

New Approaches to Catalyst Substrate Application for Diesel Engines

Meike Reizig, Rolf Brück, Roman Konieczny, Peter Treiber
Emitec GmbH

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ABSTRACT

Nearly all real Diesel engine operation is leading to low exhaust temperatures. Standard catalyst technique remains therefore for significant time below light off. To improve the conversion behavior two approaches were made: placement of tailor fitted catalysts as close as possible to the engine exhaust port before turbocharger and usage of close coupled catalysts with the so-called hybrid design. Both measures are providing visible progress in reducing Diesel engine emissions. Tests were made with modern Diesel engines both for passenger cars and heavy duty vehicles.

INTRODUCTION

Since its invention the Diesel engine became the most efficient type of power unit and it seems to be that this is true for the future too. Although Diesel engines in the past were used more as the work horses between all the engine applications this situation changed especially in Europe within the last five years. Today even racing cars [1] and luxury vehicles [2, 3, 4] are powered by Diesel engines. Reasons are as well the outstanding good fuel consumption and in some countries the attractive price of Diesel fuel as the impressive torque of modern direct injection Diesel engines with one or two turbo chargers and intercoolers. In addition to all these positive items the exhaust emission behavior is good with respect to hydrocarbon, carbon monoxide and carbon dioxide emissions. Nitrogen oxides and especially particulate emissions are the unfavorable aspects of the Diesel engine. The success in emission control on all other engines types and the rising numbers of Diesel engine driven vehicles made it absolutely necessary to improve the exhaust emissions of Diesel engines too. Challenging standards of the future [5, 6, 7, 8] gave the starting signal for intensive research and development work on Diesel engines worldwide.

With the experience of tailor fitted solutions for metallic substrates for gasoline engines automotive catalysts efforts were made to develop components which are providing substantial progress in the emission control of Diesel engines. As a result of the very efficient combustion process Diesel engines are showing relatively low exhaust gas temperatures especially under real driving conditions at partial load and speed. While at gasoline engines the main emission control problem is how to get after engine start as quick as possible light off temperature of the catalytic converter Diesel engines have an additional problem. They tend to fall below light off temperature again during deceleration and low idling modes e. g. in the European driving cycle (figure 1).

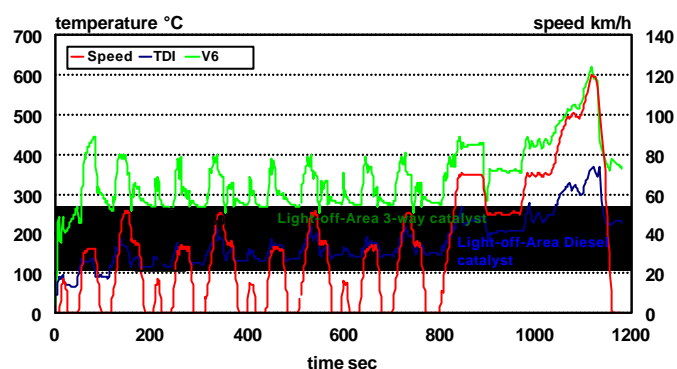


Figure 1: Temperature comparison of catalysts in underfloor position (1,9 l TDI 4-cylinder with a V6 – cylinder gasoline engine in EU III cycle)

The measures described below are taking this particularly into account.

Figure 2 depicts a scheme of an engine which shows the possible locations to install catalysts. The closest position to the engine is the catalyst in the exhaust ports of the cylinder head. The next position is the exhaust manifold leading to the turbocharger or the position right in

front of the entrance to the exhaust turbine of the turbocharger. Both locations offer the advantage of higher exhaust temperature compared to a placement after turbine because this device works as a heat sink during cold start and takes away energy during operation.

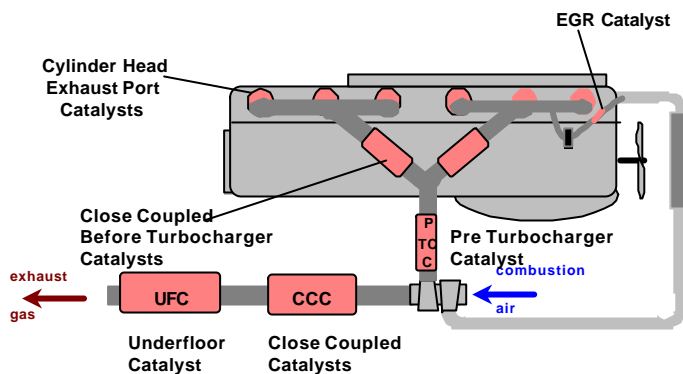


Figure 2: Possible catalytic converter positions (6-cylinder in-line engine)

Further possibilities are the close coupled position after the exhaust turbocharger and the standard underfloor position.

THE HYBRID CATALYST

The idea is to influence the light-off behavior of the catalyst by different thermal masses of the substrate. Using metal foils as the basis for a substrate it is easy to vary the foil thickness for optimization of the converter. Before running laboratory tests a computer program was used which proved to be very successful in the prediction of catalytic conversion processes.

COMPUTER CALCULATIONS – The comparison of the influence of different foil thickness was done looking on accumulated hydrocarbon emissions during second 0 to 360 of the European passenger car driving cycle. Due to the thermal mass of substrates with identical structure only varying by the foil thickness those with thin foils are showing after cold start a quick response to rising temperatures as the hydrocarbon emissions becomes nearly constant at about second 130 to 140 (figure 3).

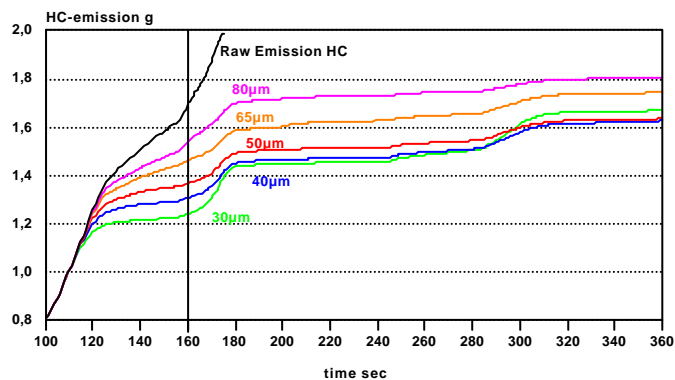


Figure 3: Catalyst calculation, influence of foil thickness (Cumulative HC - Emission with a catalyst \varnothing 100 x 130 mm, 62 cells/cm²), part of EU II cycle

Substrates with thicker foils show lower conversion at the same time of test cycle. Looking at test modes later in the cycle (e. g. at about second 300 to 320) it is to be seen that the substrate with the thin foil (30 μ m) let higher hydrocarbon emissions pass than those with thicker foils (40 and 50 μ m). Looking on the equivalent graph with conversion efficiency rates the explanation of this effect is easy to be recognized. Due to the lower thermal mass and therefore the lower heat storage the temperature and the efficiency of the substrate with 30 μ m foil material is reduced again very quickly when deceleration and idling occurs in the test cycle (figure 4).

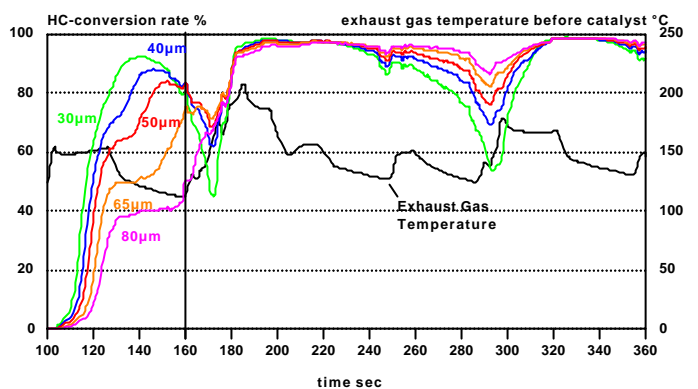


Figure 4: Catalyst calculation, influence on the conversion rate depending from foil thickness (Cumulative HC - Emission with a catalyst \varnothing 100 x 130 mm, 62 cells/cm²), part of EU II cycle

Having the behavior of substrates with foils of 30 μ m and 80 μ m in mind it is obvious to propose a catalytic converter with two or more bricks of different foil thickness (figure 5).

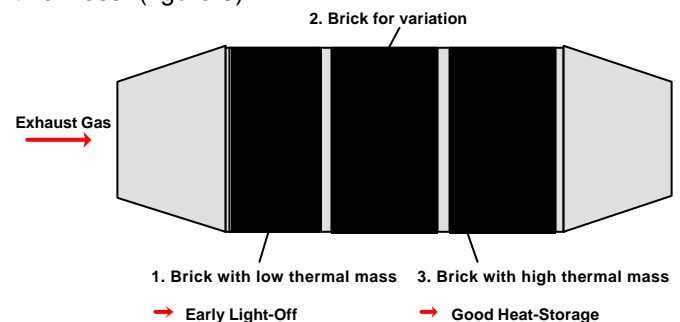


Figure 5: Hybrid catalyst

The computation was based on a catalyst with three bricks. In the first case all three bricks (no.1: length 40 mm, no. 2: length 50 mm, no. 3: length 40 mm) have the same thin foil material of 30 μ m as a reference and the link to the calculations with bricks of 130 mm length. The next step was a calculation with a last brick made from 80 μ m foil material. For the final calculation the medium

brick was made from 80 μm foil too. The results of these computations are given in figure 6.

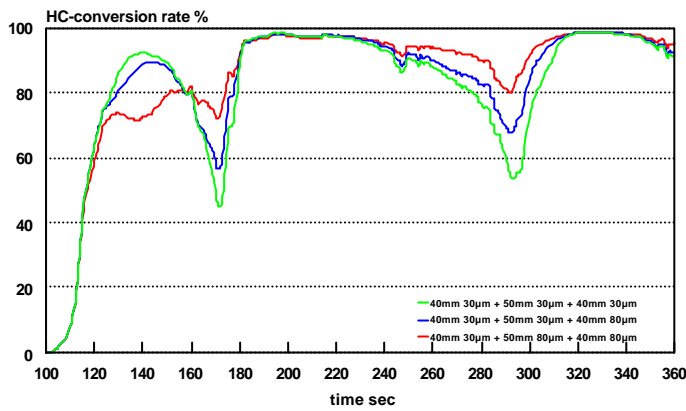


Figure 6: HC conversion rate with hybrid catalyst (part of the EU II cycle)

Although the combination with a thin foil entrance brick and two brick of relative thick foil material is showing a little disadvantage during cold start (at about second 125 to 160) the overall conversion of this arrangement seem to be very promising. Showing the same results in form of accumulated HC emissions (figure 7) the expected advantage could be seen.

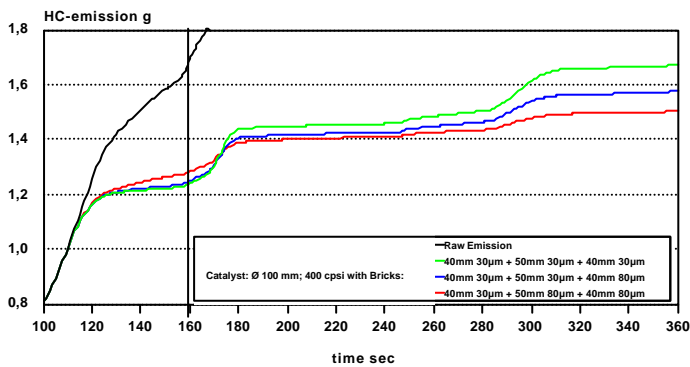


Figure 7: Accumulated HC emission with hybrid catalyst (part of the EU II cycle)

The calculation indicates a potential to reduce the hydrocarbon emissions by more than 12 to 15 % for this part of the test cycle. It can be assumed that the reduction of carbon monoxide will be enhanced to a similar degree.

MEASUREMENT RESULTS – A modern 3 litre 6-cylinder in-line engine with common-rail injection and intercooled turbocharging (turbine with variable geometry) on a test bench was used for laboratory testing. During all experiments the engine setting was unchanged. Two quick response analyzing systems were installed for modal analysis of the gaseous concentrations in the raw

exhaust and behind the catalytic converter. The exhaust system was original equipment from a medium-sized passenger car. The sequence of engine speed and torque was set according to measured values during EU III test runs on a chassis dynamometer. The hybrid catalysts were in the close coupled position of the real car instead of the original ceramic cats. The insulation of the exhaust system was taken from the car too. The exhaust mass flow was calculated by measurement of the fuel consumption and the mass flow of the combustion air on a modal basis. Two systems with identical coating were compared: the original ceramic close coupled catalyst (oval shape, diameters 90 mm x 185 mm, length 114 mm, volume 1492 cm³, 62 cells/cm², wall thickness 165 μm) and the hybrid catalyst (diameter 127 mm, 62 cells/cm², 1. brick length 31 mm with 30 μm foil thickness, 2. brick length 70 mm with 80 μm foil thickness, volume of the hybrid catalyst 1393 cm³) plus the original underfloor catalysts (volume 762 cm³ each, 62 cells/cm², foil thickness 40 μm).

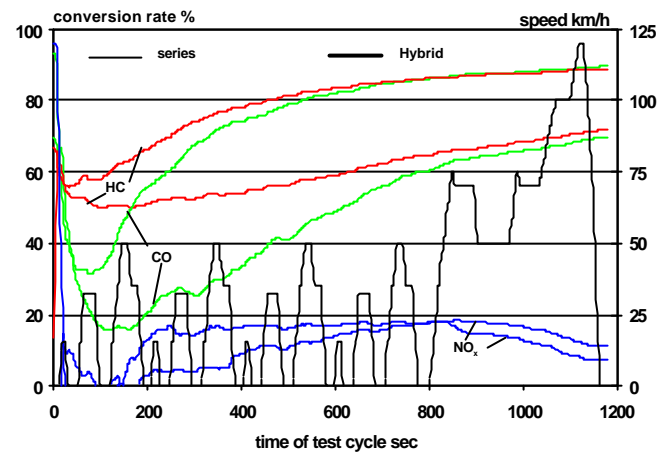


Figure 8: Comparison of cumulative conversion rates for gaseous components with ceramic and hybrid catalysts in close coupled position (EU III cycle)

The standard converter system reduces e. g. the hydrocarbon emission on the average by 60 %. The hybrid catalyst results in a reduction of 79 %. Figure 9 shows the EU III cycle results, the gaseous components were derived from the modal analysis, the particulate emission was measured by the standard gravimetric procedure.

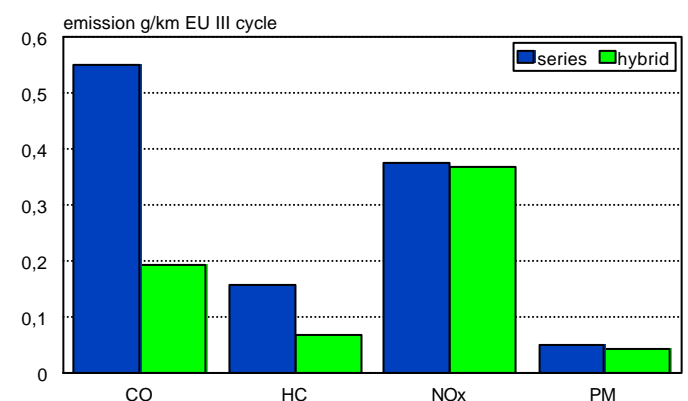


Figure 9: EU III cycle results of gaseous and particulate emissions with standard converter configuration, but with ceramic or hybrid catalysts in close coupled position

The measured lower emission values for HC and CO agree very well with the before calculated advantages.

THE PRE-TURBO CATALYST (PTC)

The most important criterion for the design of this type of catalyst is the very small space which is available in the connection of an exhaust manifold to the turbocharger. Most of the pre-turbo catalysts have substrate volumes of distinctly less than 100 cm³. Standard calculation programs will therefore lead to conversion rates of nearly zero according to the extremely high space velocities of more than 10⁶/h. The following picture (figure 10) shows a pre-turbo catalyst for a 12 litre heavy duty Diesel engine.

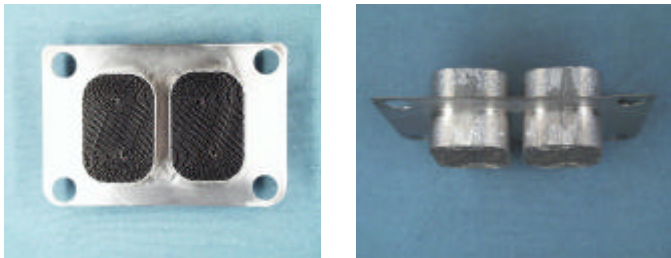


Figure 10: Pre-turbo catalyst of a HDDE (31 cells/cm², foil thickness 50 μm, length 40 mm)

CO AND HC MAPPING – Although the computer predictions were not very promising the pre-turbo catalyst was built in. The results [9] for the oxidation of hydrocarbons and carbon monoxide were astonishingly high. Figures 11 and 12 are displaying conversion rates of more than 60 % (HC) and more than 80 % (CO) in major areas of the engine maps.

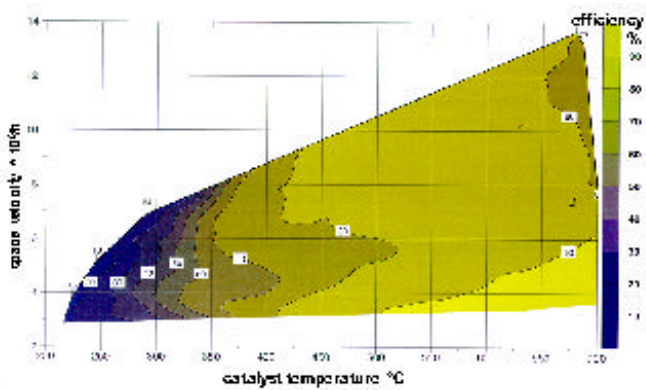


Figure 11: Engine map HC conversion rate (31 cells/cm², foil thickness 50 μm, length 40 mm) [9]

An explanation for the measured efficiency of the PTC, which was better than expected from the calculations, could be the turbulent flow characteristic, which improved the mass transfer compared to the laminar flow model that is used for computation. In addition this might be assisted by the gas pulsation and of course by the quite low engine out emissions which are leading to mass transfer limited chemical reactions.

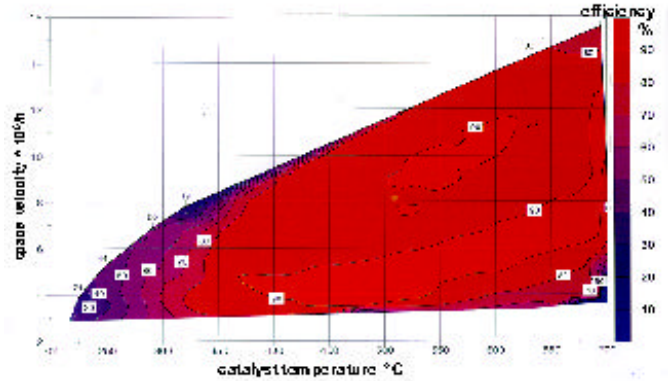


Figure 12: Engine map CO conversion rate (31 cells/cm², foil thickness 50 μm, length 40 mm) [9]

EMISSION TESTS – The most interesting question was whether the encouraging results of the mapping measurements are still valid using official emission test procedures. The answer was given by running European heavy duty test procedures, both the new 13-mode cycle ESC and the transient test ETC [10]. The engine was equipped with a PTC and an oxidation catalyst after the turbocharger in a nearly close coupled position. Figure 13 shows the improvement with reference to the residual emissions of the catalytic arrangement using the PTC to a more common configuration. Especially the CO values show a significant influence coming from the pre-turbo catalyst.

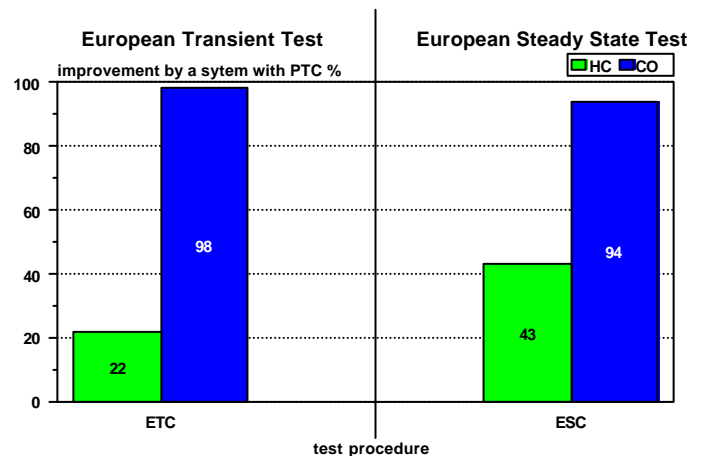


Figure 13: Improvement of HC and CO conversion rates by the system with pre-turbo-cat [10]

INFLUENCE ON NO_x AND PM – Although the HC and CO results are very positive the more important question for the emission behavior of Diesel engines is that one for the nitrogen oxides and the particulate matter. It is well known [11, 12, 13] that the share of NO₂ is of greatest importance for both aspects the oxidation of soot particles and the reduction of NO_x by selective catalytic processes. It is established that a share of about 50 % NO₂ is desirable. It could be shown [10] that it is possible to get nearly these 50 % and at least more than 30 % in a wide engine operating range (figure 14).

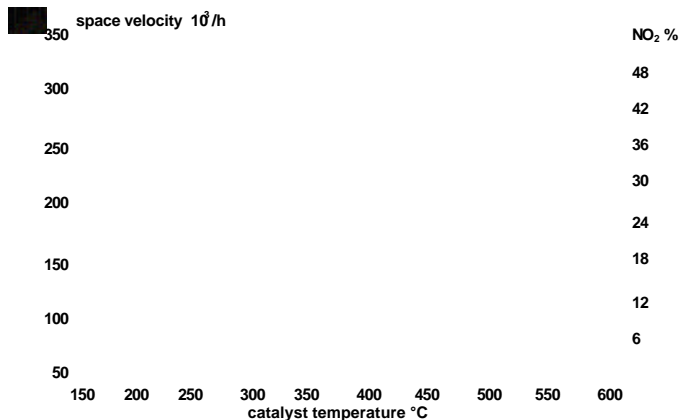


Figure 14: Percentage NO₂ of nitrogen oxides provided by the combination of an oxidation catalyst with a pre-turbo-cat [10]

The encouraging spread of relatively high nitrogen dioxide shares awakes great expectations regarding emission control devices like a continuous regenerating particulate trap system or a selective catalytic reduction system. Most of the European heavy duty Diesel engine manufacturers expect to fulfill the 2005 and 2008 standards in the 2 litre/cylinder-class without trap technique. So a SCR system was chosen to identify the influence of the pre-turbo-cat on NO_x and PM emissions. A schematic drawing of such a system is given in figure 15.

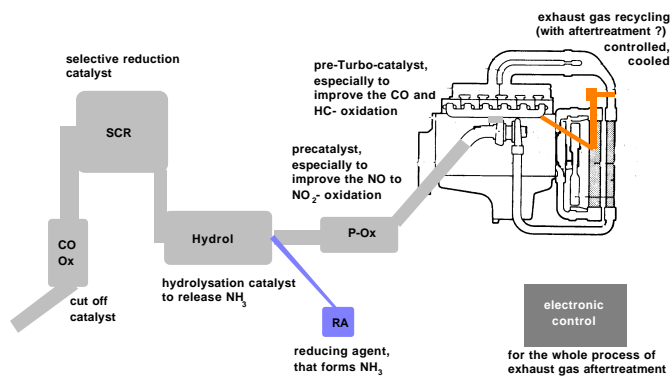


Figure 15: Principle scheme of a SCR system

The tests were carried out with sulfur-free Diesel fuel (S < 10 ppm). Although both test cycles are representing real heavy duty vehicle operation it is to be seen that the influence of the little pre-turbo-cat combined with an oxidation cat is especially positive for transient driving. With reference to the residual emissions an improvement of more than 45 % for NO_x and about 24 % for PM is remarkable. The equivalent values for the steady state test are 33 % and 19 % respectively (figure 16).

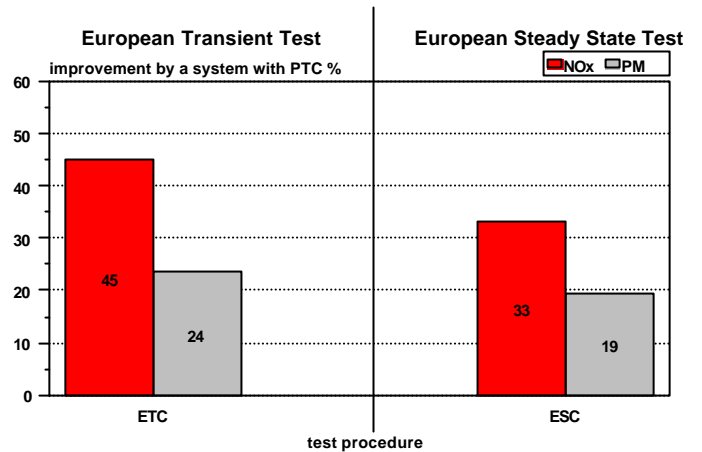


Figure 16: Improvement of NO_x and PM reduction rates by a system with the pre-turbo-cat [10]

PASSENGER CAR ENGINE APPLICATION – The same technique was used with several passenger car Diesel engines. An overview about results of the effect of additional pre-turbo-catalysts to the existing emission control system (oxidation catalyst) without change of the respective engine setting is given in figure 17. The results were obtained running the EU III cycle on chassis

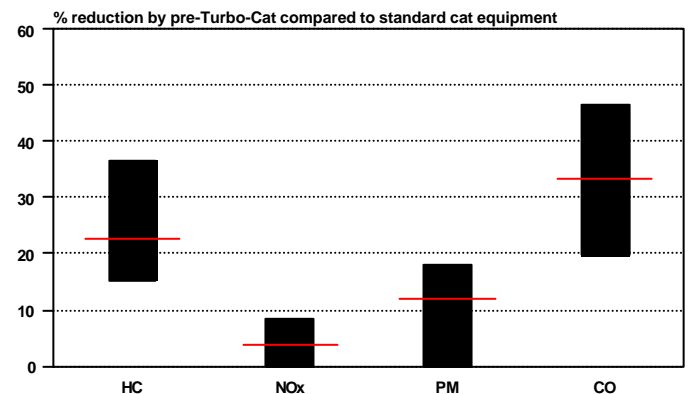


Figure 17: Improvement of the emission reduction by using a PTC on European passenger car engines (EU III cycle, spread and mean)

dynamometers with medium-seized cars powered by modern 4 and 5 cylinder in-line engines of about 2 to 2.5 litre displacement with common-rail injection systems.

Extensive tests were done using the already mentioned 3.0 litre 6-cylinder engine to optimize the parameters of

pre-turbo-catalysts. As an example the influence of catalyst volume (length) and cell density with constant foil thickness of 65 μm and loading of precious metal is shown by the conversion rates for the CO oxidation (figure 18).

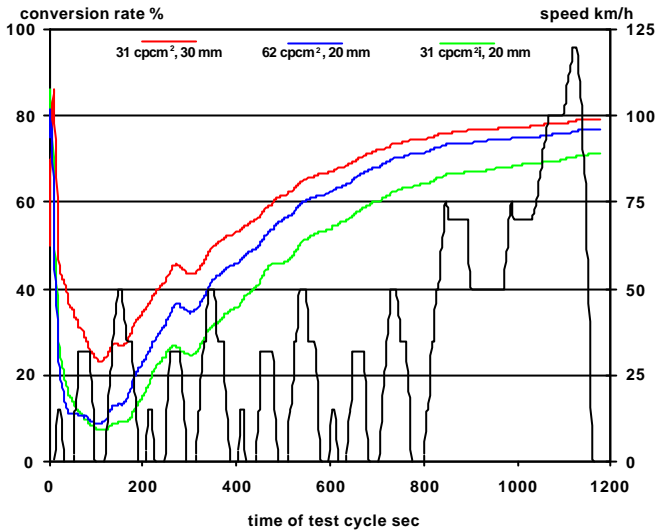


Figure 18: Improvement of the cumulative conversion rates of CO by variation of cell density and length of the PTC with oval diameters of 35x45 mm (EU III cycle)

Looking on the equivalent EU III cycle test results the following CO values were measured by modal analysis (figure 19). To have an idea about the influence on the fuel consumption through the additional installation of the PTC the measured values during the test run in l/100 km are shown in the same graph.

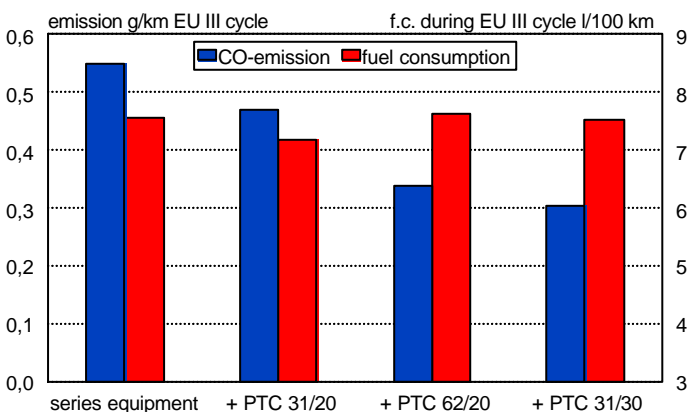


Figure 19: Reduction of the CO-emission and influence on fuel consumption by variation of cell density and length of the PTC with oval diameters of 35x45 mm in comparison to the standard converter system (EU III cycle)

To improve the performance of the PTC it is better to use a greater length (example: + 50%) than to use a higher cell density (example: + 100 %). But in the reality the final decision has to be made with respect to the available space before the turbocharger. And this is usually a question with a lot of restrictions.

OTHER PERFORMANCE ASPECTS – Introducing the pre-turbo-catalyst to customers led to the immediate question (especially from heavy duty engine manufacturers) to the influence on fuel economy and long term durability.

Fuel economy – Today there is no general answer to this question possible. The influence of each individual installation governs the results. The majority of heavy duty applications results in less than 0.5 % increase of fuel consumption although the pre-turbo-catalyst raises the flow resistance in front of the turbine significantly. On the other hand there is a rectification of turbulent flow so that the impulse going into the turbine has a more laminar, straight characteristic. That might be the explanation for the very little influence on fuel consumption with heavy duty engines. Regarding to passenger car installations all possible changes were observed. An improvement of about 5 % as well as an increase of about 2 to 3 % was measured, but more often there were no significant changes.

Durability aspects - Several hundred hours of both full load and transient operation has demonstrated the durability of the pre-turbo-catalyst. In addition one-cylinder durability tests with very high pulsation led to a relation of cell density and foil thickness that creates the necessary confidence to this technique.

CONCLUSION

It could be shown that both substrate developments the hybrid catalyst and the pre-turbo-catalyst are very helpful tools to support the reduction of exhaust emissions from Diesel engines independently whether the engine powers a light or a heavy duty vehicle.

- Using the hybrid catalyst advantages of up to 60 % for HC and up to 70 % for CO were demonstrated.
- The use of a pre-turbo-catalyst on passenger car Diesel engines improves the effect of emission control devices by about 25 % for HC and 35 % for CO.
- In case of a heavy duty application of a pre-turbo-catalysts an improvement of more than 40 % for HC and more than 90 % for CO was observed.
- With a pre-turbo-catalyst it is possible to increase the share of NO_2 in NO_x up to nearly 50 % which is

important for the improvement of NO_x-reduction techniques and the oxidation of soot.

Whether this success is great enough in helping to meet future standards could not be answered today finally. It seems to be that it is in combination with other emission control equipment a very important measure for European applications. For the future US standards the possibilities still have to be proven.

ACKNOWLEDGMENTS

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DEFINITIONS, ACRONYMS, ABBREVIATIONS

CCC	Close coupled catalyst
CO	Carbon monoxide
ESC	European steady state 13 mode test cycle
ETC	European transient test cycle
EU II cycle	European light duty vehicle test cycle with a city part (sec 0 – 820) and an extra urban driving part (sec 821 – 1220). The first 40 sec are low idling without exhaust emission measurement.
EU III cycle	like EU II cycle, but with only 11 sec low idling after start of the engine and with exhaust emission measurement from the beginning on
HC	Sum of Hydrocarbons measured with a heated flame ionisation detector
HDDE	Heavy duty Diesel engine
NO _x	Sum of Nitric oxide (NO) and Nitrogen dioxide (NO ₂)
PM	Particulate matter
PTC	Pre-turbo catalyst
S	Sulphur
SCR	Selective catalytic reduction

