Advanced Low Mass Ceramic Substrate for improved Cold Start Performance Targeting PROCONVE L8 Light-Duty Emissions Regulations

Rômulo Petrini Fogaça, Gabriel Urbani Amadei

CORNING International

Jason L. Warkins, Angus A. Craig

CORNING Inc.

Abstract

Brazilian Emissions Regulations are getting tighter in the coming years. With PROCONVE L7 in Jan-2022 and PROCONVE L8 in 2025, regulated emissions limits will significantly decrease, such as, the NMOG + NOx standard from 130 mg/km (PL6) to **50** mg/km (PL8). This challenge will necessitate better aftertreatment performance, with expected increases the catalytic converter PGM content, and consequently higher system cost.

It is understood that approximately 75% of an engine's gaseous pollutants occur during the first few seconds after a cold start, thus it is crucial to promote the emissions conversion performance during that period. One approach is to decrease the heat capacity of the catalytic system, which can be done by utilizing cordierite substrates with thinner walls or an increased material porosity. CORNING has developed an innovative technology to substantially raise the porosity of conventional ultra-thin wall substrates from 35% to 55%, while maintaining their strength. This advanced low mass design allows for a reduction of the substrate volumetric heat capacity, enabling a faster thermal response for improved catalytic function and lower tailpipe emissions.

With an aim to understand the performance of the advanced low mass substrate technology within Brazil's traditional ethanol-fuel environment, an emissions test program was performed using a modern 1.0L turbo-charged E100 engine on a transient dynamometer. The aftertreatment system consisted of 2 catalytic converters; a 1.26L converter in the closedcoupled position, and a 1.0L converter in the underfloor position. The focus of the study was to evaluate the substrate impact in the close-coupled catalyst, while the maintaining the underfloor catalyst. The baseline reference was a standard 750/2 substrate with a conventional TWC formulation in the closecoupled position. To explore the emission and cost reduction potential, samples of the low mass, high porosity substrates were coated and tested with the same TWC formulation, as well as, with reduced precious metal content. Prior to testing, all samples were oven-aged at 900°C to represent an end-of-life condition. Emission testing procedures followed the USEPA FTP75 protocols. Results from this study confirmed that the advanced low mass substrate can significantly reduce emissions (THC emissions by roughly 13%) or allow for lower PGM loadings without emissions penalty.

Introduction

With the advance of Brazilian Emissions Regulations [1], namely PROCONVE L7 and L8, new technologies must be evaluated against conventional automotive emissions aftertreatment systems to give direction on ways to achieve the impending lower certification requirements. One such promising technology is the high porosity cordierite catalytic substrate [2] which is targeted towards helping ICE-powered vehicles by providing a superior thermal response for the catalytic converter to further reduce cold start engine emissions.

This study reports on an evaluation of the standard 750/2 substrate compared against high porosity 800/3 and 900/2 substrates with different PGM load levels. To maintain baseline comparisons, aftertreatment production canning was kept for all the tests. Additionally, substrate in-channel temperatures were monitored by installed thermocouples to evaluate its temperature profile.

FTP75 protocols were used on a modern 1.0L turbocharged engine, fueled with 100% ethanol (E100) within an emissions dynamometer lab, using industrystandard analytic equipment. In this way, the authors could best compare all tested substrates (standard and high porosity) for their relative impact to engine cold start emission results.

Concept of High-Porosity Substrate

A number of methods of realizing early three-way catalyst (TWC) light-off have been considered in previous studies [2], but the main approaches are increasing the temperature of the exhaust gas or reducing the weight of the catalyst or of the substrate. However, increasing the temperature of the exhaust gas generally has a negative effect on the thermal efficiency of the engine, reducing fuel efficiency. Moreover, the rise in exhaust gas temperature also has the problem of heat deterioration of an exhaust components, e.g., manifold, etc. On the other hand, it is known that the catalytic converter weight reduction has the desired benefit of an earlier light-off. In order to reduce the weight of the catalyst, it is necessary to reduce the quantity of the wash coat. While the wash coat material itself produces a high pore volume surface to increase contact between the exhaust gas and the precious metals (PGM) in the catalyst, its reduction could lead to decline in system performance. Reduction of the wash coat also results in the accelerated sintering of the PGM. To help avoid these issues, the present research focused on the reduction of the substrate weight as a means of realizing early TWC light-off. Corresponding concerns with substrate weigh reduction include, maintaining cell structure strength and managing the effects of a lower material density in resistance to thermal shock.

Physical Properties

The new low mass material property design was developed using a systematic process allowing for scale up. A material porosity of 55% was attained for current substrate design wall thicknesses (2 and 3 mil) while meeting the other key performance requirements including mechanical strength and TWC wash coat compatibility. The new material has provided significant improvements in light-off performance to reduce vehicle emissions while ensuring that other performance targets are still satisfied. It is further understood that standard porosity substrates cannot match this low mass solution, and ceramic wall thickness below the current 2 mil wall is not commercially available today for the automotive industry.

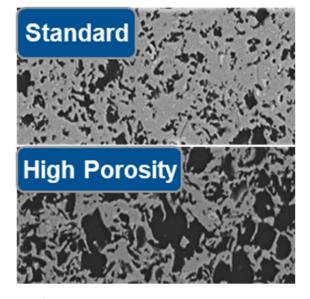
<u>Table 1</u> shows properties of the developed high porosity substrate including cell structure and ratio by weight. The realized 20% increase in porosity against the conventional substrate has allowed for a net weight reduction of 31%, which contributes to early warm-up

of the catalyst. <u>Figure 1</u> clearly contrasts cross-section SEM images of the new high porosity substrate and the standard porosity substrate.

Table 1: Comparison of properties of substrate

| | Standard Porosity Substrate (Celcor®) | High Porosity Substrate (FLORA®) | High Porosity Substrate (FLORA®) |
|--|--|---|---|
| Cell Density (CPSI) Wall Thickness (mil) | 750/2 | 800/3 | 900/3 |
| Porosity | 35% | 55% | 55% |

Figure 1: SEM images of (a) conventional uncoated substrate microstructure and (b) low-mass, high-porosity uncoated substrate microstructure

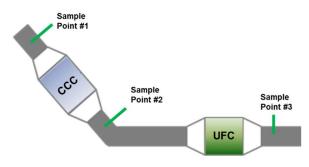


Experimental

In order to stablish the low mass ceramic substrate contribution to cold-start emissions, a modern 1.0L turbo-charged production engine was used to perform the FTP75 emissions testing. Figure 2 depicts the aftertreatment system, with the closed-coupled catalyst (CCC) using either the baseline 35% porosity substrate or the 55% porosity substrate, while the underfloor catalyst (UFC) of 35% porosity was maintained through all testing. It is noted that all CCC substrates had 1.26L of volume and the UFC substrate had 0.99L of volume. Of additional interest, the

figures show the physical locations of engine-out (#1), post-CCC (#2), and post UFC (#3) temperature and raw gas emissions sampling.

Figure 2: Schematic of Aftertreatment System setup



Three different development CC substrate technology had been selected for evaluation: a standard and 2 high-porosity substrate configurations. The variation in porosity enabled evaluation of different levels of wash coat loading (WCL), which would contribute to accelerated catalyst light-off temperatures and consequently decrease engine cold-start emissions. Table 2 shows non-coated properties of standard and high-porosity substrate used in the experiment.

Table 2: Comparison of Substrate Characteristics

| | Standard Porosity CC | High Porosity CC | High Porosity CC | Standard Porosity UF |
|--|----------------------------|------------------------|------------------------|----------------------------|
| Cell Density (CPSI) Wall Thickness (mil) | 750/2.5 | 800/3.0 | 900/2.5 | 400/4.5 |
| Part Size; diameter x length (inches) | Ø4.66" x 4.50" | Ø4.66" x 4.50" | Ø4.66" x 4.50" | Ø4.162" x 4.50" |

Catalyst Coating & Aging

As shown in <u>Table 3</u>, six (6) test systems were prepared for testing in the prescription order to the develop an understanding of the impact of material, cell geometry, and PGM loading. The PGM level was designed to be a reflection of the amount of PGM needed to meet upcoming PL8 regulation emissions targets. The "100% PGM loading" was designed by

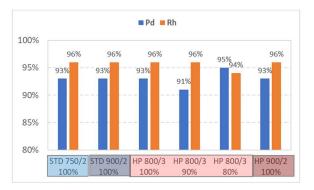
using a base PL7 PGM design and increasing the loading an additional 25% while using a total WCL representative of the actual commercial TWC application. From there, PGM thrifts of 10% and 20% on the CCC were completed on the low-mass, high-porosity 800/3.0 samples to show the impact and trade-off of PGM and emissions performance on a low-mass substrate in comparison to that of a STD conventional substrate as similar commercial geometries.

Table 3: TWC substrate systems as tested with %PGM loading

| Approach | Substrate | Product Line | PGM Load |
|----------------------|------------------|-----------------|---|
| Test 1 Commercial | Standard | 750 / 2.5 | 100% - initial design |
| | High Porosity | 800 / 3.0 | 100% - initial design 90% - proposal 80% - proposal |
| Test 2 Innovation | Standard | 900 / 2.5 | 100% - initial design |
| | High Porosity | 900 / 2.5 | 100% - initial design |

After the coatings were applied, quality tests shown in Figure 3 were made to determine the actual PGM loadings in order to ensure repeatable PGM levels across all samples in order to generate meaningful head-to-head comparison for each system tested. Parts were then aged in a high-temperature oven at an aging condition of 900°C for 50 hours at the coater to represent a full useful life (FUL) condition.

Figure 3: PGM Quality test results



Upon completion of the aging step, parts were then canned by the OEM specific canner to properly reflect the vehicle level system that would be tested onengine. For all testing CCC's were fitted with low-

mass highly durable bolt flanges at the inlet and outlet of the substrate to allow for ease of swapping through the engine test matrix. The same UFC TWC was used for the duration of all testing in order to provide repeatable test conditions and limit the impact on tailpipe emissions variability.

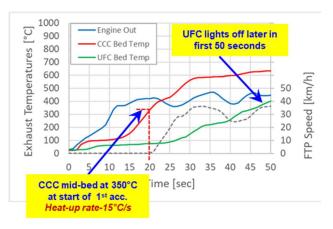
Engine Bench & Test Methodology Description

All emissions testing was completed on a current production 3-cylinder 1.0L GTDI engine via an AC electric dynamometer. The engine used was a current PL6 stock calibration and ran with E100 to be representative of performance under the regional fuel type.

Each test system was run under FTP-75 3-phase test cycle condition at ambient temperature condition (25°C) using an automated speed & torque control input to simulate the dynamics of the engine operating condition. A minimum of 4 tests were run per test system, with the initial test used as a pre-conditioning step for the subsequent tests. The results of the first test were not included in the final multi-test emissions averages.

Prior to the start of testing, baseline characterization of the engine was performed to generate a base understanding of testing conditions. This would allow a point of comparison for the alternative system designs during the course of the experiment to ensure repeatability of engine performance throughout the entire test program. Figure 4 shows engine-out and catalyst bed temperatures over the course of the first 50 seconds of cold-start for the FTP-75 cycle, as this is a critical point in the emissions cycle where a low-mass substrate is expected to deliver the most benefit.

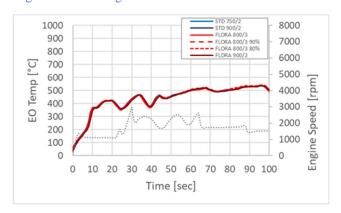
Figure 4: Baseline engine & after-treatment light-off condition



Exhaust Temperatures

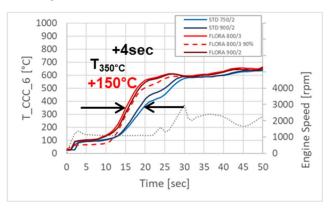
A comparison of the engine-out temperatures for all tested substrate systems is shown in <u>Figure 5</u>, from engine start to 100 seconds in the FTP75. The plotted results depict no significant variation had been observed from test to test, thus exhibiting no unexpected upstream temperature effects to the aftertreatment design comparisons.

Figure 5: A comparison of the temperature of the engine-out from engine start to 100 sec in FTP75



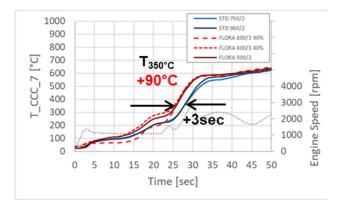
An industry-standard comparison of temperatures at 10mm from the substrate face is shown in Figure 6. This comparison shows the CCC system temperatures from engine start to 50 seconds in the FTP75. The results indicate that at 15 seconds the low-mass 900/2 substrate temperature is at 350°C, whereas the standard 750/2 substrate is much cooler at 200°C. It is additionally shown that the low-mass 900/2 substrate achieves the desired 350°C light-off and full 4 seconds faster than the standard 750/5 in the test.

Figure 6: A comparison of the temperature on the CCC from engine start to 50 sec in FTP75



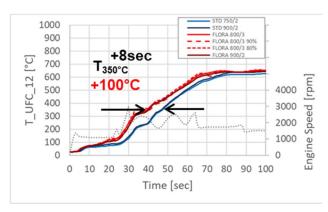
<u>Figure 7</u> compares the CCC systems similarly to above but at 10mm before the outlet face of the close-coupled catalyst. The results indicate at 25 seconds the low-mass900/2 substrate temperature at 350°C is reached 3 seconds in advance compared to Standard 750/2 substrate. It is additionally shown that at 25 seconds of engine start, the low-mass 900/2 substrate is already 350°C whereas the standard 750/2 substrate temperature is only at 240°C.

Figure 7: A comparison of the temperature of the closed-couple catalyst from engine start t0 50 sec in FTP75



Finally, Figure 8 shows the co-plotted UFC system temperatures from engine start to 100 seconds in FTP75. The temperature had been measured at 10 mm from the inlet face of the UFC. The results indicate at 40 seconds the low-mass 900/2 substrate closed-couple catalyst allowed the under-floor catalyst temperature to reach 350 °C, which is 8 seconds in advance when compared to the standard 750/2 CCC, this result is evidence of the low mass substrate contribution.

Figure 8: A comparison of the temperature on the under-floor catalyst from engine start to 100 sec in FTP75



Emissions Test Results

Modal Emissions measurements were collected as previously described and summarized in Table 2, with the focus on engine-out repeatability and tailpipe emissions performance.

In <u>Table 4</u>, engine-out repeatability statistics are shown for the two primary cold-start pollutants with a high-degree of test-to-test repeatability across the entire program. This level of repeatability, while expected from engine-dyno testing, provided a high level of confidence in being able to making meaningful comparisons of system level emissions reduction performance based on the CCC component under evaluation.

Table 4: A summary of engine-out emissions repeatability over the course of all tested systems (minimum of FTP-75 tests per system)

| System | EO THC | ЕО СО |
|-------------|--------|--------|
| (n=6 tests) | (g/km) | (g/km) |
| Average | 1.983 | 13.55 |
| Std Dev. | 0.041 | 0.32 |
| Variance | 7.0% | 7.0% |

With an understanding that test conditions were repeatable across all 6 evaluated systems, the attention then shifted to tailpipe performance results and the comparison between the standard conventional substrate and the low-mass substate. Since an importance has been placed on cold-start emissions and the potential challenges with E100 fuel, only THC and CO emissions results were the primary focus as they closely and best relate to substrate system material benefit and the previously shown temperature heat-up responses.

In Figure 9, the phase breakdown of THC emissions performance is shown for all 6 tested systems. The impact of substrate geometry is shown to have improved emissions performance, with an actual reduction of 2-3% for both the standard substrate $(750/2.5 \rightarrow 900/2.5)$ and the low-mass substrate $(800/3.0 \rightarrow 900/2.5)$. This improvement is expected based upon the increase in geometric surface area

(GSA), but this advantage is much smaller in comparison to the material impact effect that is seen between standard and high-porosity and the resulting reduction in substrate mass from the higher porosity substate. Based on material, a reduction of 11% THC emissions was observed at equivalent PGM loading conditions.

Figure 9: FTP-75 tailpipe emissions results for THC for each of the 6 tested systems.

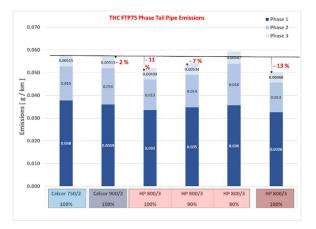
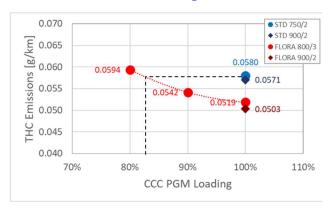


Figure 10 plots the same THC results for the 6 tested systems and shows them in a way to illustrate the way improved light-off substrates can impact tailpipe emissions performance at same or reduced PGM loading levels. As shown, the low-mass 800/3 substrate system design under reduced PGM loading levels is still performing better for tailpipe THC emissions performance in comparison to the standard 750/2 when reduced to 90% PGM loading and is just short of performing at equivalent capability to standard 750/2.5 at 80% of the PGM loading.

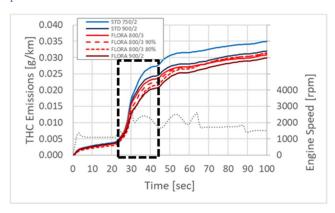
Figure 10: FTP-75 tailpipe emissions results for THC as a function of CCC PGM loading level



Specifically focusing on the cold-start portion of the FTP, is evident that the improved heat-up temperature

performance is the driving factor for reduced Phase 1 THC tailpipe emissions. As shown in Figure 11, faster heat-up times to T350°C of the low-mass substrate manifest as reduced THC emissions during the 1st set of accelerations of the FTP-75. At time=25s, the emissions traces between the standard and low-mass substrate systems separate, with geometry and PGM loading providing additional levels of improved performance within each material set. By time=45s, the emissions reductions for the lower mass systems are fully developed and these persist throughout the remainder of the full FTP-75 cycle.

Figure 11: Cold-start THC tailpipe system performance from 0-100sec of the FTP-75



For Carbon Monoxide (CO), similar trends were observed in comparison to THC tailpipe emissions data. As shown in Figure 12 and Figure 13, all lowmass CCC systems demonstrated better performance over the standard 900/2.5 system. And while the higher porosity, lower-mass systems had the best Phase 1 performance, there were also additional performance advantage gains seen in Phase 2 that provided further improvement of the low-mass systems over standard that were amplified at the higher 900/2.5-part geometry. The improved Phase 2 performance was attributed to the lower-mass substrate systems ability to get back to higher temperature operation quicker under lean, low engineload points of the second phase of the FTP. This calibration impact may not be typical for all vehicles(s)/platform(s) but does show optimization opportunities when using a lower-mass substrate in place on a standard substrate.

Figure 12: FTP-75 tailpipe emissions results for CO for each of the 6 tested systems.

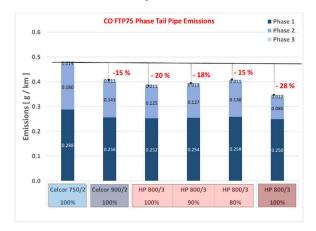
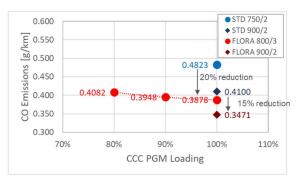


Figure 13: FTP-75 tailpipe emissions results for CO as a function of CCC PGM loading level



Conclusions

This paper examined the performance of high-porosity, low-mass substrates against conventional higher-mass substrates tested using PGM loadings that could be expected for future PL8 emissions design when using 100% ethanol fuel (E100).

As described in the emissions test results section, the high-porosity low-mass FLORA® substrate yields faster heat-up in the initial cold-start portion of the vehicle cycle which leads to lower tailpipe emissions. The reductions seen in these experiments of ~11% for THC and 20% for CO at similar / equivalent geometries are in-line with other experimental results conducted in other regions showing the benefits of high-porosity substrate.

The impact of the higher ethanol-based fuel is not seen to reduce this impact at all and continues to demonstrate that advanced substrates that reduce thermal mass can help to improve tailpipe emissions performance to lower levels or be used to reduce the higher PGM levels needed to meet future PL8

emissions targets while meeting these more stringent emissions standards.

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