

Numerical Simulation of DOC+DPF+SCR Systems: DOC Influence on SCR Performance

D. Chatterjee, T. Burkhardt, T. Rappe,
A. Güthenke and M. Weibel
Daimler AG

Copyright © 2008 SAE International

ABSTRACT

A numerical model for a diesel oxidation catalyst (DOC) is presented. It is based on a spatially 1D, physical and chemically based modeling of the relevant processes within the catalytic monolith. A global reaction kinetic approach has been chosen to describe the chemical reactions. Water condensation and evaporation was also considered, in order to predict the cold start behavior. Reaction kinetic parameters have been evaluated from a series of laboratory experiments. A correlation between the kinetic parameters and the noble metal loading was developed. The model was used in combination with a SCR-Model to study the influence of changes of noble metal loading and DOC volume on the overall transient NO_x performance of a DOC+DPF+SCR system.

INTRODUCTION

Over the last years, emission standards have become more and more stringent. To fulfill these standards, vehicle manufacturers are introducing combined after-treatment systems consisting of different catalyst technologies and DPF. One technology, which is already introduced for heavy duty applications in Europe with EURO IV, is the selective catalytic reduction of NO_x with NH_3/urea (SCR). For the design and optimization of such a complex system, a purely experimental approach is very time and cost consuming. The investigation of all possible combinations of catalyst parameters, their position in the exhaust line and the resulting interactions leads to a huge testing effort. In view of shortening development cycles and reducing development costs, numerical simulation during the development process is a key factor. A key issue for the simulation models is robustness and scalability of all models.

Future applications of the SCR technology will also include a diesel oxidation catalyst (DOC) and a diesel particulate trap (DPF). In order to comply with the stringent emission requirements all components have to be optimized in regard of system performance. The DOC and potentially a coated DPF are key components to increase the SCR performance especially at lower

temperatures. Therefore an optimized DOC setup, with respect to volume and noble metal loading, becomes a critical factor regarding performance and costs.

In previous works [1-3], a chemically and physically based, fully transient model of SCR honeycomb monolith converters was developed and discussed. This paper extends the previous modeling work by a diesel oxidation catalyst (DOC) model. During the development and parameterization of the respective chemical reaction kinetics, a correlation between kinetic parameters and noble metal loading was derived. Based on this correlation, variations of the noble metal content can be taken into account.

The DOC and the SCR models are integrated in the Daimler simulation environment *ExACT*, see figure 1. *ExACT* includes models for different types of catalysts, like SCR, DOC, LNT, TWC, DPF and provides a modular flexible platform for the simulation of complex combined exhaust aftertreatment systems.

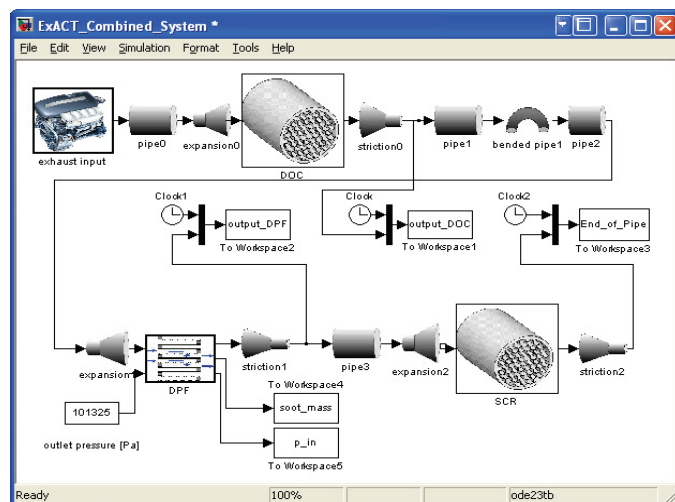


Figure 1: Scheme of the *ExACT* software environment.

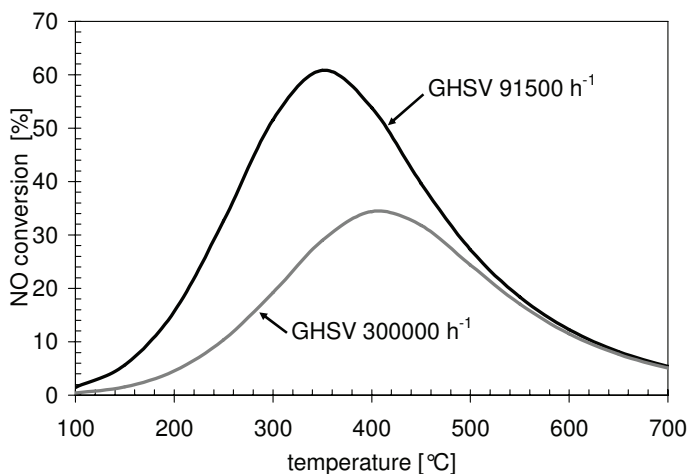


Figure 2: Steady state DOC NO conversion to NO₂ as function of catalyst temperature:

Previous works [1-3] were focused on the impact of variations of SCR parameters, like catalyst size or coating material, on the overall NO_x reduction efficiency. Within this paper a simulation study is discussed which focuses on the impact of DOC parameter variations on the overall NO_x conversion efficiency of combined DOC+DPF+SCR systems.

DOC FUNCTIONALITIES WITHIN COMBINED SCR SYSTEMS

Typically a DOC is used upstream of the SCR in combination with a DPF. A part of the NO in the exhaust gas is converted by the DOC to NO₂. However, as shown in figure 2, the NO₂ formation efficiency is strongly influenced by the catalyst temperature and exhaust mass flow. The presence of NO₂ increases the low temperature soot oxidation rate within the DPF [4] and the NO_x conversion efficiency of the SCR catalyst. Especially zeolite based SCR catalysts require NO₂ at low temperatures for good conversion efficiencies [2, 3, 5]. The optimum NO₂/NO_x ratio is 50%, see figure 3. These sensitivities require a proper adjustment of the DOC parameters to the operation conditions.

Additional functionalities are CO and HC oxidation. The latter can be used for thermal management by fuel injection in the exhaust line in front of the DOC. This is also one option to control the thermal regeneration of the DPF [6].

The important chemical reactions, which are implemented in the DOC model, are summarized in table 1. Reactions {1-4} are the oxidation of CO, C₃H₆, H₂ and NO. C₃H₆ will represent in the DOC model the various hydrocarbons. Reactions {5-8} are mainly relevant under stoichiometric or rich exhaust conditions; describing the water gas shift {5} and the NO reduction with CO {6}, H₂ {7} and C₃H₆ {8}.

Table 1: Considered set of reactions in the DOC model.

Reaction step	No
CO + 1/2 O ₂ → CO ₂	{1}
H ₂ + 1/2 O ₂ → H ₂ O	{2}
C ₃ H ₆ + 9/2 O ₂ → 3 H ₂ O + 3 CO ₂	{3}
NO + 1/2 O ₂ ↔ NO ₂	{4}
H ₂ O + CO ↔ H ₂ + CO ₂	{5}
NO + CO → CO ₂ + 1/2 N ₂	{6}
NO + H ₂ → H ₂ O + 1/2 N ₂	{7}
9 NO + C ₃ H ₆ → 3 CO ₂ + 9/2 N ₂ + 3 H ₂ O	{8}

DOC MODEL

In recent years, several proposals were made for the numerical simulation of DOC catalyst [7, 8]. The model presented in this paper combines a spatially 1D heterogeneous approach for the mass and heat balance with a global kinetic approach for the chemical reactions. A similar approach was already used for a LNT model presented in [9]. However, two additional submodels were added. To cover the wide range of space velocities in the application of the DOC model (ranging from heavy duty to passenger car) an effectiveness factor based washcoat model is included. Also, because of the large volumes in heavy duty applications, H₂O condensation in the monoliths can become significant. Therefore a H₂O condensation/evaporation model is included in the thermal balance.

TRANSPORT MODEL

The transport model assumes identical conditions within each channel of the honeycomb catalyst, with negligible axial dispersion and pressure drop, which leads to an effective, spatially 1D, heterogeneous mathematical model of the catalytic monolith [10].

The following balances are considered: Mass balances in the flowing gas, including accumulation, convection and external mass transfer (1), mass balances on the washcoat surface, including accumulation, external mass transfer and catalytic reactions (2); mass balances for accumulated species within the washcoat (e.g. for HC-Adsorption which will not be discussed in this paper and H₂O) (3); enthalpy balance of the flowing gas, including accumulation, convection and gas-solid heat transfer (4); enthalpy balance of the solid phase, including accumulation, axial heat conduction, gas-solid heat transfer, heat exchange with the surroundings and heat source from catalytic reactions (5):

$$\frac{\partial c_k(z,t)}{\partial t} = -\frac{\partial(uc_k)}{\partial z} + \frac{k_c a}{\varepsilon^g} (c_k^s - c_k), \quad k = 1 \dots K \quad (1)$$

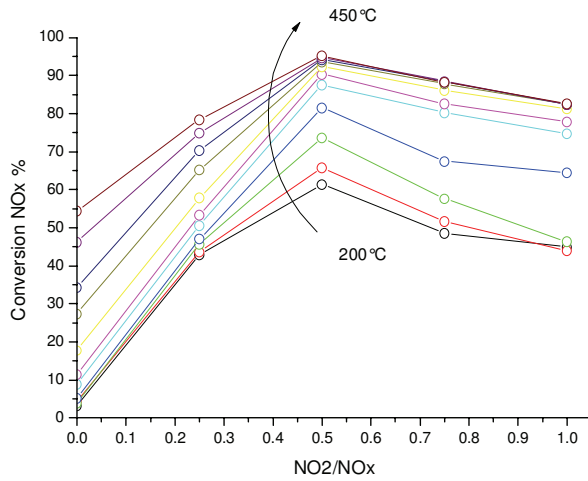


Figure 3: Effect of NO_2/NO_x feed ratio for different temperatures on the NO_x conversion performance of a zeolite based SCR catalyst. Microreactor experiments with crushed catalyst. S.V. 172.000 1/h, 1000ppm NO_x and 1000ppm NH_3 , 2 Vol-% O_2 , 10 Vol-% H_2O .

$$\frac{\partial c_k^s(z,t)}{\partial t} = \frac{k_c a}{\varepsilon^s (1 - \varepsilon^g) \phi^s} (c_k - c_k^s) + \frac{1}{\varepsilon^s} \sum_{j=1}^J v_{k,j} R_j, \quad k = 1 \dots K \quad (2)$$

$$\frac{\partial \psi_m(z,t)}{\partial t} = \frac{1}{\Psi_m^{\text{cap}}} \sum_{j=1}^J v_{m,j} R_j, \quad m = 1 \dots M \quad (3)$$

$$\rho c_p \frac{\partial T(z,t)}{\partial t} = -u \frac{\partial T}{\partial z} \rho c_p - \frac{k_h a}{\varepsilon^g} (T^s - T) \quad (4)$$

$$\begin{aligned} \rho^s c_p^s \frac{\partial T^s(z,t)}{\partial t} = & \lambda^s \frac{\partial^2 T^s}{\partial z^2} + \frac{k_h a}{(1 - \varepsilon^g)} (T - T^s) \\ & - \alpha (T^s - T^e) - \phi^s \sum_{j=1}^J \Delta H_{r,j} R_j \end{aligned} \quad (5)$$

Boundary conditions at the inlet ($z=0$) and at the outlet ($z=L$) of the monolith are:

$$T|_{z=0} = T^{\text{in}}, \quad u|_{z=0} = u^{\text{in}} \quad (6)$$

$$\left. \frac{\partial T^s}{\partial z} \right|_{z=0} = 0, \quad \left. \frac{\partial T^s}{\partial z} \right|_{z=L} = 0 \quad (7)$$

$$c_k|_{z=0} = c_k^{\text{in}}, \quad k = 1 \dots K \quad (8)$$

The inlet gas linear velocity u^{in} is calculated from the following equation:

$$u^{\text{in}} = \frac{\dot{V}^{\text{in}}}{S \varepsilon^g} \quad (9)$$

Spatially dependent external heat and mass transfer coefficients (k_h and k_c respectively) are calculated from correlations [11]. The storage phenomena are characterised by the maximum effective storage capacity Ψ^{cap} and temperature-dependent relative saturation coverages $\psi^{\text{eq}}(T)$.

The reaction rate for NO-oxidation (4) is multiplied by the so-called effectiveness factor η . This takes into account the influence of the washcoat diffusion on the respective reaction [12, 13]. The effectiveness factor is calculated from the dimensionless quantity called *Thiele modulus* (ϕ), with the following equation:

$$\eta = \frac{\tanh(\phi)}{\phi} \quad (10)$$

The *Thiele modulus* is calculated by equation (11).

$$\phi = L \sqrt{\frac{R_4}{D_{\text{eff}} c_{\text{NO}}}} \quad (11)$$

As detailed in [12], equations (10) and (11) are only exact from a mathematical standpoint, if the reaction rate R_4 is first order. A preceding numerical analysis, which is beyond the scope of this paper, with a 1D washcoat reaction/diffusion model, revealed however, that under the relevant operating conditions, equations (10) and (11) provide a good approximation. The effective diffusion coefficient D_{eff} is calculated from a random pore model [12, 13, 14]. The washcoat thickness L is estimated from microscopic pictures.

H₂O CONDENSATION AND EVAPORATION

Water condensation from the exhaust gas onto the monolith and evaporation back to the exhaust influences the temperature during light off. Especially H_2O which condenses before engine start might slow down the light off.

The model assumes that the condensed water on the surface is in thermal equilibrium with the water steam in the gas phase. In order to integrate the model into the framework described by equations (2) and (5) simple H_2O adsorption (12) and desorption (13) rates are used.

H_2O condensation/adsorption:

$$R_{\text{H}_2\text{O},\text{Ads}} = k_{\text{Ads}} (\Psi_{\text{H}_2\text{O}}^{\text{eq}}(T) - \Psi_{\text{H}_2\text{O}}) p_{\text{H}_2\text{O}}, \quad R_{\text{H}_2\text{O},\text{Ads}} \geq 0 \quad (12)$$

H_2O evaporation/desorption

$$R_{\text{H}_2\text{O},\text{Des}} = k_{\text{Des}} (\Psi_{\text{H}_2\text{O}}^{\text{eq}}(T) - \Psi_{\text{H}_2\text{O}}) (p_{\text{H}_2\text{O}} - p_{\text{H}_2\text{O}}^0(T)), \quad R_{\text{H}_2\text{O},\text{Des}} \geq 0 \quad (13)$$

The rates are included in the mass (2) and heat balances (5) with the respective heat of condensation/evaporation.

REACTION KINETICS

A combination of global pseudo-stationary kinetics has been applied for the CO, H₂, C₃H₆ oxidation (reactions {1}-{3}) and the NO reduction reactions (reactions {6}-{8}). For the NO oxidation (reaction {4}) and the water gas shift (reaction {5}), the backward reactions are explicitly considered by using the temperature dependent equilibrium constants. This is for the NO₂ formation essential as typically the conversion efficiency of a DOC above 350 °C is limited by the thermodynamic equilibrium. The kinetic parameters k_j and inhibition factors $K_{a/b,i}$ are given in Arrhenius-type expressions:

$$k_j = A_j \exp\left(-\frac{E_{a,j}}{R^s T}\right) \quad (14)$$

$$K_{a/b,i} = A_{a/b,i} \exp\left(-\frac{E_{a/b,i}}{R^s T}\right) \quad (15)$$

The parameters are evaluated from experiments with catalyst samples in a laboratory reactor. Using only two different inhibition terms G_1 and G_2 enables the simulation of the complex chemical system with a relatively low number of kinetic parameters; keeping the parameter estimation effort on a reasonable level.

Table 2: Reaction rate equations.

No.	Reaction Rate
{1}	$R_1 = k_1 \frac{y_{CO} y_{O_2}}{G_1}$
{2}	$R_2 = k_2 \frac{y_{H_2} y_{O_2}}{G_1}$
{3}	$R_3 = k_3 \frac{y_{C_3H_6} y_{O_2}}{G_1}$
{4}	$R_4 = k_9 (y_{NO} y_{O_2}^{0.5} - \frac{y_{NO_2}}{K_{y,9}^{eq}}) \frac{1}{G_2}$
{5}	$R_5 = k_4 (y_{CO} y_{H_2O} - \frac{y_{CO_2} y_{H_2}}{K_{y,4}^{eq}})$
{6}	$R_6 = k_6 y_{CO} y_{NO}^{0.5}$
{7}	$R_7 = k_7 y_{H_2} y_{NO}^{0.5}$
{8}	$R_8 = k_8 y_{C_3H_6} y_{NO}^{0.5}$

$$G_1 = (1 + K_{a,1} y_{CO} + K_{a,2} y_{C_3H_6})^2 (1 + K_{a,3} y_{CO}^2 y_{C_3H_6}^2) (1 + K_{a,4} y_{NO_x}^{0.7}) T,$$

$$G_2 = (1 + K_{b,1} y_{CO} + K_{b,2} y_{C_3H_6})^2 (1 + K_{b,3} y_{CO}^2 y_{C_3H_6}^2) (1 + K_{b,4} y_{NO_x}^{0.7}) T$$

The model has been implemented in Fortran. Finite differences method with semi-implicit approximations of time derivatives, first-order Taylor's expansion of reaction rates and adaptive time-step control is used to solve the set of partial differential equations (1-5). On a typical current desktop computer, the computation is approximately 3-15 times faster than the net run of a corresponding experiment. The Fortran program has been linked into Matlab Simulink as a dynamic link library (*.dll) to form a part of the *ExACT* software environment.

EXPERIMENTS AND EVALUATION OF KINETIC PARAMETERS

Three different DOC technologies were studied. All technologies were analysed with different noble metal loadings in degreened (600°C, 5h, real exhaust) and aged states (700°C, 200h, hydrothermal oven aged), see table 3. Laboratory data using an integral reactor is used to calibrate the reaction kinetics. With regards to NO oxidation it is learned that steady-state engine bench data could also be used to calibrate reaction {4}. A large set of data, regarding NO₂ formation, was available from a heavy duty test bench and was therefore used for calibration of reaction {4}.

Table 3: Catalyst technologies used for calibration

	Catalyst1	Catalyst2	Catalyst3
Noble metal	Pt	Pt	Pt/Pd
Loading [g/ft ³]	20	35, 70, 90, 180	27, 41, 55
Monolith	400cpsl, 6mil	300cpsl, 5mil	300cpsl, 5mil

Integral reactor experiments:

The conversion efficiencies of CO, C₃H₆, NO, were investigated under isothermal conditions within the range 100 – 600 °C. A monolith sample with 400/4 cpsl/mil cell density was used. Different lean mixtures were used as reactor input. The concentration of NO was between 500ppm and 1000 ppm, CO levels were 100ppm and 5000ppm, C₃H₆ concentration was 100ppm and 1000ppm. O₂ levels were 2, 4, 8 Vol.-%. H₂O and CO₂ were fixed at 8 Vol.-%. The space velocity was varied from 50000h⁻¹ to 300000h⁻¹ with nitrogen as balance. A temperature ramp with 2 K/min was applied to measure the quasi steady state conversion efficiencies. The following measurement equipment was used: CO was detected by an infrared analyser, C₃H₆ by FID and NO_x by chemiluminescence techniques

Engine test bench experiments

The NO conversion efficiency under steady state conditions were measured using a heavy duty engine test bench. Monoliths with 10.5" diameter and 3"-6" length were used. The engine was operated at constant load and speed until steady state conversion in the DOC was established. The measured operating points covered a wide range of operating conditions (S.V. 30.000-230.000 1/h, T_{exh.} 150-550°C). NO and NO₂ was measured before and after the DOC by means of a chemiluminescence analyzer.