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Evaluation of catalytic converter aging for vehicle operation with ethanol

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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

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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	1.398×10^{-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

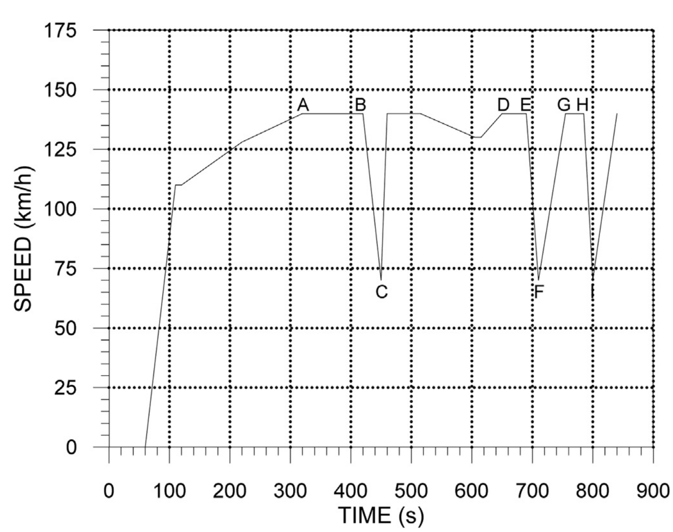

Fig. 1. Catalytic converter aging test driving cycle [15].