

Enhancement of Diesel Soot Combustion with Oxygen on Particulate Filters After Injection of Dicyclopentadienyl Iron (Ferrocene) in the Exhaust Pipe

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ABSTRACT

For the regeneration of diesel particulate filters with oxygen, temperatures above 550 °C are normally required. The increase of the exhaust gas temperature to temperatures above 500 °C demands a large amount of energy, so that strategies to reduce the regeneration temperature have to be considered. One option is the injection of a catalyst, which reduces the required regeneration temperature. Hence, a system was developed at HJS Emission Technology GmbH to inject catalyst-precursor into the exhaust gas pipe, whereby the catalysts are generated due to decomposition of the precursor in the hot exhaust gas. A technique based on the calculation of apparent activation energies was developed to characterize the soot combustion on the filter. In the first step metal oxide catalysts, like cerium(IV)oxide, manganese-oxide and iron(III)oxide were investigated after injection of their nitrate precursors dissolved in water. These catalysts showed poor activities, by the reason of the low specific surfaces of the catalyst particles, which were achieved from the decomposition of the nitrate precursors. In the next step ferrocene (dicyclopentadienyl iron) dissolved in toluene was used as a precursor for the generation of the iron(III)oxide catalyst. The advantage of dicyclopentadienyl iron is the fact that it sublimates into the gas phase at temperatures above 90 °C. The catalyst is then generated from gaseous ferrocene in the exhaust pipe, whereby catalyst particles far below 1 µm can be achieved. Experiments revealed much higher activities of the iron(III)oxide catalysts generated from dicyclopentadienyl iron compared to the nitrate precursor. Additionally the dependency of the catalyst performance on the catalyst-soot-ratio was investigated in detail. An

iron(III)oxide-soot ratio of 4 wt% was determined to be a reasonable value for the regeneration of the diesel particulate filter.

INTRODUCTION

Diesel engines are widely used in heavy duty vehicles, construction machines, electric power generators, trains and ships due to their high efficiency and low fuel consumption compared to petrol engines. On the contrary diesel engines have the drawback of nitrogen oxide (NO_x) and particulate matter (PM) emissions. The high demand of diesel engines worldwide necessitates inner engine measures and / or a treatment of the exhaust gas to eliminate the NO_x and the PM-emissions to prevent the environment from severe pollution.

European emission standards define the acceptable limits for exhaust emissions of new vehicles sold in EU member states. The emission standards are defined in a series of European Union directives staging the progressive introduction of increasingly stringent standards. Currently, emissions of nitrogen oxides (NO_x), total hydrocarbon (THC), non-methane hydrocarbons (NMHC), carbon monoxide (CO) and particulate matter (PM) are regulated for most vehicle types, including cars, trucks, trains, tractors and similar machinery.

Table 1 shows the emission standards (Euro 1 - 6) for passenger cars [1] and it can be seen, that an almost complete removal of the particulate matter is demanded for the most recent standards.

Table 1. European emission standards for passenger cars [g/km]

Tier	Date	CO	THC	NO _x	HC + NO _x	PM
Diesel						
Euro 1	July 1992	2.72 (3.16)	-	-	0.97 (1.13)	0.14 (0.18)
Euro 2	January 1996	1.0	-	-	0.7	0.08
Euro 3	January 2000	0.64	-	0.50	0.56	0.05
Euro 4	January 2005	0.50	-	0.25	0.30	0.025
Euro 5	September 2009	0.50	-	0.18	0.23	0.005
Euro 6 (future)	September 2014	0.50	-	0.08	0.17	0.005

For the removal of the particulate matter, diesel particulate filters (DPF[®]) are employed. HJS Emission Technology GmbH normally uses Sinter Metal Filters (SMF[®]), the principle is illustrated in [figure 1](#) (top). A filter with an area of 1.8 m², as it is commonly used in light duty vehicles, is pictured at the bottom of [figure 1](#). The filter is consisting of 60 filter pockets and has a length of 250 mm and is capable to capture more than 99 % of the particles. The particulate matter is accumulated on the filter and has to be removed continuously by oxidation.

unacceptable high backpressures. For applications that cannot assure this requirement, active approaches have to be considered to remove the soot from the filter.

As stated above, for a significant non-catalytic oxidation of diesel soot with oxygen temperatures between 500 °C and 650 °C have to be employed, i.e. for the combustion of the soot on the filter the exhaust gas temperature has to be raised to that level. This can be done by a burner, in which diesel fuel is injected and combusted. Unfortunately, the burner requires additional energy, which increases the CO₂ emissions, additional space and a supply of compressed air.

Another technique to remove the soot from the filter is the SMF[®]-AR system. The SMF[®]-AR system enables the regeneration of the filter in every operation condition. The SMF[®]-AR combines the usage of catalytic additives with an electrical heater. A catalyst-precursor is added to the fuel and in the piston of the motor the catalyst particles are generated during fuel combustion. The catalyst is significantly reducing the ignition temperature of the particulate matter on the filter, so that the soot can be ignited at temperatures between 350 °C and 400 °C. This is done by an electrical heater with 80 A power demand during the ignition procedure of approx. 150 seconds. The SMF[®]-AR system is described in detail in [2].

However, the usage of a fuel borne catalyst has the disadvantage of the denial by many motor and injection nozzle manufacturers due to a possible fouling in the injection nozzles and due to a lack of compatibility with bio-diesel.

Hence, a novel technique has been considered for the catalytic soot combustion, namely the injection of the catalyst precursor into the exhaust gas. With such a system, the above mentioned concerns could be eliminated and a wider acceptance of additive based regeneration techniques can be assured. The principle is illustrated in [figure 2](#). The diesel engine produces exhaust gas containing soot particles. The soot particles are captured in the filter. Upstream of the filter a catalyst-precursor solved in a liquid solution (= additive) is injected and in the exhaust gas the catalyst is formed and captured with the soot on the filter. The activities of catalyst soot mixtures depending on the solvent, the catalyst, the soot-

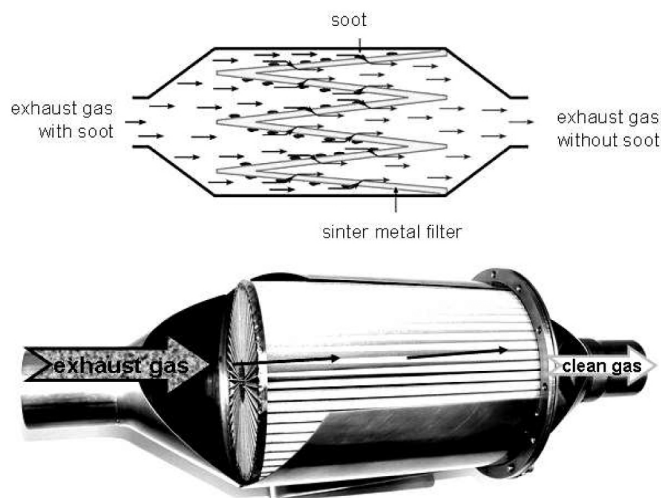


**Figure 1. Principle of the HJS Sinter Metal Filter (top).
Photograph of a 1.8 m² sinter metal filter (bottom).**

A CRT[®]-system (continuously regenerating trap) is a passive filter regeneration device, which uses the reaction between NO₂ and the particulate matter, which is significantly higher than the reaction of the particulate matter with oxygen. The NO₂ is generated by a platinum loaded catalyst upstream of the filter, which oxidizes the NO present in the diesel exhaust gas to NO₂. A significant reaction of NO₂ with the particulate matter normally takes place above 250 °C, on the contrary the oxidation with O₂ requires more than 500 °C. This means for the CRT[®] system with a sinter metal filter that more than 35 % of the temperature profile have to be above 250 °C to avoid overloading of the filter with soot, which results in

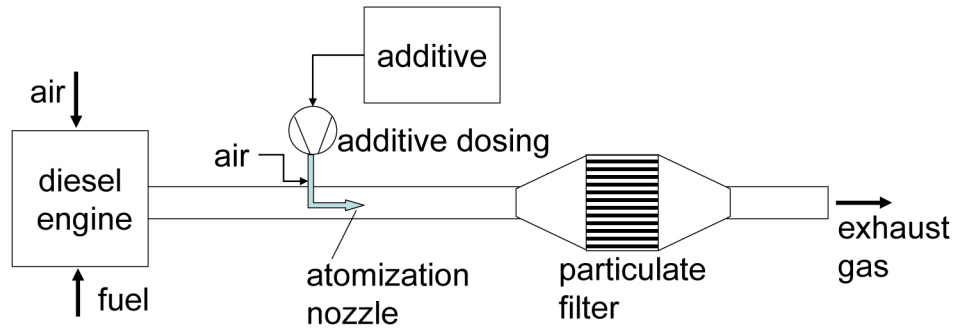


Figure 2. Principle of catalyst injection in the exhaust gas.

catalyst ratio and the operational conditions are discussed in this paper.

CALCULATION OF THE SOOT LOADING

To characterize the regeneration performance, it is important to know about the soot loadings in every time step of the data acquisition to balance the build up and the oxidation of the soot on the filter. Unfortunately the soot loading can only be measured directly by weighing the complete filter module, which can only be performed at distinct weighing intervals, so that the oxidation behavior cannot be described satisfying.

Hence, a calculation of the soot on the filter module by the available data is essential for the characterization of the soot oxidation kinetics. The well known Darcy model, which describes the pressure drop over porous material should therefore be employed for the calculation of the soot loading.

$$\text{Darcy Equation: } \frac{\Delta p}{L} = B_0 \cdot \eta \cdot w \quad (1)$$

In equation (1) Δp describes the pressure drop, L the depth of the porous medium, B_0 the resistance coefficient, η the dynamic viscosity and w the superficial gas velocity. As the filter is consisting of filter material with the depth L_F and a filter cake with a depth L_C , the pressure drop can be calculated with:

$$\Delta p = (B_{F,0} \cdot L_F + B_{C,0} \cdot L_C) \cdot \eta \cdot w \quad (2)$$

The depth of the filter cake L_C under the assumption of a homogeneous distribution can be expressed by

$$L_C = \frac{M_S}{\rho_S \cdot \varepsilon \cdot A_F} \quad (3)$$

[M_S : soot mass on the filter, ρ_S : soot density; A_F : filter area]

The superficial gas velocity through the filter cake is:

$$w = \frac{\dot{M}_L \cdot R \cdot T}{A_F \cdot p} \quad [\dot{M}_L : \text{exhaust gas mass flow through the filter, } T: \text{temperature; } p: \text{pressure; } R: \text{universal gas constant}] \quad (4)$$

Under the assumption that the bed porosity and the depth of the filter material remains constant, the resistant coefficients $B_C = B_{C,0} / \varepsilon$ and $B_F = B_{F,0} \cdot L_F$ can be defined.

The pressure drop over the filter can be then estimated by:

$$\Delta p = \left(B_F + B_C \cdot \frac{M_S}{\rho_S \cdot A_F} \right) \cdot \eta \cdot \frac{\dot{M}_L \cdot R \cdot T}{A_F \cdot p} \quad (5)$$

In preliminary experiments the soot cake turned out to have a much higher pressure drop characteristic than the filter material: $B_C \gg B_F$, so that the soot mass M_S can be calculated by the measured pressure drop above the filter:

$$M_S = \frac{\Delta p \cdot A_F^2 \cdot p \cdot \rho_S}{B_C \cdot \dot{M}_L \cdot R \cdot T \cdot \eta} \quad (6)$$

Equation (6) was employed for the experiments in this paper to calculate the soot mass on the filter during operation on the engine test bench. The viscosity η was calculated by the Sutherland formula [3]. The pressure drop Δp , the static pressure before the filter p , the mass flow and the temperature before the filter T are measured directly. With the resistance coefficient B_C the soot mass can be calculated.

MODELLING THE REACTION KINETICS OF THE SOOT OXIDATION

For the characterization of the soot oxidation on the particulate filter the selection of a suitable model, which takes all the used parameters into account is essential. For this reason the soot oxidation should be characterized by an Arrhenius approach as it is frequently done in the literature [4,5,6].

Yezerets et. al. [4] proposed a model to characterize the soot oxidation by:

$$r = k \cdot [O_2]^\beta \cdot [C] \quad (7)$$

where r is the reaction rate [mol/s], k the reaction rate constant and $[O_2]$ and $[C]$ are the concentration of oxygen and the moles of soot on the filter, respectively. The reaction order of oxygen is set to $\beta = 0.63$ [4].

The reaction rate constant k can be described by an Arrhenius equation

$$k = A \cdot \exp\left(\frac{-E_a}{RT}\right) \quad (8)$$

with the pre-exponential factor A and the apparent activation energy E_a . From the experimental data provided by Yezerets [4] a pre-exponential factor $A = e^{17}$ 1/min was calculated and used in this work. The activation energies were assumed to be independent to the temperature in the investigated range between 300 °C and 500 °C. The determination of the apparent activation energy E_a was carried out by the linearization of the reaction rate constant k by

$$\ln(k) = -\frac{E_a}{R} \cdot \frac{1}{T} + \ln(A) \quad (9)$$

The reaction rate k was determined from the soot conversion rate, the measured oxygen concentration and from the amount of carbon on the filter. Plotting the reciprocal temperature $1/T$ versus $\ln(k)$ gives the regression line from which the activation energy and the pre-exponential factor A can be calculated.

Besides the activation energy, the so called “balance point” can be applied for the characterization of the soot oxidation. The balance point is the temperature at which the soot production of the engine equals the soot oxidation on the filter, i.e. the soot mass $M_S = \text{const.}$

SIMULATION MODEL OF THE ADDITIVE INJECTION

The prediction of the fluid mechanics of the exhaust gas and especially of the soot and catalyst particles is essential to achieve a homogeneous soot-catalyst mixture in order to reach high catalyst efficiencies. Therefore the fluid mechanics of the catalyst should be identical to the one of the soot particles. The aim of the simulation is to find a maximum particle diameter at which the catalyst particles are following the same streamlines as the soot particles. For the simulation the CFD-software CFX[®]12 (ANSYS Germany GmbH, Otterfing, Germany) was applied and the fluid mechanics of the exhaust gas flow modeled as air were calculated.

In this paper the simulation of the gas flow in the filter module, i.e. the filter and the housing containing inlet and outlet cones, is presented as well as the trajectories of the soot and catalyst particles. Figure 3 is showing the geometry of the filter module used in the CFD simulation. On the left side the complete filter module is pictured corresponding to the real filter on the engine test bench. As the filter is axial-symmetric, a simulation of one filter pocket (i.e. a consideration of a 6°-segment) is sufficient to predict the fluid mechanics of the complete filter.

The following components in the simulation were used:

Inlet: At the inlet the mass flow is defined. As only a 6°-segment is considered, the mass flow in the simulation is only 1.67 % of the mass flow through the complete filter. Particles are injected randomly distributed in the inlet surface, which represents the soot and the catalyst particles. The injected particles are calculated by CFX[®] by Langrangian particle tracking after the calculation of the flow pattern, i.e. the particles are assumed of having no influence on the fluid mechanics. The particles are modeled as spheres.

Filter pocket: The filter pocket was defined as a porous medium. The pressure drop over the filter material was modeled by a linear resistance coefficient $B_{F,0} = 10^{-9} \text{ m}^2$ perpendicular to filter surface. This resistance coefficient represents the pure filter material without a soot cake.

Flange (wall): The flange is modeled as a wall at the end of the filter pocket. The flange acts as a barrier and forces the flow to pass through the filter pocket.

Side walls (between filter pockets): The side walls of the segment were all modeled as symmetry planes, the remaining walls were defined as no slip boundaries.

The flow pattern is solved by CFX using the Navier Stokes equations, i.e. the mass balances, the momentum balances

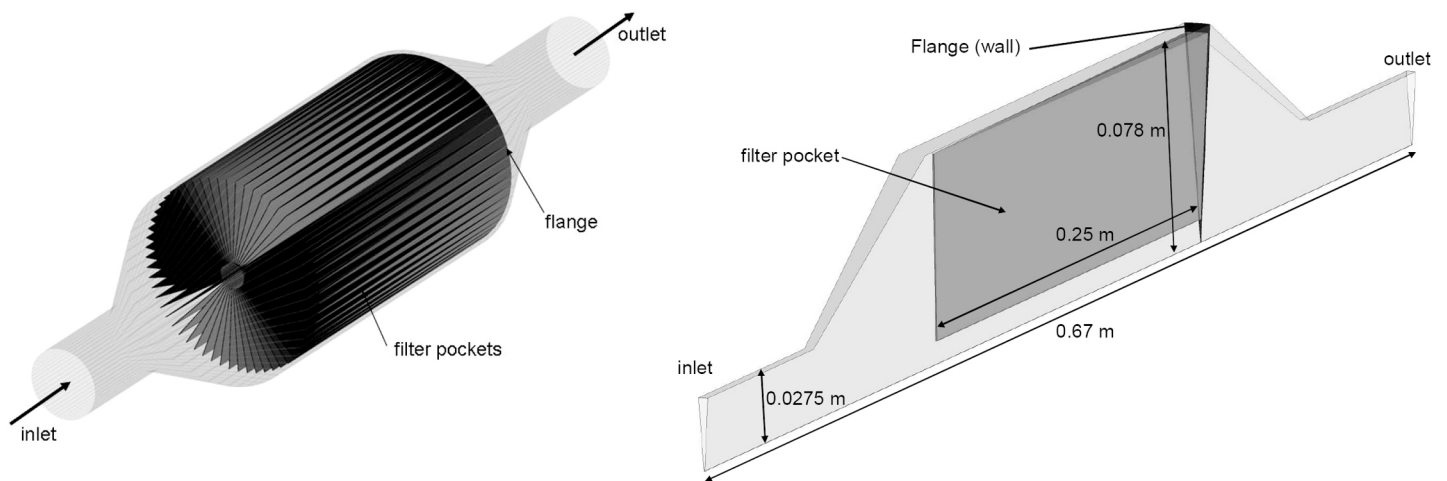


Figure 3. Geometry of the filter module for the CFD-simulation (left: the complete filter module; right: the 6°- segment of the filter module, in which the simulations were carried out).

and the k- ϵ turbulence equations are calculated in each cell of the body, presented in [figure 3](#) on the right hand side.

EXPERIMENTAL

The experiments were carried out at the engine test bench at Iserlohn University of Applied Science, a sketch of the experimental setup and a photograph are shown in [figure 4](#).

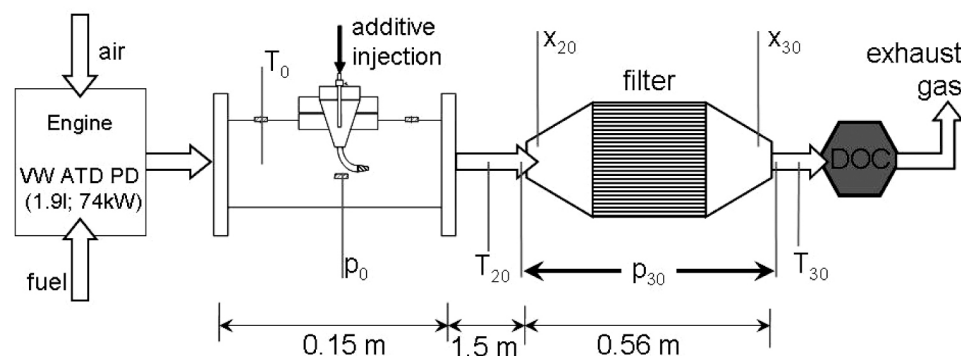
For the generation of the exhaust gas and the soot a VW motor (ATD PD; 1.9 l; 74 kW) was used. The exhaust gas pipe was covered by an insulation to avoid temperature losses and to ensure an approximately constant temperature profiles in the radial and the axial directions. Behind the motor the injection unit was installed, consisting of a hollow cone nozzle (Lechler GmbH, Metzingen, Germany) with a 30° spraying angle. The atomization characteristics of that nozzle with ethanol as testing material at 4 bar air pressure is shown in [figure 5](#). The dosing of the precursor - solution was conducted by a screw feeder (Eco Pen 450, Vieweg GmbH, Kranzberg, Germany), which can be operated in the range between 0.005 - 6 ml/min. Before the atomization in the nozzle, the solution was mixed with air at 4 bar to ensure a proper transportation to the tip and to ensure an appropriate atomization. The soot and the catalyst particles are collected on a sinter metal filter (HJS Emission Technology GmbH, Menden, Germany) with an area of 1.8 m². The filter consists of 60 filter pockets, each with an area of 300 cm², which are welded into a flange. For the filter the SMF[®]-AR housing (HJS Emission Technology GmbH, Menden, Germany) was used to enable a swift installation of the filter. Behind the filter an oxidation catalyst (DOC) was installed to ensure a complete elimination of hydrocarbons before leading the exhaust gas to the environment.

In order to evaluate the experiments temperature, pressure sensors and gas analysis are necessary. Temperature sensors

were therefore installed right before the injection of additive (T_0), directly in front (T_{20}) of the filter and behind it (T_{30}). The gauge pressure (p_0) in the exhaust pipe at the position of the injection unit and the pressure drop above the filter (p_{30}) were measured. With the help of the gas analysis it is possible to determine the content of CO, CO₂, NO/NO₂, O₂ and hydrocarbon in the exhaust gas in front of and behind the filter. The soot loading on the filter was calculated from the filter pressure drop, the exhaust gas mass flow and exhaust gas temperature by [equation \(6\)](#). The pressure drop resistance coefficient B_C was adapted to the weighted soot loading at the beginning and at the end of the regeneration procedure. From the average resistant coefficient $B_C = 2.5 \cdot 10^{15} [1/m^2]$ a deviation up to $\pm 8 \%$ was observed.

The catalysts used in this paper were oxides of the transition metals cerium, manganese and iron, which were found in literature to be catalytic active in soot conversion [7; 2]. The precursors of the catalyst particles were either the nitrates of iron, cerium and manganese, which were all solvable in water (Fe(NO₃)₃, Mn(NO₃)₂, Ce(NO₃)₃) and cyclopentadienyl iron (= ferrocene) as iron oxide precursor, which is solvable in the most organic solvents.

For loading up the filter with soot, the engine was always operated at a constant engine torque of 25 Nm and at an angular speed of 3110 rev/min, resulting in 170 kg/h exhaust gas and approximately 2-3 g/h soot mass flow. Under these operating conditions temperatures of about 300 °C in front of the filter were reached. The additive was injected continuously into the exhaust gas at a constant rate. Analysis of the filter soot after the experiments revealed that at temperatures of above 280 °C all of the injected iron was captured in the filter cake, so that it can be expected that temperatures of above 280 °C in front of the filter are



temperature ports:

T_0 : after engine/before injection
 T_{20} : before filter
 T_{30} : after filter

pressure ports:

p_{30} : filter pressure drop
 p_0 : system pressure at injection

gas analysis

x_{20} : gas port 1
 x_{30} : gas port 2

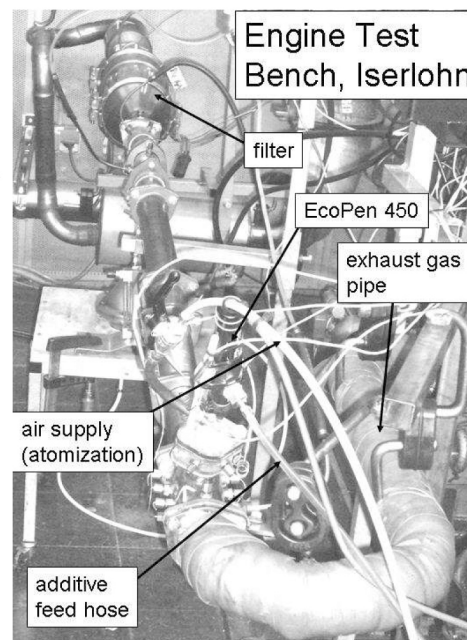


Figure 4. Setup of the engine test bench (left: sketch of the setup; right: photograph of the engine test bench).

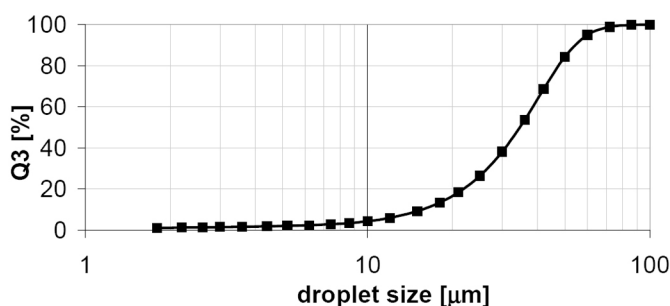


Figure 5. Spray characteristics of the SCR-nozzle operated at 4 bar with ethanol.

required to ensure a complete conversion of the precursor into the catalyst before the filter.

The regeneration of the filter was conducted after the filter was loaded with soot and catalyst for 12 h by increasing the exhaust gas temperature from 275 °C to 550 °C in 25 °C steps by increasing the engine torque accordingly. The soot conversion during the regeneration procedure was mainly employed to characterize the efficiency of the catalyst particles. After the experimental procedure on the engine test bench, the remaining soot was combusted in an oven to determine gravimetrically the soot mass on the filter at the end of the experiment. With the soot burned off, it is possible to investigate the catalyst distribution on the filter.

ESTIMATION OF THE REQUIRED CATALYST PARTICLE SIZE BY THE RESULTS OF THE CFD-SIMULATION

The simulation of the flow through the filter was conducted for typical conditions of engine operations. In this paper the results for an exhaust gas mass flow of 200 kg/h is presented, which is representative for diesel engines in the power range between 75 kW and 90 kW under heavy duty conditions. The simulated exhaust gas mass flow is slightly higher than applied one at the engine test bench. However, as the simulation should give a rough estimation of the required particle size, the simulated results are transferable to the experimental ones. Normally these conditions result in exhaust gas temperatures in front of the filter of approximately 280 °C, which was therefore used in the