitted to different aging treatments under simulated exhaust gases, Ind. Eng. Chem. Res. 39 (2000) 272–276.

[7] G.W. Graham, A.E. O'Neill, A.E. Chen, Pd encapsulation in automotive exhaust-gas catalysts, Appl. Catal. A Gen. 252 (2003) 437–445.
[8] M. Moldovan, S. Rauch, G.M. Morrison, M. Gómez, A.M. Palacios, Impact of ageing on distribution of platinum group elements and catalyst poisoning elements in automobile catalyst, Surf. Interf. Anal. 35 (2003) 354–359.
[9] J.H. Baik, H.J. Kwon, Y.T. Kwon, I.-S. Nam, S.H. Oh, Effects on catalysts aging on the activity and selectivity of commercial three way catalysts, Top. Catal. 42–43 (2007) 337–341.
[10] R.A. Silva, M.M. Viana, N.D.S. Mohallen, Structural, morphological and textural characterization of new and used automotive catalysts, Cerâmica 55 (2009) 170–176.
[11] D.C.D. Silva, F.M.Z. Zotin, R. Neumann, C.E. Hori, M.J.B. Cardoso, Thermal aging effect in oxi-reduction properties and catalytic activity of CZ and Pd-CZ catalyst, Quím. Nova 35 (2012) 291–296.
[12] A.L. Nakamura, R.G. Monteiro, R.O. Altoé, R.A. Marques, Z.V. Silva, E.M.R.S. Xavier, Determination of the Aging State of an Automotive Catalyst to Define the OBD Br-2 Calibration Strategy, 2011. SAE Tech. Paper 2011-36-0353.
[13] S.K. Matam, E.H. Otal, M.H. Aguirre, A. Winkler, A. Ulrich, D. Rentsch, A. Weidenkaff, D. Ferri, Thermal and chemical aging of model three-way catalyst $Pd/Al_2O_3$ and its impact on the conversion of CNG vehicle exhaust, Catal. Today 184 (2012) 237–244.
[14] R.C. Costa, J.R. Sodré, Hydrous ethanol vs. gasoline-ethanol blend: engine performance and emissions, Fuel 89 (2010) 287–293.
[15] FIAT Auto Normazione, Fatigue of Anti-emission System on a Chassis Dynamometer, 2006. Chapter 7-T4126, Torino.
[16] ABNT, Light Duty Road Vehicles – Determination of Hydrocarbons, Carbon Monoxide, Oxides of Nitrogen, Carbon Dioxide and Particulate Matter in the Exhaust Gas, NBR 6601 Standard, Brazilian Association of Technical Standards, Rio de Janeiro, 2012.
[17] FIAT Auto Normazione, Trivalent and Oxidant Monolithic Catalyst for Catalytic Converters, 2005. Chapter 9.02165/02, Torino.
[18] H. Bayraktar, Theoretical investigation of flame propagation process in a SI engine running on gasoline-ethanol blends, J. Renew. Energy 32 (2006) 758–771.