Structured Foil Catalysts: A Road Map to Highly Effective, Compact Aftertreatment Systems

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ABSTRACT

While emission standards are becoming more stringent with every new legislation level, the engineering of compact aftertreatment system is becoming extremely challenging. This paper outlines a road map for cost-effective, compact aftertreatment systems through use of catalysts with standard and structured foil substrates. The longitudinal-structure (LS) foil disrupts laminar flow regimes within channels enhancing mass transfer and gas reconditioning.

The presented results were applied to DOC catalyst functionality including parameters such as cross-section, substrate type and substrate volume. The catalysts were degreased and tested on a production 15ltr ISX Cummins engine calibrated for US 1998 emissions. Various load points were selected to determine catalyst performance as a function of exhaust gas temperature, exhaust flow rate (space velocity) and exhaust gas composition. A HC injector system was used to characterize oxidation performance at various concentration levels.

The presented results show the trade-off between converter efficiency in mass transfer limited catalyst function and back pressure. The LS-Metalit showed superior performance with high potential for down sizing based on a high volumetric efficiency.

INTRODUCTION

In an effort to minimize the impact of vehicular traffic on the environment and the people living in it, the regulatory authorities are passing more stringent legislation regulating exhaust gas pollutants. For on-road heavy duty diesel engines (HDD engines) the year 2007 saw a significant reduction in the amount of PM-emissions. Particulate reduction technology in conjunction with advanced engine calibration is being utilized in order to comply with US07 standards. In a further step that will take effect in the year 2010 a large reduction in the NO\textsubscript{x}-emissions will be required. This NO\textsubscript{x}-reduction can be achieved with the help of NO\textsubscript{x}-reduction systems like selective catalyst reduction (SCR) systems that used liquid urea injection in addition to the PM-reduction system that is already in place [1].

The diesel oxidation catalyst (DOC) plays a very critical role in the function of the modern after treatment system by taking on a multitude of different functions. First there is the oxidation of unburned hydrocarbons (HC), carbon monoxide (CO) and organic fractions of diesel particulates for tail pipe reduction of these emissions. Low temperature combustion processes like HCCI will also require an oxidation catalyst for the higher HC and CO emissions. Second the DOC increases the amount NO\textsubscript{2} in the engine-out NO\textsubscript{x}. The NO\textsubscript{2} is important for two reasons: First for passive regeneration of a particulate filter (like the Emitec PM-Metalit), in which the trapped soot is oxidized with NO\textsubscript{2}. Second, is the Fast-SCR reaction that takes place at low temperatures at a high reaction rate when there is an equal amount of NO and NO\textsubscript{2} present. The third function of the DOC is to provide exotherms during active regeneration. The active regeneration of a particle filter (wall-flow type) is achieved by injection of additional fuel either into the cylinder after combustion or the exhaust gas system upstream of the DOC. These additional hydrocarbons are
oxidized on the DOC and create exotherms to raise the exhaust gas temperature above the soot combustion temperature. Once the soot has been ignited it will combust in the presence of oxygen. The conversion efficiency of the DOC will dictated not only how much fuel has to be injected to reach the soot combustion temperature but also how much hydrocarbon slip will take place, resulting in tail pipe HC emissions.

With the addition of new safety and comfort equipment on modern vehicles less space is available for the after-treatment system. This yields divergent paths of the space that is available for after-treatment system and high conversion efficiencies that is required of the modern system [2].

During catalyst operation, mass transfer is the rate limiting step [3]. Since the catalytic reaction only takes place in the walls of the catalyst, the pollutants in the exhaust gas have to diffuse to the wall, where they can undergo reaction. The state-of-the-art ceramic and metal catalysts that are in use today, utilize straight channels that run from one side of the catalyst to the other. Straight channel substrates have good mass transfer at the inlet of the channel, where the flow is still in a turbulent regime. However, the mass transfer rapidly drops as the flow becomes laminar along the channel. In laminar flow the highest concentration of pollutants is at the center of the channel, furthest from the wall. The pollutants have a long diffusion path to access the active reaction sites at the wall. Figure 1 shows the mass transfer in a straight channel:

As stated the mass transfer drops rapidly as the flow proceeds along the channel. A long distance is needed to convert all the pollutants in the exhaust gas.

The purpose of Emitec introducing advanced metallic substrate with structured channels is to increase mass transfer. Several “turbulent-like” catalyst products have been introduced into the market and are now in serial production. The LS structure (longitudinal structure) has a counter-correlation that forms blades in the center of the channel [4]. These blades have a two-fold advantage: First, the blade moves catalytically active material into the center of the channel. As mentioned earlier the highest pollutant concentration is in the center of the channel. So the LS structure moves the active material to location at which it is needed. The second benefit is that the blades inhibit the formation of laminar flow in the channel. When the flow reaches the beginning of a blade the mass transfer increases and again decreases as the exhaust gas travels along the blade. At the end of the blade the mass transfer rises again as the flow leaves the blade. This increases the mass transfer and the specific efficiency of the catalyst. For a given volume, a catalyst with a higher efficiency will have a higher specific efficiency. A diagram of the mass transfer in an LS channel is shown in figure 2:

When compared to the mass transfer in the standard channel, the LS channel has the increase in the mass transfer at the beginning and end of each blade. This yields a product with a higher specific efficiency.

**ROAD MAP TO HIGH-PERFORMANCE DOC SYSTEMS**

The substrate technology for diesel aftertreatment system is a key component to address the challenging performance needs. Innovative substrates are used for oxidation catalyst, fuel reformer systems, NO\textsubscript{x} adsorber, hydrolization and reduction catalyst. While catalyst manufacture focus on optimization of storage parameters and long term catalytic activity, substrate manufacture concentrate on tuning following design parameters for robust cost-effective systems:

- substrate cross section, e.g. elliptical and non-road shaped substrates
- substrate volume, length and cross section
- substrate wall thickness, open frontal area to minimize flow restriction
- substrate cell density and geometric surface area to maximize catalyst usage.
- and advanced channel structure to maximize probability for gas wall interaction

The combination of such parameters determines fluid dynamic properties and flow restriction and catalyst effectiveness. Maximization of heat transfer and mass transfer during operation is essential for system robustness and substrate heat capacity determines light-off characteristics and thermal response of downstream components. Following functions were studied:

- restriction and conversion efficiency as function of cross section and substrate length
- influence of substrate structure on effectiveness and restriction
- influence of space velocity
- parameters influencing gas mass transfer

The function was studied on very compact diesel oxidation catalyst installed on a relatively large engine to simulate high mass flow rates and therefore extreme space velocities at different temperatures. The results are very helpful to overcome packaging challenges, converter effectiveness and exhaust flow restriction.

Figure 3 shows the expected back pressure and efficiency performance of three substrate types. In a first step the substrate cross-section is increased by a more rectangular shape. The length is reduced to keep catalyst volume constant. The back pressure is expected to be reduced. Since the GSA is the same and the mass transfer coefficient decreased for the new design, catalyst efficiency is expected to drop. In a second step the mass transfer rate is increased through the LS foil technology. The feature is expected to increase volumetric efficiency of the catalytic converter and a reduction in length is feasible to minimize exhaust flow restriction. Development of such an efficient product leads to the most cost-effective solution for DOC system.

Figure 3 shows a road map to a compact, high-efficiency after-treatment system.

**EXPERIMENTAL SETUP**

**ENGINE SPECIFICATION**

The engine used for this testing was a CUMMINS ISX Signature 600 diesel engine.

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<th>Parameter</th>
<th>Specification</th>
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<tr>
<td>Engine Model</td>
<td>ISX Signature 600</td>
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<tr>
<td>Displacement</td>
<td>14.94L</td>
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<td>Peak Power (Rated)</td>
<td>455 kW @ 1800 rpm</td>
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<tr>
<td>Peak Torque</td>
<td>2880 Nm @ 1250 rpm</td>
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<td>Governed Speed</td>
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<td>Table 1: Engine Specification</td>
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</tbody>
</table>

**FUEL SPECIFICATION**

All tests were run using US 2007 specification ULSD (Ultra Low Sulfur Diesel) fuel.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
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<tr>
<td>Sulfur</td>
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<tr>
<td>C/H ratio</td>
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<tr>
<td>Density</td>
<td>0.8412 g/mL @ 15.56°C</td>
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<td>Lower Heating Value</td>
<td>42.582 MJ/kg</td>
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<tr>
<td>Table 2: Fuel Specification</td>
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EXHAUST SYSTEM LAYOUT & INSTRUMENTATION

Two exhaust system layouts were used for the project. One layout was used during the degreening process and one layout was used during testing. The degreening configuration consisted of an in-exhaust fuel injection system and a warm-up catalyst to generate high exhaust temperatures (650°C) upstream of the specimen DOC (figure 4). After the degreening phase was complete, the warm-up catalyst was removed and replaced with a dummy pipe (figure 5). A valve downstream of the test catalyst was used to ensure that the exhaust gas system back pressure was the same for all test samples. Exhaust temperature and pressure was monitored at the turbine outlet, and at the inlet and outlet of the specimen DOC. Two AVL CEB-II combustion emissions benches were used to sample exhaust gas upstream and downstream of the DOC.

HYDROCARBON DOSING SYSTEM

The low HC engine-out emissions made an investigation of the HC-conversion performance difficult. An in-pipe injector system was developed to study oxidation characteristic as a function of simulated HC levels. An air assisted system was chosen to facilitate delivery of the fuel into the exhaust pipe and improve the atomization. An automotive low pressure port injection fuel injector was used to meter the fuel flow into the air stream. Control of the injector was handled by the AVL PUMA test bed control system. The injector duty cycle was varied between 0 and 80% on a fixed 10Hz firing frequency. For testing, the fuel was injected right at the turbocharger turbine inlet to provide maximum mixing of the fuel with the exhaust gasses. For the degreening phase, the fuel was injected downstream of the turbocharger to avoid any possible damage to the turbine caused by extended exposure to raw fuel.

DOC DEGREENING

Degreening of the DOC prior to testing is important to stabilize its conversion behavior during the test. EPA guidance is that on-engine degreening of a catalyst subjected to diesel exhaust gas should be between 25 and 125 hours duration [5]. However, research has shown that the DOC can reach stable operation with as little as six hours of degreening if DOC inlet temperature is elevated to 650°C with the use of hydrocarbon injection (or post injection) and a heat-up catalyst upstream of the DOC to be degreened [6]. For the purposes of this study, accelerated degreening was chosen for a total duration of six hours per specimen DOC. The engine operating point for degreening was chosen to have the lowest possible exhaust mass flow-rate to maximize the exothermic reaction in the warm-up catalyst and minimize the hydrocarbon slip into the specimen DOC (Table 3).

| Engine Speed   | 1000 rpm   |
| Engine Load   | 1000 Nm    |
| DOC Inlet Temp | 650-670°C  |
| DOC Inlet HC  | 350-450 ppm|
| Exhaust Mass Flow | 630 kg/hr  |

Table 3: Operating Point for Degreening

TEST PARTS

In order to investigate the influence of the different parameters on the performance of the devices, several parameters were varied in the test parts. These include cross sectional area, length, volume, cell density and channel structure. All substrate samples were coated with a specific PGM loading of 40 g/ft³ platinum-only
After coating the test parts were canned with cones (20° inlet cone angle) that included Marmon flanges for easy change-over in the experimental setup.

**TESTING**

For this program, a specially devised steady-state 12 mode test was created to compare the performance characteristics of all the DOCs. The strategy of the 12 mode test is to subject the DOCs to a controlled inlet hydrocarbon concentration while varying inlet temperature. The targeted load points are shown in table 5 and sketched out in figure 6 compared to ESC 13-mode load points. As a result the performance of the catalysts can be evaluated at different space velocities while keeping the temperature similar for three test intervals. The interval 1 is at 325°C, interval 2 at 400°C and interval 3 at 475°C. The history of the test cycle is shown in figure 7. The temperature was held within 10%. In a light-off test the HC $T_{50}$-temperature was found to be 260°C. This light-off test was done on the test engine by slowly increasing engine torque and speed thus raising the exhaust gas temperature. The HC concentration upstream and downstream of the test part was monitored and used to calculate $T_{50}$. Hence the lower temperature of 325°C is sufficient to evaluate the HC-conversion performance. Each 12 mode test was repeated three times: Once with fuel injection off, once with fuel injection controlled to produce 1000ppm HC concentration upstream of the DOC and once with fuel injection controlled to produce 8500ppm HC concentration upstream of the DOC.

During the test cycle each of the mode points was set and run for 5 minutes to allow the catalyst to stabilize. The data was recorded with a sampling frequency of 1Hz during the entire test cycle. The last 30 seconds of each mode was averaged to yield the values for each mode. An analysis of the variance of the data showed that the
standard deviation was less than 0.7% within this 30 second period.

NO₂-FORMATION

The formation of NO₂ is strongly dependent on the temperature. Figure 8 shows the formation of NO₂ as a function of the temperature.

The range shaded in red on the diagram is temperature range in the test cycle. An inlet temperature of 325°C is at the optimum temperature for NO₂-formation. At temperatures above 325°C the NO₂-Formation rapidly decreases due to the thermodynamic limitations. For this reason mainly the NO₂-formation at 325°C will be discussed further.

RESULTS / DISCUSSION

The results will be presented in three groups; the first being the downsizing potential of the LS structure; the second being the influence of the cross section; finally both will be combined into the road map to a compact, high-efficiency after-treatment system.

LS TECHNOLOGY VS STD TECHNOLOGY

Starting off the road map is the downsizing potential of the LS structure. Two catalysts having the same diameter of ø254mm were compared (group 1 in table 4). The state-of-the-art catalyst had a cell density of 200 cpsi. The “advanced” catalyst increased the cell density to 300 cpsi and introduced the LS structure. The catalyst length and volume of the LS catalyst were reduced by 50%. The blades in the channels that are formed by the counter-corrugation breakup the formation of laminar flow, increasing the mass transfer. This gives the LS structure a higher specific efficiency. This downsizing is meant to show the potential for volume reduction and PGM savings and represents an extreme case. Figure 12 and 13 show the HC-conversion of both devices at in test cycle intervals 1 & 3. The space velocity for the 200cpsi reference system is calculated 180k 1/hr and for the downsized 300LS substrate 360k 1/hr at the highest load point.

In figure 12 (inlet temperature 325°C) the downsized LS catalyst shows better HC-conversion than the standard catalyst in all load points. At higher mass flows (space velocities) the benefit of the LS-structure increases from about 5% at lower mass flows to around 30% at high mass flows. Comparing this with figure 13 (inlet...
temperature 475ºC), the HC conversion efficiency is higher. The same trend between the standard and LS catalysts is also seen. The HC-conversion of the LS catalyst is about 3% higher at low mass flows and 20% higher at high mass flows. As the flow rate increases, the flow in the catalyst becomes more “turbulent” and the mass transfer increases. The LS structure “makes up” for the reduction of the volume by 50% and the surface area by 30%.

Figures 14 and 15 show the NO2-formation of both devices in intervals 1 and 3 of the test cycle:

The pressure drop of the LS catalyst is similar to that of the standard catalyst at lower flow rates. The pressure drop of the LS catalyst increases more rapidly as the mass flow increases. However, since the test catalysts were chosen to be under sized for the engine the space velocities that are represented by the high mass flow rates are not common in “normal” catalyst operation. Given the size of the catalysts a mass flow above 1500 kg/h is outside the operating range of a “well designed” catalyst system.

**INFLUENCE OF CROSS-SECTION AND SUBSTRATE LENGTH AT EQUAL CATALYST VOLUME**

The important of catalyst cross section on the pressure drop is widely recognized by the industry. Two catalysts that had approximately the same volume but different cross-sections were compared (group 1 in table 4). The first catalyst had a round cross section. The second catalyst had a “theta” shaped cross section, which looks like a square with rounded corners. The pressure drop of both devices is show in figure 17:
Figure 17: Pressure Drop of 300cpsi Standard Structure with equal volumes but different cross sections in Interval 1 of Test Cycle

Figure 17 shows that the “theta” shaped catalyst has a significant pressure drop advantage. The pressure drop can be lower by more than 1/3 at high mass flows. This is due to two factors: First, the catalyst is shorter, yielding a lower flow restriction due to the channel. Secondly, the larger cross-section has a larger open frontal area, which also reduced the flow restriction.

Figures 18 and 19 show the HC-conversion efficiency of both devices in intervals 1 and 3 of the test cycle. Figure 20 shows the HC-conversion of both devices over the entire test cycle:

Figure 18 shows that the catalyst with the smaller cross-section (ø200x130mm) shows an approximately 10 to 15% better HC-conversion efficiency in test interval 1. Figure 19 shows the same trend with the HC-conversion efficiency of the small cross section part being 10% higher at low mass flows and about 20% higher at high mass flows. Even though the space velocities are similar, the longer distance the exhaust gas travels along the channel, at a higher velocity results in a higher mass transfer and consequently a higher HC-conversion efficiency. The exhaust gas has a longer channel to flow
through and there is more time for the pollutants to diffuse to the channel wall. This result is consistent with figure 2 that shows the mass transfer along the channel in a straight channel substrate. The high mass transfer due to the turbulent inlet flow decreases rapidly as the laminar flow pattern is formed. Figure 20 shows that the HC-conversion of the smaller diameter part is consistently higher than that of the larger cross-section part throughout the test cycle.

Figure 21 shows the NO\textsubscript{2}-formation of both devices in interval 2 of the test cycle:

![Figure 21: NO\textsubscript{2}-formation of 300cpsi Standard Structure with Equal Volumes but Different Cross-Sections in Interval 2 of Test Cycle](image)

As shown in figure 21 the NO\textsubscript{2}-formation of the smaller cross section part is higher than that of the large cross section part. The advantage is about 13% through out the interval. Both catalysts show a decrease NO\textsubscript{2}-formation with increasing mass flow. Both seem to decrease at the same rate.

PUTTING THE ROAD MAP TOGETHER

After looking at the tools that are available, it is time to look at how these tools can be used to build a compact, high-efficiency after-treatment system. As already shown in figure 17, the change to a non-round shape with a larger cross-section will result in a lower back pressure device. The effect of this change on the performance was discussed in the cross-section section i.e. lower HC-conversion efficiency due to lower mass transfer. The LS-structure can be used in order to increase the mass transfer. The higher specific efficiency brought on by the blades in the channels will give the desired increase in mass transfer. Using a combination of the LS structure with the larger cross-section, a device with similar pressure drop but higher HC conversion efficiency and smaller size can be realized. Two catalysts of similar volume using standard technology, one with a round cross section of 200mm and the other with a “theta” shape that has an equivalent round cross-section of 209mm, were already compared earlier in the results section. A “theta” shaped catalyst with of 209mm equivalent round diameter using LS structure was compared to the two catalysts with standard technology. The length of the LS catalyst was also reduced by 20% compared to the “theta” shaped standard catalyst. The HC conversion of the three devices (group 3 in table 4) in question is shown in figure 22:

![Figure 22: HC-Conversion of Catalysts with Different Cross-Sections and Channel Structures with in Interval 1 of Test Cycle](image)

Figure 22 shows that the HC-conversion decreases with increasing mass flow, i.e. increasing space velocity. This is to be expected since the residence time decreases and there is less time available for the pollutants to diffuse to the channel walls. The benefit of the smaller size is associated with a decrease in HC-conversion for the catalysts with standard technology. Both show similar behavior in the decrease of the HC-conversion. The introduction of LS-technology improves the HC-conversion efficiency above the level of the original catalyst. Keeping in mind that the LS catalyst was 20% shorter than the standard catalyst of same cross section, the benefit of the higher mass transfer is clearly shown. At higher mass flows the benefit of the LS-structure becomes more defined. Here the internal “turbulent-like” flow is stronger and the mass transfer is higher.

Figure 23 shows the pressure drop of all three devices in interval 1 of the test cycle:
The pressure drop shows similar trends. The “theta-shaped” catalyst has a lower pressure drop. This is due to the larger cross-section and open frontal area, which yield a lower flow restriction. The catalyst with LS-technology has a pressure drop that lies between the two catalysts with standard technology at lower flow rates. The blades in the channels increase the flow restriction along with increasing the mass transfer. As the flow rate increases, the pressure drop increases faster for the LS catalyst. The pressure drop of the LS-catalyst becomes greater than the pressure drop of the standard catalyst. However, this happens in an area of operation that would not be encountered during regular operation of a “correctly” sized engine/catalyst combination.

CONCLUSION

It has been shown that there are several tools available in designing a cost-effective compact after treatment system:

- The LS structure, that utilizes blades in the channels, will yield a catalyst with a higher specific efficiency. This will lead to a compacter after-treatment system, saving space and PGM cost.

- A downsizing of 50% is possible utilizing the LS structure with an increased cell density. Both the HC conversion and NO\textsubscript{2}-formation of the smaller LS catalyst are higher that the standard catalyst.

- For a given catalyst volume, an increase in cross-section by using non-rounded parts will yield a significant back pressure advantage through a larger open frontal area and shorter channels.

- When an increased cross-section is combined with the LS structure, a very compact after treatment system can be designed that does not increase the back pressure or sacrifice conversion efficiency.

ACKNOWLEDGMENT

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REFERENCES