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ABSTRACT

The tightening of emissions regulations has required changes in many areas of vehicle systems, including calibration strategies, catalytic converter strategies and exhaust configurations. Engine calibration strategies can be engineered to complement the performance parameters of the converter. Knowledge of the precise window of converter performance for different substrates can therefore provide guidance in targeting engine calibration strategies as well as selecting compatible converter systems within calibration constraints.

In a previous paper [5], we explored the effect of thermal mass on emissions performance in the context of the FTP. This paper expands on the previous work and explores the effect of the aging cycle and thermal mass differences on CO-NOx crossover and light-off profiles. This analysis provides a tool to assist in design by defining a window of performance in the converter to be used in matching to a window of operation in the calibration.

The substrate configurations studied in the analysis are 400/4, 900/2 and 900/1. These represent a direct comparison of constant cell density on the one hand and constant bulk density on the other. The air/fuel sweeps and light-off ramps were performed at steps throughout the aging cycle, yielding information not only on the comparison between the products but also on how their relative performances change over the life of the converter. Emissions and temperature were examined to evaluate the performance.

INTRODUCTION

Previous work by Day[1] has suggested through modeling that as a monolith increases in cell density, the increased reaction activity will result in higher temperatures which will result in faster thermally induced catalyst deactivation. The importance of this parameter lies in the design of new systems wherein a converter with a greater resistance to thermal aging may be a better choice for a higher temperature application such as a close-coupled location.

Therefore, this study was designed to understand and quantify the differences between the aging curves of three different cell density and wall thickness configuration products with respect to the operating window defined by the air/fuel sweep tests and the light-off region of performance.

The information given in this paper and the conclusions drawn are intended to supplement previous data in confirming the recommendations made in the design process to select a substrate optimized for each application. A firm foundation in selecting substrates can save significant time and money in experimental iterations for platform development.

EXPERIMENTAL PLAN

SAMPLE MATRIX

This experiment studied three systems with substrate configurations in the thin wall and ultrathin wall areas. Table 1 shows the configurations used in the experiment with nominal attribute values.

System Name	Cell Density (cpsi)	Wall Thick (mil)	Bulk Density (g/l)	GSA (m^2/l)	OFA (%)
400/4	400	4.5	279	2.87	82.8
900/2	900	2.5	271	4.37	85.6
900/1	900	1.5	165	4.51	91.2

Table 1: Test Matrix

This matrix was designed to provide comparisons of constant bulk density between the 400/4 and 900/2 systems while comparing constant GSA between the two 900 cell systems. These two comparisons will allow us to separate the variables in the contributors to aging and performance.

SAMPLE PREPARATION

The systems tested in this experiment comprised 4.33" inch diameter substrates, 3.94" in length, yielding 0.93 liters of converter volume.

These were coated with nominally 226 g/l of washcoat, incorporating 51 grams of 9:1 bimetal catalyst formulated for close-coupled applications. The precious metal (PM) loading is in the standard range, but at the low end because of the possible thrifting expected in the 900 cell products, so this will amplify results. The bare and coated substrate measurements are shown in table 2 below.

System Name	Bare		Coated		
	Wall Thick (mil)	Weight (g)	Wall Thick (mil)	Weight (g)	Bulk Density (g/l)
400/4	4.24	265.3	4.55	476.0	513
900/2	2.76	276.9	3.24	486.4	524
900/1	1.92	204.3	2.21	411.3	443

Table 2: Substrate Attributes

The data in table 2 show actual substrates in the range of sample manufacturing. It is important to note that the 400/4 sample is in the low range of nominal and the 900 cell products are both in the upper range. This is relevant since the coated actual bulk density of the 400/4 and 900/2 have, while still very close to each other, changed rank.

AGING

Aging was performed using the RAT-A(805) protocol [2], a four-mode rapid aging cycle. The reason for choosing this lower temperature aging cycle was to have better control over the aging process during this step-wise examination, knowing that we would be creating a half-life aging for a close-coupled system and a full-life aging with respect to an underbody environment. The inlet control temperature was 805°C and the exhaust flow of each converter was 80 scfm. The bed temperature was permitted to float according to the aging protocol. California certification fuel was used for aging.

The converters were aged in pairs, 400/4 with a spare converter together and 900/2 and 900/1 together.

Since the inlet was kept to 805°C and the total aging time tested to date is 100 hours, what we have simulated at this point can be considered an approximation of 100,000 miles on a cooler system – underbody, six-cylinder. When applied to a hotter system such as a close-coupled four cylinder, we estimate that aging has simulated between 25,000 and 35,000 miles. Knowing from previous work [1] that the thermal deactivation of a catalyst follows a logarithmic pattern, we can thereby see the entire expected life of a cooler system while still having measured the area of greatest change on the hotter system.

ENGINE

After the catalyst systems were engine-aged, they were installed in the test cell for evaluation. An engine dynamometer test has been developed to characterize performance differences between converter systems during the light-off phase. While the engine is running at a steady state operating point, temperature ramps are controlled using a heat exchanger. The flow rate can be adjusted by controlling the flow between a test and dump leg [3].

This configuration allows repetition of A/F sweep and light-off experiments in rapid succession and reduces variability between tests significantly. Moreover, constant inlet conditions (flow rate, back pressure, heat-up rate, emissions levels, A/F ratio) can be set independently of the installed converter system, which yields an unbiased relative comparison of aftertreatment systems.

Light-off tests were performed with a lean A/F ratio (14.9). The temperature was ramped to 400°C in about 50 seconds and then held constant. The flow rate, A/F ratio and engine-out emissions were kept constant. To obtain representative results, the test was repeated four times on each system. The average has been used for comparison. The fuel control was set to create ±0.5 A/F ratio swings around the set-point in one hertz cycles. Previous work [4] summarizes the good repeatability of the inlet conditions.

Air-Fuel Sweep tests were performed using the same engine and while holding temperature and flow rate constant, varying the air to fuel ratio (AFR) by increments of approximately 0.1 AFR from rich (13.5) to lean (14.7).

TEST MATRIX

In order to understand the effects of cell density on aging, the samples were aged for a certain period, and then tested in the test cell for 4 repeats at each of two flow rates as shown in table 3.

Cumulative Aged Hours	AF Sweep 30CFM	Light Off Tests 30CFM	AF Sweep 60CFM	Light Off Tests 60CFM
10	4	4	4	4
20	4	4	4	4
40	4	4	4	4
100	4	4	4	4

Table 3: aging intervals

RESULTS

AGING

The first paper describing this work discussed the hypothesis that the higher cell density parts would age with a higher exotherm due to their increased catalytic activity. However, this was not born out in statistically significant values in the thermal profiles from the aging cycles. The results are again shown here to provide context for the emissions studies presented.

While a higher inlet temperature for 80% of the measurement points was present for the 900/2 samples during aging, this was only a difference of 5 degrees, well within the norm or +/- 10°C for an aging cycle. Inlet temperatures are shown in figure 1. The peak temperatures are also different and this would predict a difference on the severity of aging. But again the magnitude of the difference is on the order of 5 to 10°C, a normal range for a typical aging cycle. Since backpressure was equalized on the samples using a downstream valve, and since the two aging exhaust streams are from a mixed source and therefore should be equivalent, this inlet temperature variation is likely due to thermocouple placement or proximity to the engine in the aging cell.

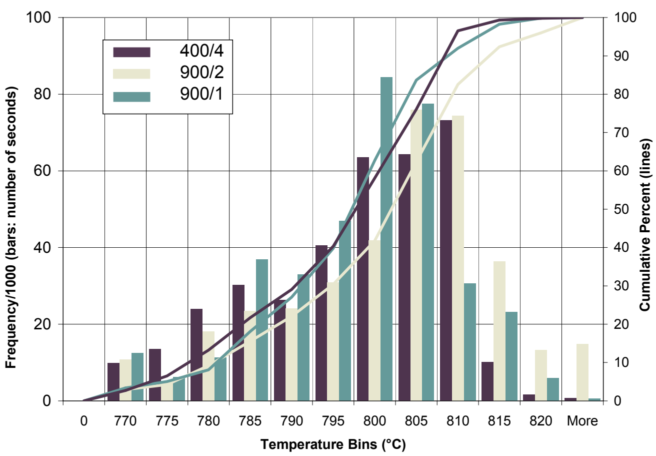

Figure 1: Histogram of inlet temperatures during aging

Inside the substrate at a depth of 1 inch, we see in Figure 2 that the 900/2 continues to have a higher temperature for 80% of measurements in response to the higher inlet as shown in Figure 2. But again the magnitude of the difference at that point is less than 10°C and is therefore considered a normal range. Also important are the peak temperatures of the systems, where we see that the 400/4 and the 900/2 see higher temperatures more often than the 900/1. While the range is larger, the +/-10°C spread is still within the normal variation.

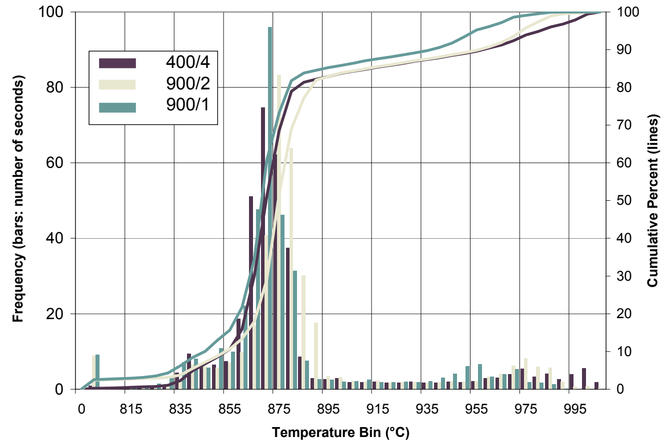

Figure 2: Histogram of bed temperatures 1" deep during aging

The histograms also show that the exotherms of the three systems are not substantially different. Looking at the temperature under which each system spent 80% of its time, for both inlet and 1" deep as seen by the cumulative temperatures line, we can build the following table:

	400/4	900/2	900/1
inlet 80%	803	812	802
substrate 80%	885	890	881
exotherm °C	82	78	79

Table 4: Exotherm of each system during aging

We can see that the bulk density appears to have more of an effect on aging than the GSA. This is good news for the higher GSA products and their long term performance.

LIGHT OFF RAMPS

The light off responses show that even in a light-off test the trend seen in the total FTP [5] is present. Here the light-off curves of the systems at 60CFM from 10 hours of aging to 100 hours show the 900 cell parts having an initially faster deactivation, but that it slows over the aging process to result in a more robust system over time, as we had seen in the FTP tests.

Looking at the aging steps individually, starting with the 10 hours of aging graph below, shows rank as expected with 900/1 performing best and 400/4 having the highest accumulation.

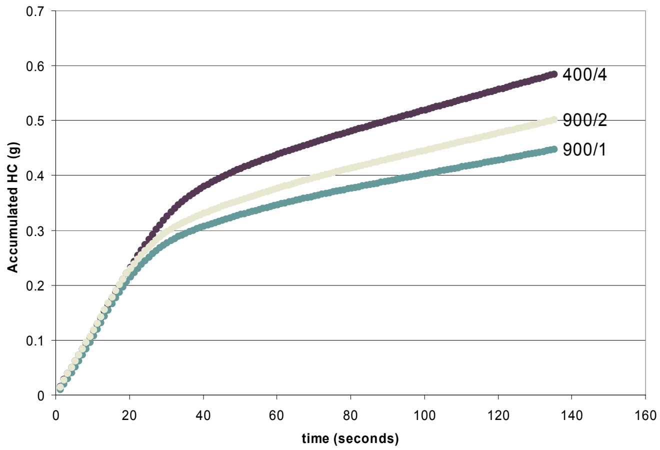

Figure 3: Accumulated Hydrocarbons - 10 hours of aging

The twenty hours graph in figure 4 below shows the 900 cell systems as nearly equivalent to each other and the 400 cell still with higher emissions. This result is in line with that seen on an FTP cycle reported in the previous paper where the 900 cell systems showed an accelerated aging only in the first 20 hours of aging and then became more stable for the remainder of the aging cycle.

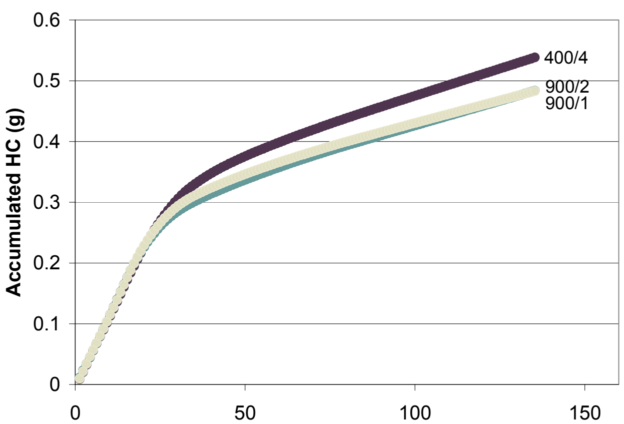

Figure 4: Accumulated Hydrocarbons - 20 hours of aging

Figure 5 shows the accumulated emission in the light off test with forty hours of aging on the systems. Here we can see the 900/2 as the best performer. An anomaly is present for the 900/1 system where the accumulated emissions are higher than the 400/4 system. This is an artifact of the test variability which is confirmed by its resolution in the 100 hour results and its absence in the AF sweep results. So again we see the gap widening as the aging progresses

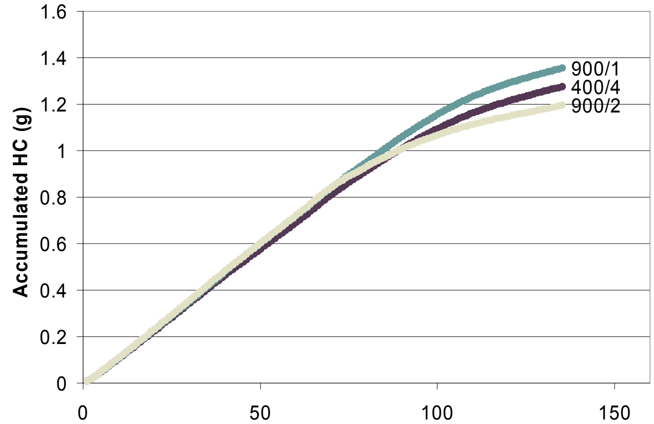

Figure 5: Accumulated Hydrocarbons - 40 hours of aging

As in the previous work, we can see the progression to 100 hour aging shown in figure 6 expanding this difference as the 400 cell parts suffer more from aging and the 900 cell parts maintaining more of their activity. Comparing to the previous figure, the anomaly present at the 40 hour data resolves for the 100 hour test.

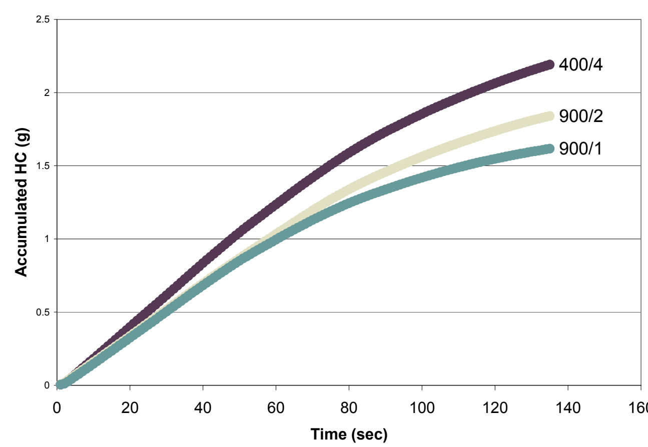

Figure 6: Accumulated Hydrocarbons - 100 hours of aging

In figure 7 below, the total accumulated hydrocarbons are compared to show the progression of aging through the lens of light off performance for both 30 and 60 CFM flow rates. The 900 cell is most favorable, while the 900/1 anomaly shows at both flow rates in 40 hours, but shows the best performance at 100 hours, confirming the predicted rank.

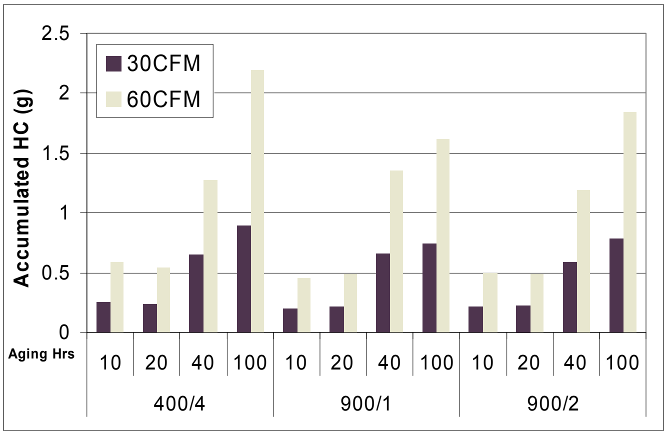

Figure 7: Comparison of accumulated hydrocarbons for both flow rates over steps in 100 hours of aging

Overall the higher GSA systems confirm in the light off regime what what seen in the 3-bag totals earlier. That the deactivation curves of the two different GSA products are a different shape, with the high GSA showing more rapid deterioration in the early part of the catalyst life, but stabilizing and become more robust than the 400 cell systems over the longer life.

This is particularly relevant to the PZEV regulations where maintaining activity over an even longer life is critical to meeting the new, tighter standard.

AIR-FUEL SWEEPS

The air-fuel sweeps provide a look at the operating window of each system. The conversion efficiency at the crossover between the NOx and CO curves are shown in this section, along with the crossover conversion efficiency (CCE) between NOX and HC. The combination of the two CCEs represents a "window" of operation between the highest conversion efficiencies of all three species.

The graph below shows an example of the results in the air-fuel sweep test, demonstrating the repeatability of the tests.

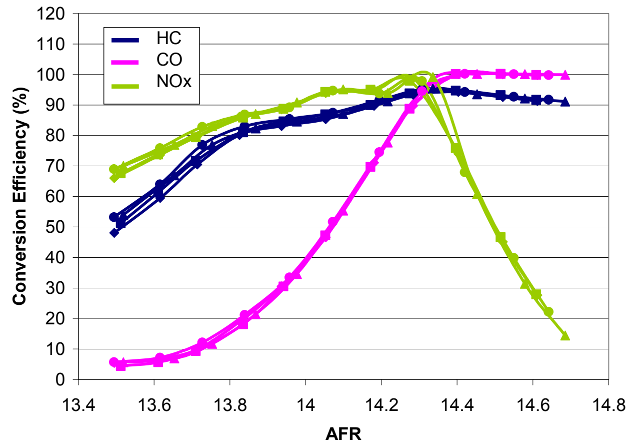

Figure 8: example of AFR sweep results for one system, all four repeats plotted to show good repeatability

The four repeats are averaged and the CCE for each system is tabulated from the sweep charts. These tabulated CCE values are then charted to show the trends between the systems and over time. These data are shown for 20, 40 and 100 hours of aging.

The trend that we see in the next 3 graphs shows the initially high aging effect for the 900 cell products, which stabilizes and by 100 hours of aging retains more of its conversion efficiency than the 400 cell, with the lower bulk density 900/1 product maintaining it's advantage through the sequence.

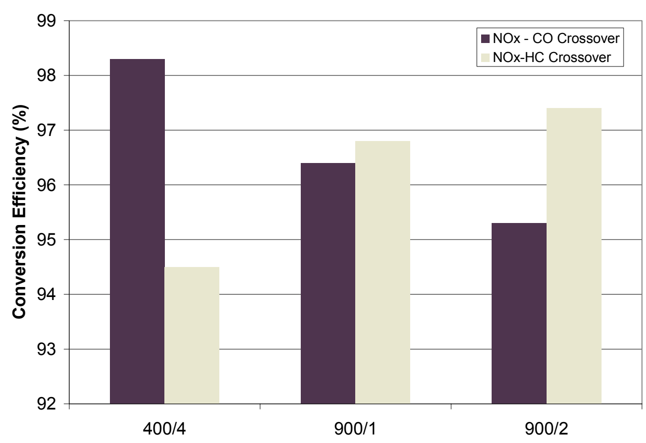

Figure 9: Crossover Conversion Efficiencies 20 hours of aging

One thing that is determined by the sweeps is how the CO-NOx efficiency of the 400/4 system is what starts to give it a light off advantage because of the exotherm from that activity, while its HC-NOx efficiency is still lower than the higher GSA products.

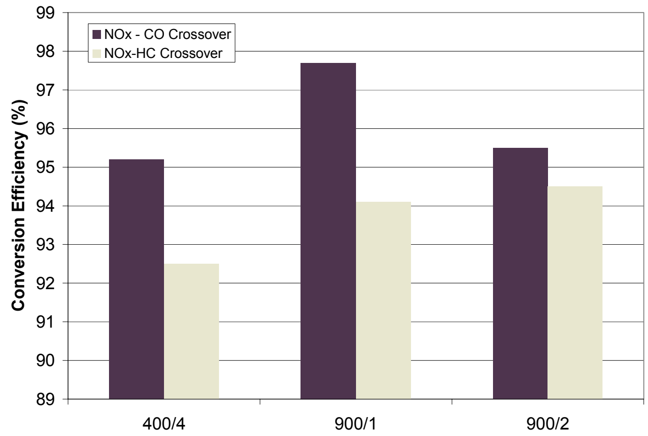

Figure 10: Crossover Conversion Efficiencies 40 hours of aging

The trend continues in the 40-hour aging sweeps in figure 10, where the CO-NOx CCE is reduced in the 400/4 system, but maintained by the 900 cell systems.

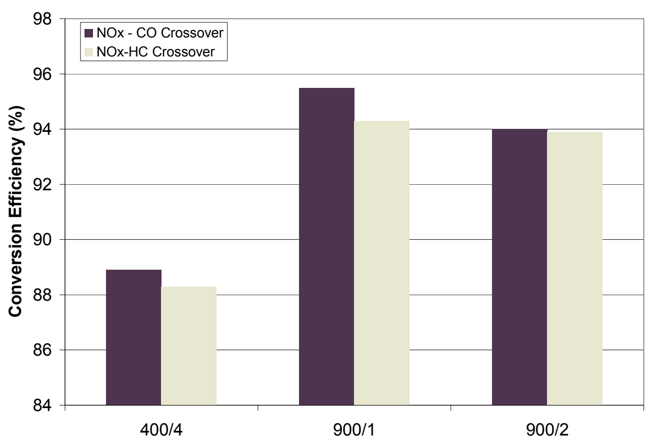

Figure 11: Crossover Conversion Efficiencies 100 hours of aging

At the 100-hour aging stage the deactivation again is most dramatic in the 400 cell system while the 900 cell systems, with the 900/1 still performing better than the 900/2 system as predicted by calculations.

CONCLUSION

During aging, higher cell density converter systems do not experience significantly higher temperature durations when the inlet conditions are held constant. While there is a slight elevation in peak temperature for the higher surface area substrates, this does not result in overall greater thermal exposure over the aging duration.

During testing, the 900/1 maintains its superior light off performance and higher overall conversion efficiency in the air-fuel sweeps. There is a slight acceleration in aging in the first 10 hours, but by the final aging set, the performance remains ranked according to predicted results, with 900/1 outperforming the others in all emissions species. The equal bulk density 900/2 and 400/4 comparison does not show the higher peak temperature resulting in accelerated aging overall at the end of the aging at 100 hours, suggesting an effective robustness due to the increased exposed catalyst surface area and how that translates into performance.

This demonstrates that the GSA-only model of deactivation does not completely describe the aging process we see here. A more likely mechanism based on these data is the maintaining of sufficient active sites by the higher available surface area throughout the aging process. Indeed, this demonstrates a measure of robustness to the 900 cell products. Specifically, the lower bulk density 900 cell system enjoys the benefits of both the robust maintaining of catalytic activity and the shorter duration of peak temperatures mitigating the aging effects in the first place.

This ability to better withstand the thermal aging process bodes well for applications targeting the PZEV regulation which requires continued high conversion performance for longer life applications. In addition, this robustness can become a design advantage in higher temperature applications such as those in a close-coupled location or a high flow-rate application.

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