Potential of Catalyst Concepts for Achieving the SULEV Limiting Values for Emissions

Dipl. Ing. Wolfgang Maus, Dipl. Ing. Rolf Brück, Dipl. Ing. Peter Hirth, Dipl. Ing. Jan Hodgson and Dr. Ing. Manuel Presti
EMITEC GmbH, Germany

Abstract

Compliance with future limiting values for exhaust gases, e.g. with the SULEV legislation in California, will have a decisive influence on the introduction of alternative drive concepts and fuels. In order to safeguard these ultra low emissions, it becomes necessary to develop new, more effective catalyst systems. In a test programme, passive metal catalysts with different cell densities and foil thicknesses and heated catalyst systems were compared in the FTP test on a dynamic engine test bench. Catalyst calculations with engine-out emissions of different engines highlight the potential for complying with future SULEV limiting values for exhaust gases.

1. Introduction

The industrial development of the prosperous nations and the division of labour which accompanied this led to a great need for individual mobility which appears to be approaching saturation there today. In this respect, the political focus in the countries of the triad was shifted, as from the sixties, from increasing the prosperity to improving the living conditions. Particularly in the conurbations, evident environmental problems experienced a high level of public attention and emphasis was placed on measures for health and environmental protection. In the industrialised countries, this led, at an early stage, to air-conservation regulations and to the stipulation of limiting values for exhaust gases from motor vehicles. Following the European and American example, it is now possible to observe a similar trend in the developing countries. In the case of the two-wheelers, countries such as Taiwan, India and China are even assuming a pioneering role in the question of the emission regulations and exhaust-gas aftertreatment.

Especially because of the immission situation in the Los Angeles basin, California continues to strive for the lowest emission values for automobiles. Instead of only still pursuing the previous ultimate objective of a zero emission vehicle as a battery vehicle, alternative concepts such as hybrid and fuel-cell drives are now being taken into consideration as well. Here, the "provisional end" of the exhaust-gas legislation for spark-ignition engines is being reached with the so-called SULEV vehicles ("Super Ultra Low Emission Vehicle"). One vehicle concept whose emissions are identical to those of an electric vehicle was presented to the public as early as 1997 [1]. In urban areas with increased immissions, such a vehicle is in a position to produce negative emissions. It can clean the surroundings with regard to hydrocarbon immissions.

Table 1: SULEV limiting values

	HC [g/m]	CO [g/m]	NOx [g/m]	PM [g/m]
Limiting values	0.01	1.0	0.02	0.01

At the moment, any further tightening-up of the limiting values for emissions would not justify the attainable benefits due to overproportional costs, energy input and raw-material consumption. In comparison, because of the energy storage which is still expensive, short-lived and weight-intensive today, electric vehicles do not constitute an alternative to vehicles with such optimised internal-combustion engines [2]. At present, fuel-cell drives with a reformer do not exhibit any advantages in the overall-efficiency chain, not least due to the additional weight of the whole system as well as to the energy consumption of the necessary auxiliary units.

Measures in order to improve the effectiveness of the spark-ignition engine (such as a reduction in the friction power, variable valve control systems, CVT gear units or lean concepts) lead not only to a decrease in the fuel consumption and thus in the CO_2 output but also to a reduction in the absolute engine-out emissions.

In spite of a very low assumption of 1.5 g/m for the engine-out emissions in the American FTP test (including the cold start), compliance with the above SULEV limiting values already demands a catalyst effectiveness of more than 99.3 % throughout the test. With regard to the calculation of the overall test result, the so-called bag results (Bag 1: cold start; Bag 2: condition warm from operation; Bag 3: hot start) are weighted according to the following equation.

E = total FTP emissions [g/m]
EM1 = emissions in Bag 1 [g]
EM2 = emissions in Bag 2 [g]
EM3 = emissions in Bag 3 [g]

In practice, it has already been possible, in optimum conditions, to prove conversion rates of 99.95 % in the condition warm from operation. In the case of the above engine-out emissions, this corresponds to HC emissions of 0.0027 g in Bag 2 and of 0.0029 g in Bag 3. This results in maximum permissible residual HC emissions of 0.16 g for the cold start and the light-off phase in Bag 1. Such high conversion rates of 99.95 % in the condition warm from operation can only be achieved with optimum mixture control, above all in the transient condition. Because of the limited oxygen storage capacity of the catalysts, "fat peaks" lead to a reduction in the HC and CO effectiveness, especially in the aged condition. Due to the rapidly decreasing nitrogen-oxide conversion rate in the lean range, "lean peaks" have an extremely critical effect on the compliance with the limiting values for NOx. Single-cylinder lambda control permits not only the correction of tolerances for the injection quantities but also the possibility of operating individual cylinders in a slightly fat or lean form in a targeted way which may lead to an increase in the catalyst effectiveness.

As mentioned above, the engine-out emissions determine the necessary catalyst effectiveness and thus the scope of the exhaust-gas aftertreatment to be carried out. However, in the case of SULEV vehicles, the important factors are not only the engine-out emissions in the condition warm from operation but also, in particular, the HC emissions in the first seconds after the engine start. Fig. 1 shows the cumulative HC engine-out emissions of various mid-range vehicles and the necessary $t_{99.95}$ (point in time by which, at the latest, a 99.95 % conversion rate is achieved).

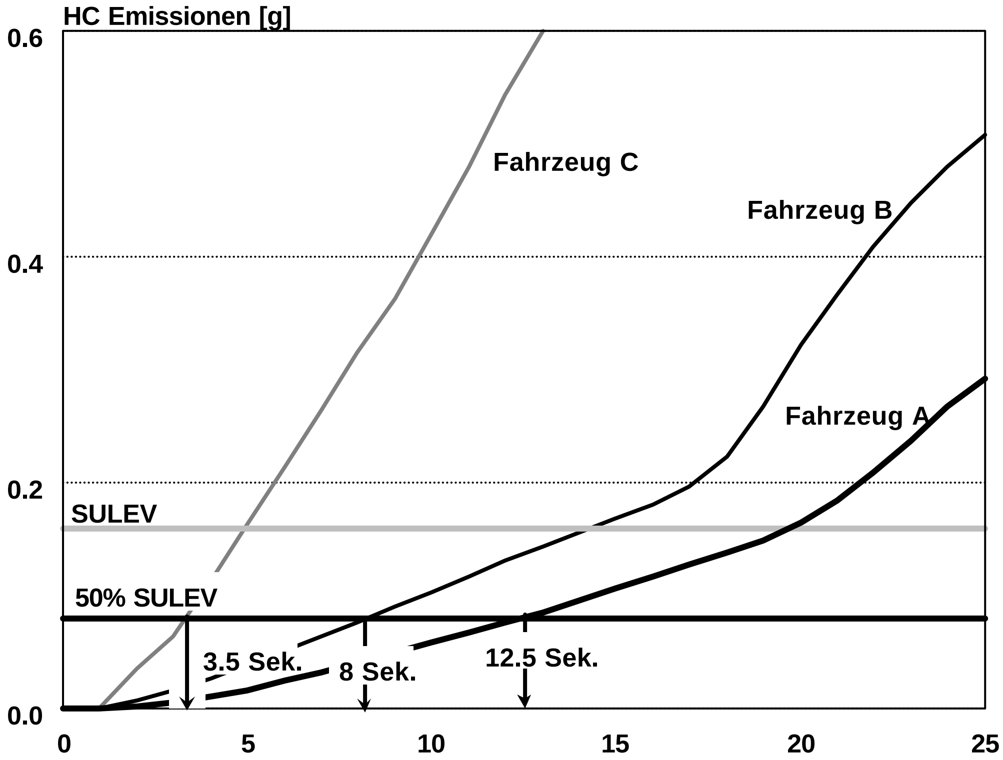

Fig. 1: HC emissions of various mid-range vehicles over the first 25 seconds of the FTP test and necessary $t_{99.95}$ light-off times

The development objective of 50 % of the emissions of the permissible limiting value was defined as the assumption for a non-aged system. According to Fig. 1 and depending on the engine-out emissions, this results in times of 3.5 - 12.5 seconds in order to achieve a conversion rate of 99.95 %. These light-off times are indispensable in order to avoid exceeding the SULEV limiting value in the further course of the exhaust-gas test.

In the case of a passive catalyst system, the catalyst is only heated up by the exhaust gas. Fig. 2 shows gas temperatures upstream of a catalyst close to the engine with various engine and cold-start concepts. With these temperatures and a constant exhaust-gas mass flow of 25 kg/h, the $t_{99.95}$ times of a metal catalyst with the dimensions of ∅ 90 x 90 mm, 800 cpsi and a foil thickness of 0.03 mm were calculated with the aid of a catalyst-calculation program.

It can be recognised that light-off times of 18 seconds are required even in the case of an extremely rapid increase in the temperature upstream of the catalyst. If these are compared with the times which are necessary until a conversion rate of 99.95 % is reached and are shown on Fig. 1, it is apparent that only vehicles with extremely low engine-out emissions can achieve the aspired limiting value solely with catalysts close to the engine (i.e. without an EHC).

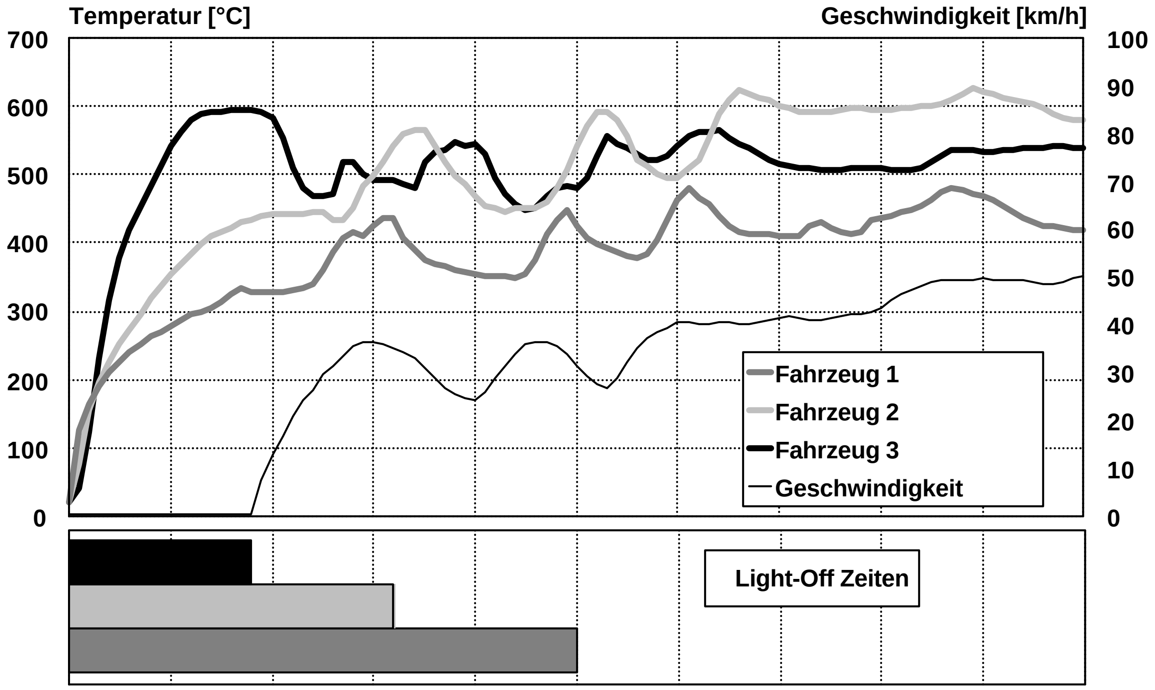

Fig. 2: Gas temperatures upstream of the catalyst in a position close to the engine with various engine and cold-start concepts and $t_{99.95}$ light-off times of a metal catalyst (Æ90 x 90 mm; 800 cpsi)

However, since such ultra low emission engines may also have power and stability disadvantages or it may well not be possible to develop them in a new form in the time available until 2003, alternatives must also be considered on the exhaust-gas aftertreatment side and must be developed until they are ready for series production.

2. Exhaust-Gas Aftertreatment Concepts

In the past, a large number of passive and active exhaust-gas aftertreatment measures (e.g. catalysts close to the engine, HC adsorbers, integral adsorbers, burners, exhaust-gas ignition, electrically heatable catalysts and latent-heat accumulators) have been investigated in exhaust-gas tests [3, 4, 5, 6, 7, 8 and 9]. However, in addition to the limiting values to be complied with for emissions, crucial significance is also attached to the long-term durability and to the diagnosis possibilities (OBD II). Furthermore, the exhaust-gas aftertreatment system must function permanently not only in the specific, well-known exhaust-gas test but also in daily operating conditions. Systems which, in comparison with the exhaust-gas test, discharge considerably more cold-start emissions after the engine start in practical conditions and thus emit much more in the field because of the shortening of the idling time cannot be used in terms of responsible environmental protection. Therefore, in addition to catalysts close to the engine, only hydrocarbon adsorbers and electrically heatable catalysts have currently reached a development stage which will allow them to be introduced into series production in the MY of 2003. Calculations about these concepts and their specific requirements have already been presented in the past [10].

In summary, it may be said that HC adsorbers are certainly capable of storing the cold-start HC emissions intermediately until the downstream EHC has been heated up for the conversion process. However, one disadvantage in this respect is that increased electrical heating capacities are also necessary due to the thermal mass of the adsorber [13]. Other approaches for solutions are formed by so-called integral adsorbers whose thermal stability has not yet been proven, above all when they are used close to the engine. Even by-pass systems with complicated flap designs in the exhaust-gas line must still provide evidence of their suitability for series production. An EHC system close to the engine may be regarded as a feasible alternative to passive catalyst concepts [10].

First of all, the design criteria for a passive SULEV converter system close to the engine were investigated in a test programme.

3. Design Criteria

The theoretical and practical conversion capacities for catalysts which were located close to the engine and exhibited different diameters (60 - 127 mm), diameter/length ratios and cell densities (100 - 600 cpsi) have already been investigated in the past [12]. An advantage was found for catalysts with an adapted small diameter and high cell densities. However, an increase in the cell density to 600 cpsi was only beneficial in the cold start if there was a simultaneous reduction in the foil thickness from 0.05 mm to 0.04 mm and thus in the specific heat capacity.

In the meantime, new material developments have allowed the film thickness of metalites to be decreased to 0.03 mm in series production [12] and even to 0.025 mm for prototypes (in comparison: paper thickness = 0.1 mm). The following figure shows the cold-start assessment factor of the "geometrical surface area / heat capacity" [13] of different catalysts with high cell densities.

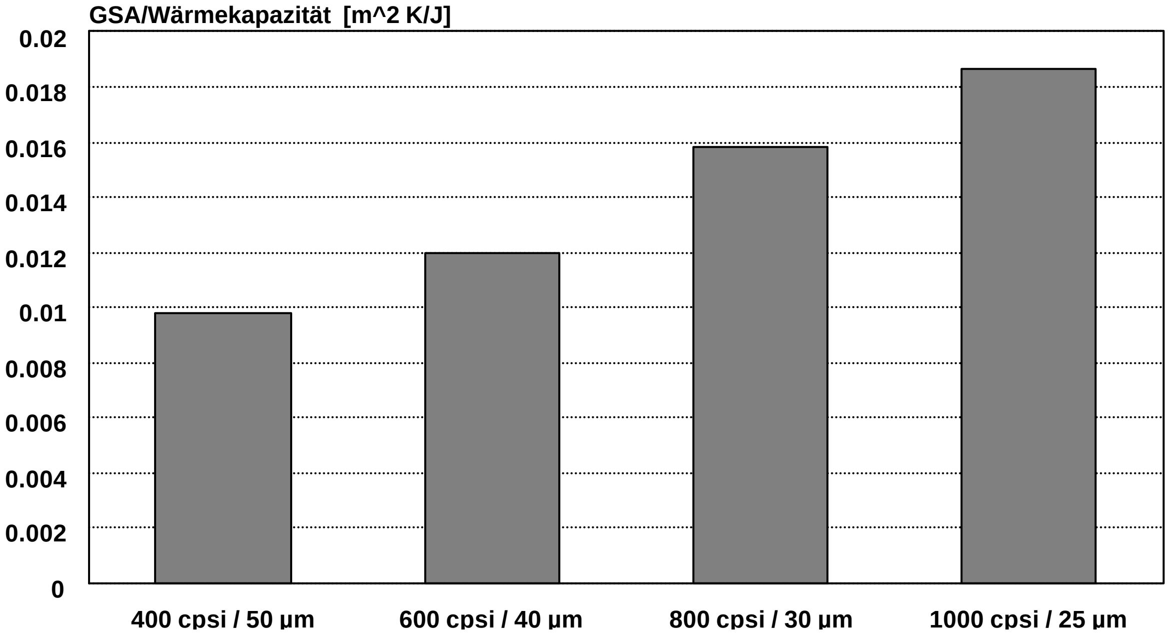

Fig. 3: Cold-start assessment factor of the "geometrical surface area / heat capacity" [13] of different catalysts with high cell densities (400 - 1000 cpsi)

With the aid of ultrathin foils, it was possible to achieve a further improvement in the cold-start assessment factor right up to 1000 cpsi catalysts.

In a test programme, the cold-start characteristics of different catalyst substrates in the new condition were investigated in the FTP test. The tests were performed on a dynamic engine test bench with modal exhaust-gas measurement upstream and downstream of the catalyst. A six-cylinder engine (TLEV compliance) with three-in-one manifolds served as the test substrate.

3.1 Cold-Start Behaviour

3.1.1 Influence of the Cell Density and of the Foil Thickness

In order to examine the influence of the (theoretical) cold-start assessment factor on the cold-start emissions, the catalysts shown in Table 2 were measured in the FTP test. All the metal catalysts had the dimensions of ∅ 98.4 x 74.5 mm and were installed as single catalysts in the exhaust-gas line.

Table 2: Test catalysts

Cell density [cpsi]	400	600	800	1000
Foil thickness [mm]	0,05	0,04	0,03	0,025
Cold-start factor	0.0098	0.0119	0.0158	0.0186

The following figure shows the HC conversion rates in the first 100 seconds of the FTP test. The results should be understood as the average of several measurements.

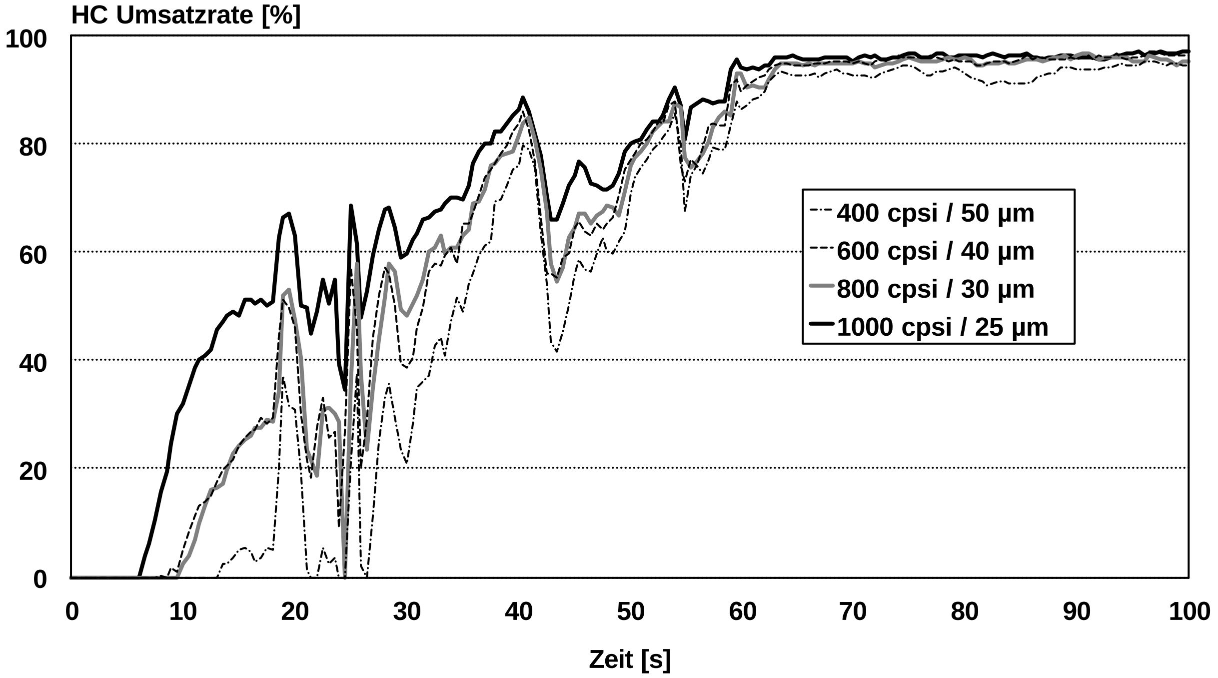

Fig. 4: HC conversion rates during the first 100 seconds of the FTP test

The 1000 cpsi catalyst with a foil thickness of 0.025 mm exhibits the best cold-start behaviour in the comparison. Corresponding to the cold-start assessment factor (Fig. 3), the 400 cpsi standard substrate exhibits the worst result.

In order to improve the representation of the cold-start emissions, Fig. 5 shows the cumulative HC emissions.

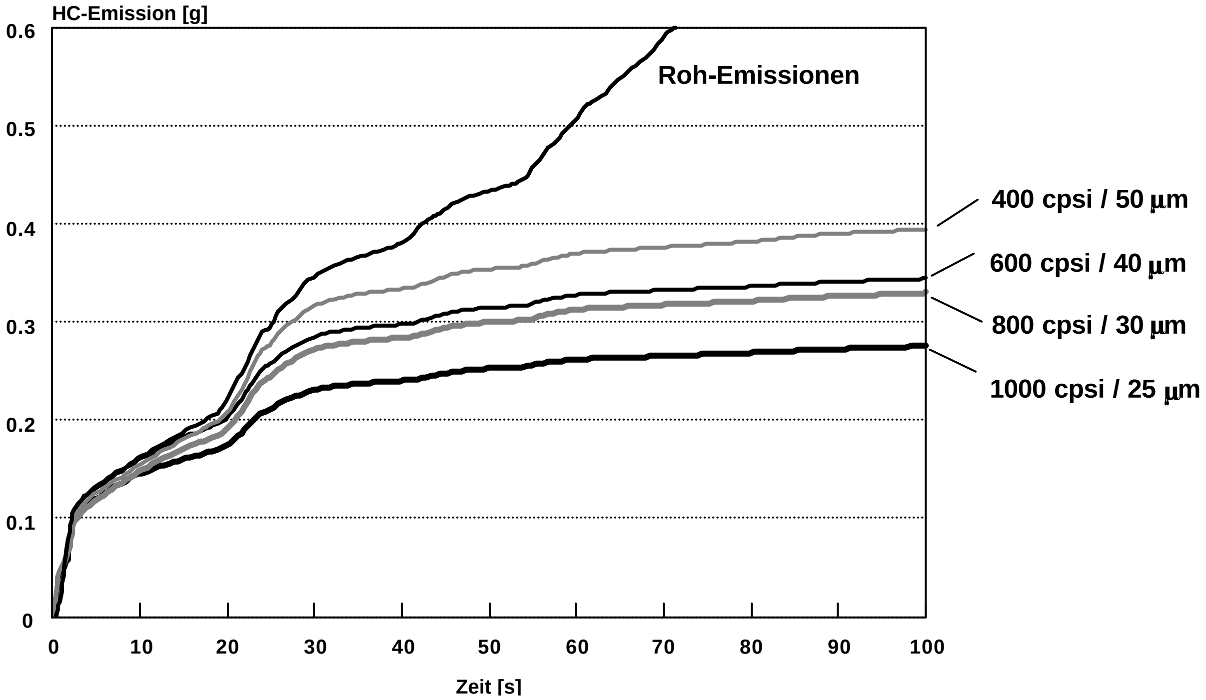

Fig. 5: Cumulative HC emissions during the first 100 seconds of the FTP test

After 100 seconds, the emissions advantage of the 1000 cpsi catalyst amounts to 18.6 % over the 800 cpsi substrate and to 22.6 % over the 600 cpsi substrate. Compared to the 400 cpsi / 0.05 mm standard catalyst, the HC emissions were improved by 33.6 % in this first period of time.

3.1.2 Heated Catalyst

The tested heated catalyst with a downstream back-up catalyst is described in Table 3. The heating capacity was 2000 W with a heating time of 20 seconds after the engine start. Investigations showed that this heating capacity can be provided by a standard battery without any restriction on the service life [14].

Table 3: Heated-catalyst data

Heated catalyst	Back-up catalyst	Catalyst volume [l]
Ø 98,4 x 10 mm 400 cpsi; 0,04 mm	Ø 98,4 x 67 mm 800 cpsi; 0,03 mm	0,59

The cumulative HC emissions in the cold start of the FTP test are shown on Fig. 6.

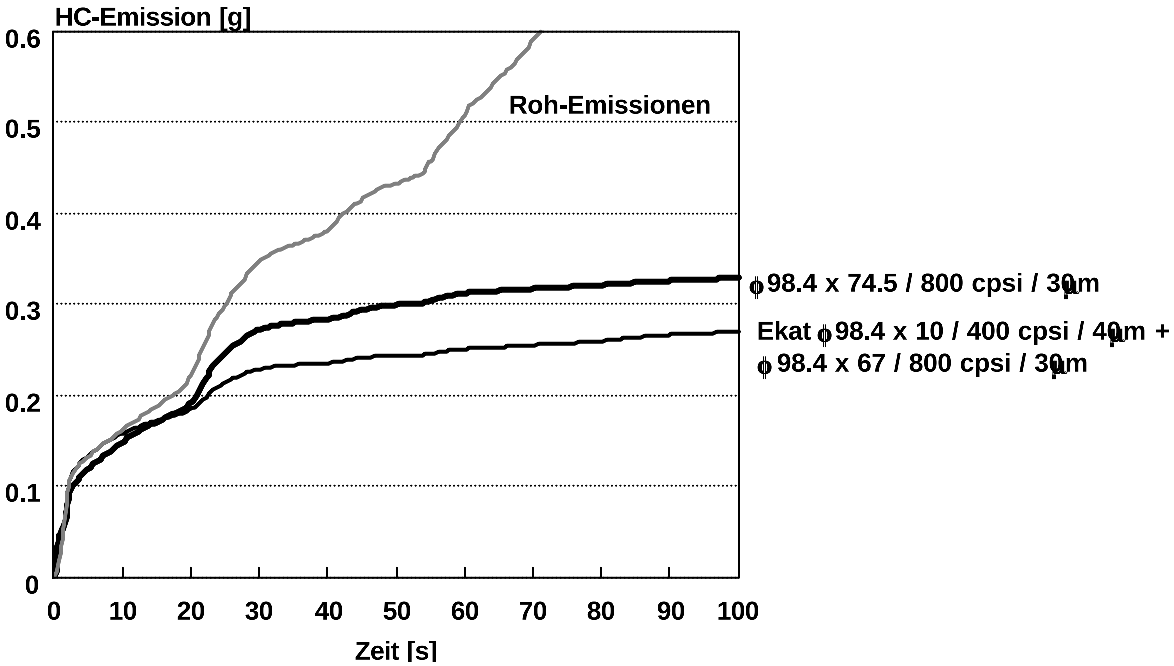

Fig. 6: HC emissions during the first 100 seconds of the FTP test on the passive catalyst in comparison with the corresponding heated-catalyst system

If the heated-catalyst variation is compared with the corresponding (cell density and foil thickness) passive variation in the first 100 seconds, the active heating leads to a 20.2 % improvement in the HC emissions. It must be pointed out that the heated catalyst was heated using a separate battery, similar to a two-battery system, and that the provision of the electrical power thus did not have any influence on the engine-out emissions, exhaust-gas temperature or exhaust-gas mass flow.

3.2 Condition Warm from Operation

The influence of the cell density (catalyst variations from Table 2) in the condition warm from operation was established in the second step. For this purpose, the conversion rates were evaluated from 100 seconds after the engine start to the end of Bag 1.

Fig. 7 shows the HC conversion rates and Fig. 8 the NOx conversion rates of the individual test catalysts.

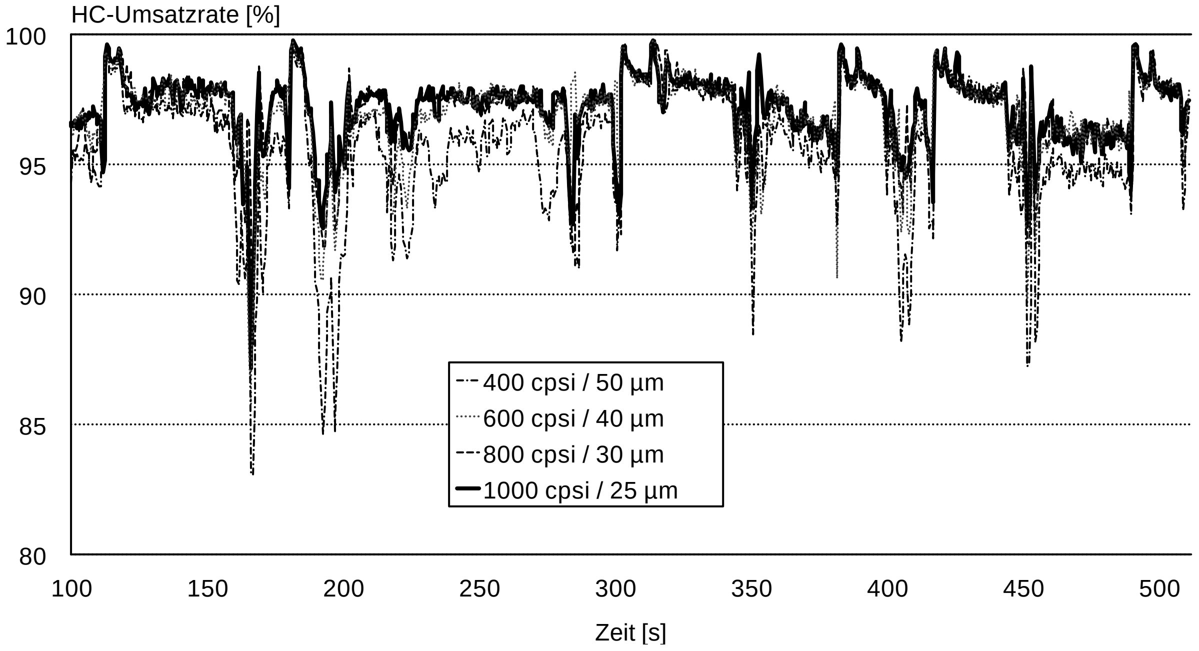

Fig. 7: HC conversion rates of the individual test catalysts in the condition warm from operation

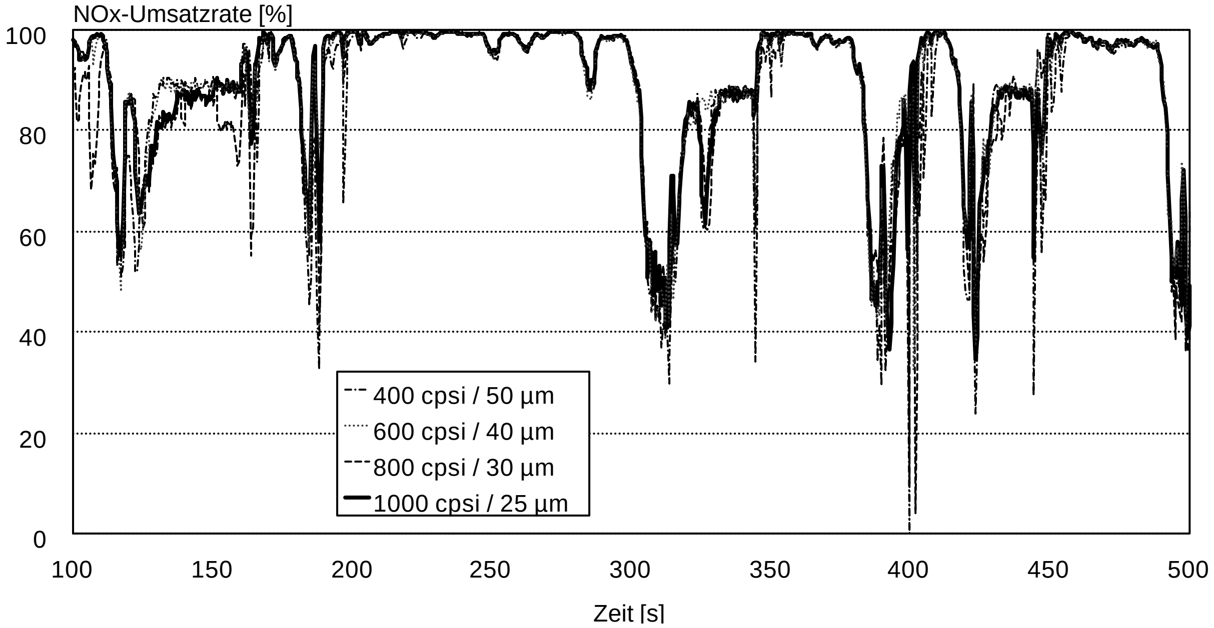

Fig. 8: NOx conversion rates of the individual test catalysts in the condition warm from operation

In order to improve the representation, the respective averages of the conversion rates were calculated and shown on Fig. 9.

In the test range warm from operation, the use of a 1000 cpsi catalyst leads to a 35.3 % reduction in the residual HC emissions in comparison with the 400 cpsi substrate. With the 800 cpsi catalyst, it was possible to achieve an improvement of 14.4 %. The NOx tailpipe emissions were improved by 21.7 % from the 400 cpsi standard catalyst to the 1000 cpsi substrate.

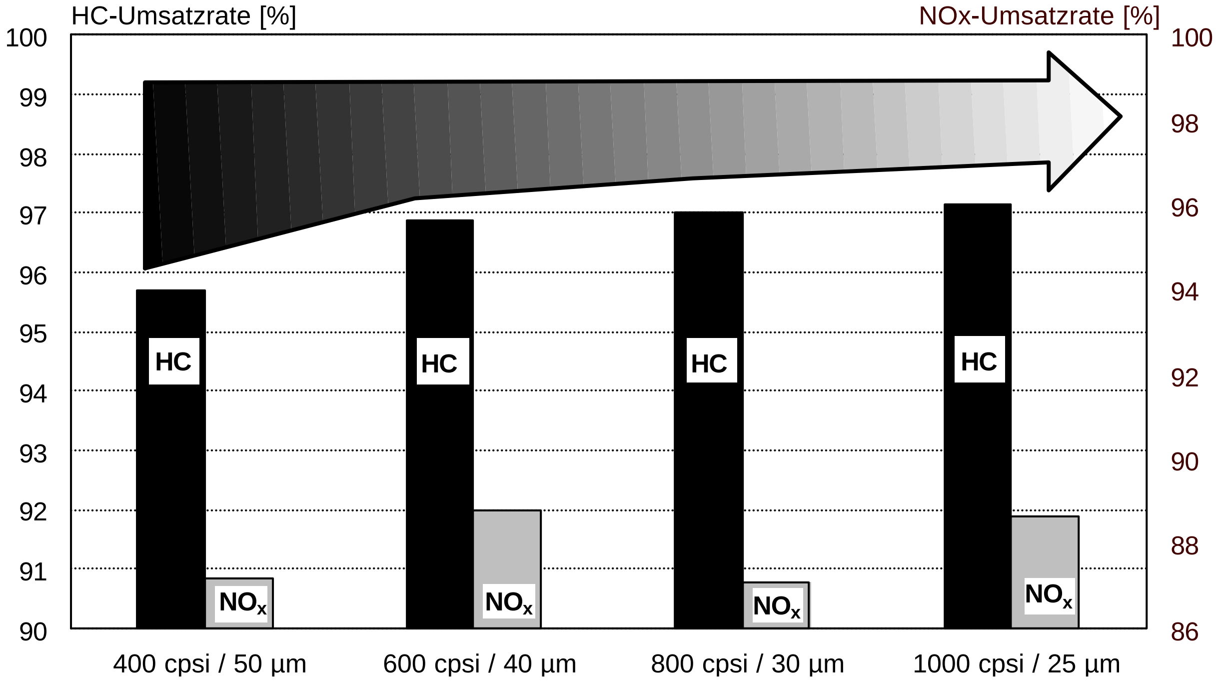

Fig. 9: Averages of the HC and NOx conversion rates in the condition warm from operation

4. Catalyst Calculations

In an earlier comparative programme, it was shown that it was possible to improve the cold-start behaviour by using small catalyst diameters [12]. Because of the very high pressure loss with small diameters, the use of cascade systems constitutes an effective compromise. For this reason, cold-start calculations were made below with the best catalyst (1000 cpsi; 0.025 mm) and with the heated catalyst (∅ 80 x 12 + 50.8 mm, 1000 cpsi / 0.03 mm) in order to determine the potential for complying with the SULEV legislation depending on the engine-out emissions. The T_{50} light-off time (50 % conversion achieved) of the catalytic coating was assumed to be 230°C.

The calculations were made with the aid of the Katprog finite-volume program developed at Emitec. The exhaust-gas temperatures upstream of the catalyst, the exhaust-gas mass flow as well as the engine-out emissions of Vehicle A (very low engine-out emissions) and of Vehicle B (European production vehicle) from Fig. 1 served as the input data. The fuel/air mixture was specified immediately after the engine start with lambda = 1.

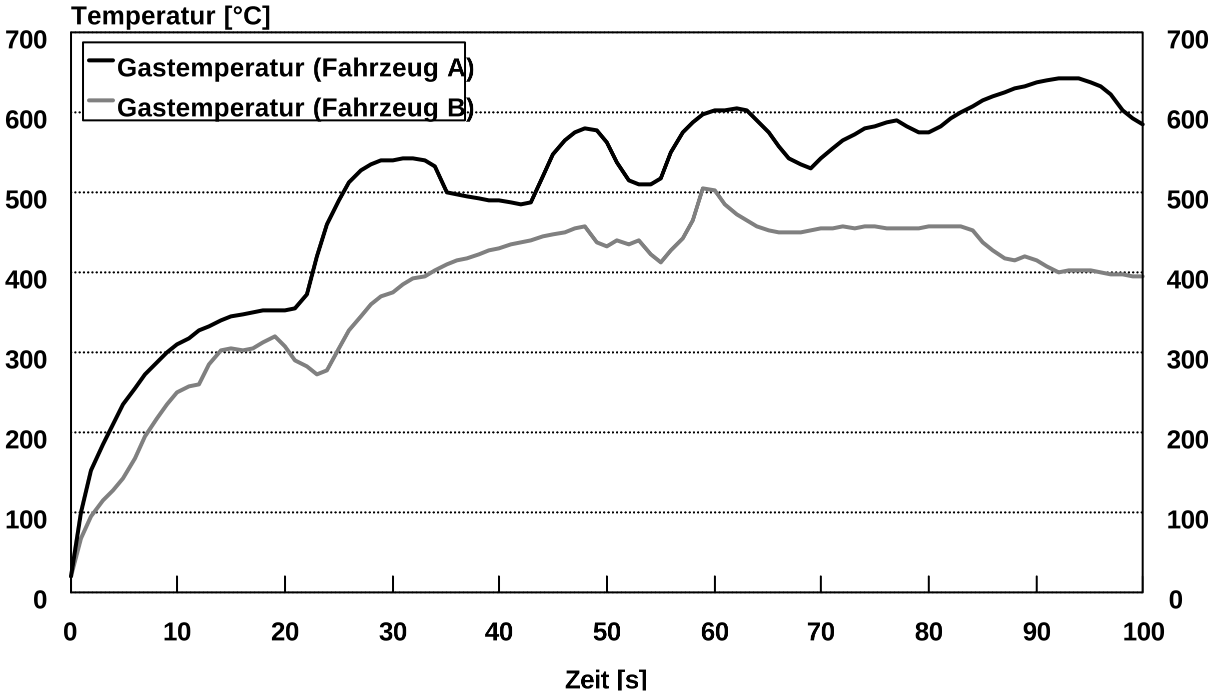

Fig. 10: Exhaust-gas temperature of the SULEV calculations

Fig. 11 shows the cumulative HC emissions not only of a catalyst cascade which was located close to the engine and was equipped with substrates with the dimensions of ∅ 80 x 62.8 mm and ∅ 98.4 x 120 mm, 1000 cpsi and a foil thickness of 0.025 mm but also of a heated-catalyst system in which the first substrate of the cascade was replaced by an EHC with the dimensions of ∅ 80 x 12 + 50.8 mm, 400/1000 cpsi, a foil thickness of 0.03 mm and 2000 W. The heating time was 20 seconds after the engine start.

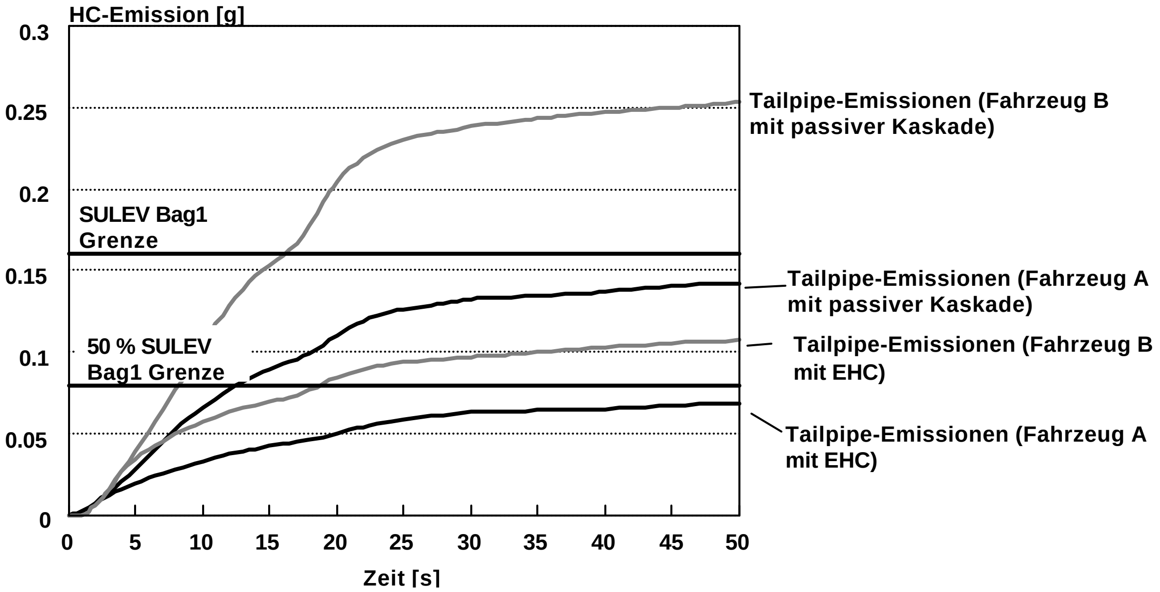

Fig. 11: Calculated cumulative tailpipe emissions of a catalyst cascade close to the engine and of an EHC system depending on the engine-out emissions of the vehicle

The calculation result shows that, with low engine-out emissions (Vehicle A), it is possible to achieve SULEV values even with a passive cascade in the new condition. However, in order to comply with that safety margin to the limiting value which is necessary for the ageing rate known today (above development objective: 50 % of the limiting value), it is necessary to use a heated catalyst. Although the SULEV limiting value can be achieved with a heated catalyst in the case of higher engine-out emissions (Vehicle B), the specified safety margin is too narrow.

By means of improved engine management and the connected lower ageing rate (because of temperature peaks which do not occur in the transient driving operation), it would be possible to substantially reduce the planned safety margin to the limiting values. It may be concluded from the calculations that SULEV limiting values could also be achieved with passive exhaust-gas aftertreatment systems by further reducing the engine-out emissions to 0.8 - 1.0 g/m (as a representative value for the cold-start emissions). On the other hand, it may be deduced that SULEV limits can hardly be complied with in the case of engine-out emissions of more than 2.0 g, even with a heated-catalyst system.

It may be concluded from this that the engine-out emissions will, in future, be a decisive influencing factor for the complexity and costs of the exhaust-gas aftertreatment system to be applied.

Brief preheating of the catalyst (in certain circumstances, in conjunction with a low secondary-air flow) may be used as a possible solution in order to compensate for unavoidably high engine-out emissions. The task of the secondary air is to transport the heat of the heating disc into the downstream catalyst, thus leading to a larger preheated catalyst volume depending on the preheating time and on the engine-out emissions.

In order to prevent a catalyst preheating process from entailing a loss of comfort for the driver, it would be appropriate to carry out targeted preheating via door, seat and belt contacts.

5. Summary

The development of a SULEV system places the most stringent requirements on the engine, on the engine control system and on the exhaust-gas aftertreatment system. Deliberations about the necessary conversion rates and engine-out emissions showed that max. 0.16 g of HC may be emitted for already low engine-out emissions of 1.5 g/m in the cold start. Depending on different engine-out emissions, this results in light-off times ($T_{99.95}$ %) in the range of 3.5 - 12 seconds. For the optimum designing of highly efficient catalyst systems, emission measurements were taken on metallic catalyst substrates with cell densities between 400 cpsi and 1000 cpsi and with foil thicknesses of 0.05 - 0.025 mm. This led to the following results.

- The increase in the cell density from 400 cpsi to 1000 cpsi with a simultaneous reduction in the foil thickness from 0.05 mm to 0.025 mm confirms the cold-start assessment factor found earlier and gives rise to a 33.6 % improvement in the cold-start emissions.

- In the condition warm from operation, it was possible to reduce the residual emissions by up to 35.3 % by improving the mass transport in the substrates with higher cell densities.

- Calculations of the cold-start emissions with optimum catalyst substrates reveal the possibility of achieving SULEV values with a passive catalyst system depending on the engine-out emissions.

- In the simulations carried out, it was only possible to attain the development objective of achieving 50 % of the SULEV limiting values in the new condition with very low engine-out emissions, optimum lambda control and an active exhaust-gas system in which the first substrate was replaced by a heated catalyst.