

Synergetic DOC-DPF System Optimization Using Advanced Models

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ABSTRACT

Modern ‘DOC-cDPF’ systems for diesel exhaust are employing Pt-, Pd- as well as Pt/Pd alloy- based coatings to ensure high conversion efficiency of CO, HC even at low temperatures. Depending on the target application, these coatings should be also optimized towards NO₂ generation which is involved in low temperature soot oxidation as well as in SCR-based deNO_x. Zeolite materials are also frequently used to control cold-start HC emissions. Considering the wide variety of vehicles, engines and emission targets, there is no single optimum coating technology. The main target is therefore to maximize synergies rather than to optimize single components. At the same time, the system designer has nowadays a wide range of technologies to choose from, including PGM alloyed combinations (Pt/Pd), multiple layers and zones applicable to both DOCs and DPFs. This paper attempts to deal with the specific problem of optimizing such complex synergies, using advanced modeling techniques and exploiting a large number of ‘virtual’, rather than ‘real’ experiments. A systematic study of simple (single-PGM, single-layered) coating technologies is the starting point to generate a reaction model database, which is then used to simulate more complex, multi-component, multi-zoned and multi-layered systems.

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INTRODUCTION

Nowadays, the design and control of diesel exhaust aftertreatment systems are becoming more and more complex, in order to meet the stringent emission regulations and to ensure their optimum operation over time. Moreover, due to the strong pressure for CO₂ emissions reduction, the average exhaust temperature is expected to decrease, posing significant challenges to the exhaust after-treatment technology. This leads to lower exhaust gas conversion efficiency of oxidation catalysts. A common way to address the matter is the use of higher amount of noble metals for their preparation; however, the production cost is significantly increased.

In order to face this problem, catalyst manufactures are investing on research into applying the main idea of optimal combination of noble metals [1]. Platinum (Pt) is the most common noble metal and is widely used along with zeolite for the adsorption of hydrocarbons during the cold start phase. In recent years, the prevailing technologies are based on mixing platinum (Pt) with palladium (Pd), due to Pd’s capability to stabilize the Pt on catalyst’s washcoat and thus increasing the durability of catalyst at high operating temperatures [2, 3].

Moreover, new system configurations have been suggested, which use multiple monolith substrate zones, coated by different catalyst formulation (axially and/or radially) within the same device. Usually, the stronger (and more expensive) noble metal is placed in front zone in order to exploit the higher temperatures of the exhaust gas during cold start phase [4, 5]. Through radial zoning, it could be envisioned that more precious metal can be put in the monolith areas where the gas flow rate is usually higher as a result of flow maldistribution [6].

Segregated washcoat technologies have been developed to physically separate noble metals by fixing them on a particular base metal oxide of the washcoat, before the washcoat is applied to the substrate [7]. Such technologies are used when the co-existence of more active metals in the same coating may interact with each other, with washcoat components, or with the support material and to produce undesired, catalytically inactive compounds.

To reduce catalyst development cost, computational optimization methodologies are widely applied, especially during the last years. These methods rely mostly on chemical kinetic models using mathematical expressions of reaction rates, which face the catalytic coating as a ‘black box’ regardless of its type and complexity of the

catalytic coating. Usually, they are based on reference kinetic models for Pt-catalysts, which are re-calibrated to match the performance of the catalyst under investigation [8, 9, 10]. This methodology leads to increasing kinetics parameter calibration needs, since it fails to predict the combinational effect of multiple active metals concentration.

The systematic investigation of these phenomena requires the study of 'reference' catalytic samples, whose catalytic coatings contain certain variety of noble metals. In order to ensure that this research is conducted using catalytic materials with perfect catalytic coatings which would not be possible to be implemented using commercial products, 'reference' catalytic species have been supplied for this reason in the frame of a collaboration agreement.

In order to determine the catalytic kinetics parameters, the simulation model has to be calibrated with the help of experimental data. In principle, exhaust model calibration can be performed using engine bench experimental data under steady state and transient conditions with full scale catalysts [11, 12]. However, using this approach it is rather difficult to identify the chemical mechanisms and to develop a standard calibration procedure. A systematic methodology for model calibration based primarily on synthetic gas tests with small scale catalysts has been proposed in [13] and was used as a basis in this work. The main target is to define a process to transfer the information obtained from synthetic gas tests, to full-scale tests with real exhaust gas, which it is not a straightforward process due to the complex hydrocarbon speciation. Particular emphasis is given to the design of experiments, targeting on adsorption-desorption phenomena of hydrocarbons [14, 15, 16], as well as in species inhibitions and self-inhibitions phenomena of reactions, as a consequence of very high CO and HC concentrations in exhaust gas.

The main target of this work is to support a new methodology for the design of diesel after-treatment systems selecting optimized catalyst combinations. This methodology makes use of a combined consideration of experiments and computational simulations and includes testing of small-scale samples of simple catalysts tested on a series of steady-state protocols at lab scale to calibrate the reaction models, which are then validated in full-scale catalysts tested on steady-state and transient engine tests.

In a second step the paper attempts to deal with the specific problem of optimizing multi-component, multi-layered and multi-zoned 'DOC-cDPF' systems. A systematic study of simple (single-PGM, single-layered) coating technologies is the starting point to generate a reaction model database which is then used to simulate more complex, multicomponent and multi-layered systems.

The individual steps of this methodology are summarized below:

1. Initially an experimental investigation of 'reference' catalysts with a single active material, platinum (Pt) or palladium (Pd) is performed. These measurements are used to obtain the chemical kinetics of these simplified configurations.
2. Experimental investigation and modeling of adsorption/desorption of hydrocarbons.

3. Measurement of catalysts configuration with 'complex' catalytic coatings containing more than one active metal. Check if the model can predict complex formulations using the kinetics of the simple coatings without recalibration from scratch.
4. Validation of the approach under more complex operating modes.

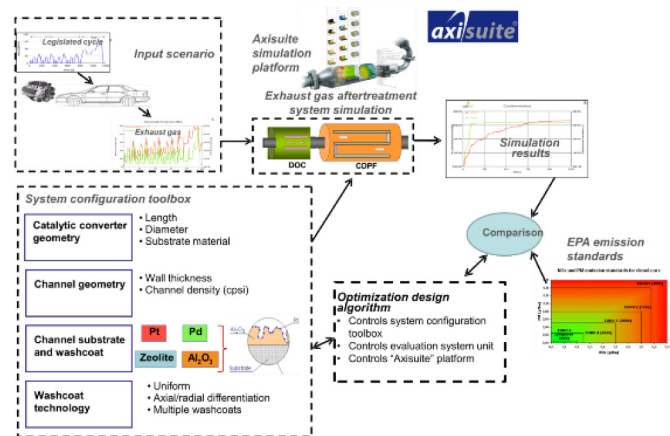


Figure 1. Catalyst optimization design methodology concept.

Scope of this approach is to develop a full optimization design methodology, whose concept is presented in Figure 1. An integrated system configuration toolbox will assist the user to evaluate optimized complex catalytic configurations under real world conditions, by setting only the catalytic system configuration parameters, such as converter geometry (length, diameter, substrate thickness etc), channel geometry (wall thickness, channel density), channel substrate and washcoat formulation (Pt, Pd, zeolite etc) and washcoat technology (uniform, axial/radial configuration, multiple washcoats etc.).

In this study, DOC modeling is performed using the commercial "Axisuite®" platform. This platform is a modular software for the simulation of exhaust aftertreatment devices and systems, consisting of specific modules for simulation of wall-flow particulate filters, flow-through catalytic converters, foam-based or fiber-based filters and connecting pipes [17].

EXPERIMENTAL SETUP

Samples

A number of DOC research samples were supplied and studied for this work. The active metal (PGM) components are Pt and Pd in various combinations. Apart from single-layer catalysts, zeolite catalysts were also prepared in order to study the effect of adsorbed hydrocarbons on catalyst efficiency. Alloyed-type, multi-zoned and multi-layered catalysts were also specially prepared, in order to study the behavior and efficiency of more complex configurations. Table 1 presents the full list of the used samples.

All samples have the same geometrical and material properties, which are given in Table 2. Based on information from the catalyst supplier, the additional components such as alumina were part of the washcoat. All samples were aged at 700°C for 10 hours.

Table 1. List of DOC samples used in experiments.

DOC catalytic samples codification	
C1	Pt-only
C2	Pd-only
C3	Pt zeolite
C4	Pt/Pd (2:1) alloy
C5	Pt/Pd (2:1) alloy zeolite
C6	2-zone: front Pt / back Pd
C7	2-layers: lower Pt / upper Pd

Table 2. DOC properties.

Geometrical data	
Cell density	400 cpsi (62 cells/cm ²)
Wall thickness	6.5 mils (0.165 mm)
Material properties	
Substrate material	Cordierite
Specific loading	150 g/l
PGM loading	2.825 g/l

In order to address the applicability of methodology in catalyzed particulate filters (cDPF), two different filter samples were prepared (Table 3). *S1* sample is a simple catalyzed filter with a Pt-only uniform coating. *S2* is a Pt/Pd- alloy catalyzed filter with lower level PGM loading. Both samples had the same geometrical and material properties, which are presented in Table 4. All samples were aged at 700°C for 12h in air.

Table 3. List of cDPF samples used in experiments.

cDPF samples codification	
D1	Pt-only uniform coating. PGM loading: 0.35 g/l
D2	Pt/Pd (12:1) alloy. PGM loading: 0.18 g/l

Table 4. Catalytic DPF properties.

Geometrical data	
Cell density	200 cpsi (31 cells/cm ²)
Wall thickness	12 mils (0.305 mm)

Synthetic Gas Bench Tests

Experimental Setup

Small-scale specimens (diameter: 20 mm, length: 37 mm) were extracted from all DOC samples configurations described above. Each specimen was measured, being placed in an electrically heated high temperature tube furnace which can be fed with synthetic gas. As it can be seen in Figure 2a, a gas mixer (EnviroNics S-2000) which can mix up to six different gases was used for the preparation of the inlet gas mixture. In selected experiments, controlled amounts of heavy liquid HCs were introduced by a syringe pump (ColeParmer 74900

dual syringe pump). A ‘saturator’ was used to humidify the reaction gas. It consists of a glass flask filled with distilled water. The flask is placed on a magnetic heated stirrer which keeps the water temperature constant with the help of a control thermocouple. As it passes through the flask, the gas stream gets saturated with the amount of water which corresponds to the selected water temperature. For tests with liquid HCs and without water the ‘saturator’ is by-passed.

The inlet and outlet concentrations of the different species (CO, CO₂, HC, NO/NO_x) were measured using a multi-gas analyzer (AMA i60). Specifically for the HC adsorption tests, an ultra-fast HC analyzer (MEXA-1 210FRF, T90 less than 2ms) with two sampling channels was used to continuously monitor the inlet and outlet concentrations.

Temperature inside the test piece was continuously monitored using a set of K-type thermocouples. Thermocouples are placed in various points inside the specimen to study the temperature distribution. The thermocouple positions inside the specimen are presented in Figure 2b.

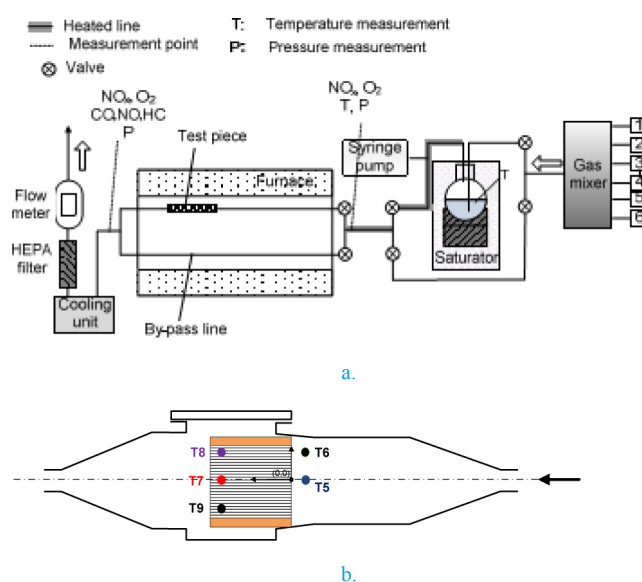


Figure 2. SGB tests: (a) Experimental setup sketch, (b) DOC thermocouple positions for SGB tests.

Test Protocols

Chemical reaction rates are different for each catalyst and depend on the catalyst's ageing status. Thus, they have to be defined for the specific catalyst used for the study. A common way to define such parameters is to measure the experimental input ('in') and output ('out') catalyst conditions (mass flow rate, temperature and species concentrations) and then to determine the parameters which minimize the deviation between experimental ('exp') and simulation ('sim') results. This process is commonly referred to as 'model calibration'. The model prediction accuracy can be afterwards checked via full scale experiments with real exhaust gases under various transient conditions.

A pre-conditioning of the DOC was performed prior to each test. Preconditioning consists of a heat-up phase up to 450°C under N_2 . Then a mixture of 200 ppm NO / 10% O_2 / 0% H_2O is allowed to flow through the sample for 15 min. Finally, the test piece was cooled under N_2 .

Light-off (L/O) and Cool-down (C/D) is a typical test, where the temperature of the test piece is initially increased up to 450°C (L/O phase) and then decreased (C/D phase), while a constant composition feed gas passed through the sample. The catalytic oxidation activity is frequently characterized by the temperature to reach a certain conversion efficiency. In our case, the characteristic temperature is evaluated at the entrance of the DOC (' T_{in} '). The correlation of conversion efficiency vs temperature depends on the direction of temperature change. The L/O temperature during temperature increase is typically higher than the C/D temperature. For the evaluation summary presented here, we use the temperature where 50% CO (' T_{50-CO} '), 80% HC (' T_{80-HC} ') and 20% NO (' T_{20-NO} ') conversion is observed during the C/D phase.

Another important test is Concentration Scan (C/S), where the temperature of the test piece is kept constant while the concentration of the species of interest (CO or NO) is changed stepwise in a predefined concentration range. The concentrations of the other species present in the feed gas are kept constant.

An overview of the HC/ H_2O Adsorption (ADS) / Desorption (DES) test is presented in Figure 3. After the preconditioning of the catalyst, a mixture of N_2 , $C_{12}H_{26}$ and water are fed into the catalyst at constant space velocity and temperature until outlet HC concentrations reaches approximately inlet concentrations, indicating complete saturation (adsorption phase). When the outlet HC concentration reaches the inlet concentration, only N_2 is driven through the sample and the furnace temperature is first kept constant and equal to the adsorption temperature for a few minutes. Then the temperature is increased again under N_2 , to achieve full desorption of the HC. At the end, the sample is cooled again under N_2 to the next temperature to be tested.

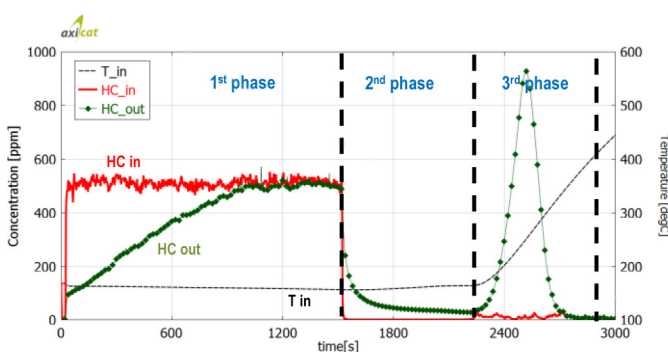


Figure 3. DOC C3. Adsorption/desorption test protocol description. 1st phase: adsorption. 2nd phase: desorption under constant temperature. 3rd phase: desorption with increasing temperature. Feed gas composition given in Table 5.

More details about the specifications of the protocols (temperature, feed gas, flow rate) are presented in Table 5.

Table 5. Description of project's protocols (SGB tests).

Protocol	Temperature	HC (C1) [ppm]	CO [ppm]	NO [ppm]	O ₂ [%]	CO ₂ [%]	H ₂ O [%]	GHSV [h ⁻¹]
L/O / C/D	50° - 450°C L/O ramp: 15 deg/min	500 C ₃ H ₆ or C ₁₂ H ₂₆	1000	100	10	5	4.2	78,000
ADS/ DES	240°, 200°, 160°C	(ads) 500 C ₁₂ H ₂₆	-	-	-	-	4.2	78,000
C/S	T50 & T80	500 C ₃ H ₆	var.	100	10	5	4.2	78,000

Full-Scale Transient Tests

The experimental setup used for the transient full-scale tests includes the engine, the exhaust line where all the emission, temperature and pressure measurements are performed and the catalytic system configuration. This consisted of a DOC sample followed by a cDPF sample when applicable. A EURO 5 compliant 1.4l turbo diesel engine was used for the experiments.

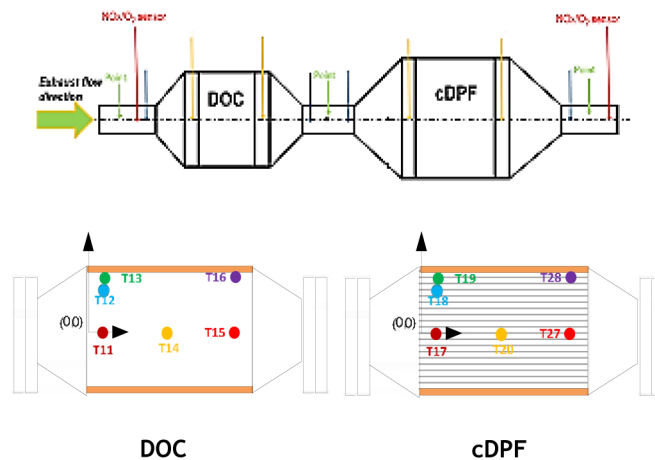


Figure 4. DOC and cDPF thermocouple positions during engine bench tests.

Two measuring positions were determined: a) upstream of the system (DOC inlet) and b) downstream of the system (outlet of the catalytic system). Each driving cycle was repeated twice, first time setting the AMA i60 multi-gas analyzer measuring the CO, CO₂, HC, NO emissions at the first position, and the following time setting the analyzer measuring the corresponding emissions at the second position. The majority of the experiments were repeated accurately. Aside this analyzer, additional NOx sensors were used to monitor NOx and O₂ inlet and outlet concentrations continuously during the experiments.

Three samples (C1, C2 and C4) were used for experiments (144mm x 75mm). The exact positions of the thermocouples are depicted in Figure 4.

MATHEMATICAL MODEL

Model Description

The present simulation study was performed using the commercial "Axisuite®" platform [17].

DOC modeling was performed using the “Axical” module of the platform, a general tool for modeling all types of flow-through catalysts. The governing model equations have been presented and discussed in relevant publications [14, 18, 19, 20] and are given here as a reference (Figure 5). The model is equipped with intra-layer discretization to account for the coupling between reaction and diffusion phenomena. These phenomena play an important role in the case of multi-layer washcoats as well as in the case of extruded catalysts [21].

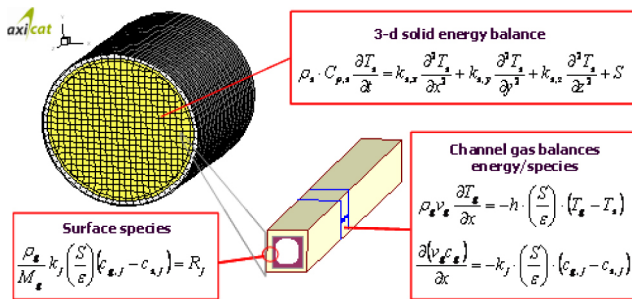


Figure 5. Flow-through catalyst schematic and basic model equations.

DPF modeling was performed using “Axitrap” module of the platform. This module is used to simulate bare and catalyzed DPFs in terms of filtration efficiency, pressure drop, and catalytic reactions. With the aid of sophisticated 3-dimensional heat and mass transfer models coupled with suitable reaction models for soot combustion, the model is able to predict the evolution of DPF regeneration events, incl. temperature field predictions. The basic differential model equations are summarized in Figure 6, whereas more details can be found in relevant publications [22, 23, 24].

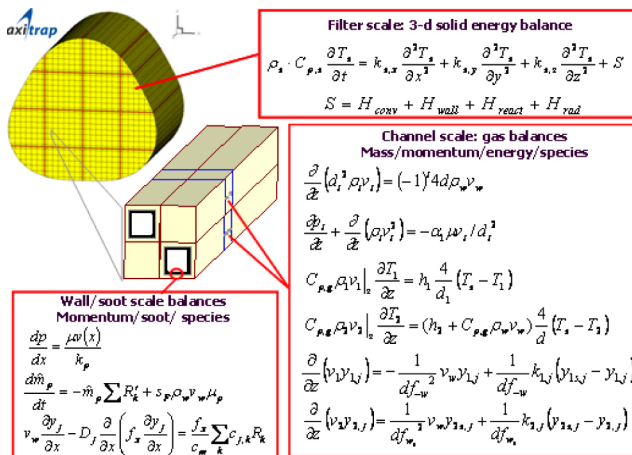


Figure 6. Wall-flow DPF schematic and basic model equations.

Reaction Scheme

The chemical reactions accounted for in the DOC mathematical model are listed in Table 6. These include oxidation reactions for CO and HC. For HC oxidation both O₂ and NO₂ reactions are considered. In addition, the HC de-NO_x mechanism has been added (reaction d) to account for observed NO_x reduction in the presence of HC. The

oxidation of NO to NO₂ also takes into account the chemical equilibrium between the NO₂ formation (reaction e) and NO₂ decomposition (reaction f). Moreover the reaction between CO and NO is considered (reaction g). Inhibition terms are used for all reactions. The analytical relationships for these terms are presented in [13].

Table 6. Reaction scheme used in DOC model.

CO + 1/2 O ₂ → CO ₂	(a)
C _x H _y + (x+y/4) O ₂ → x CO ₂ + y/2 H ₂ O	(b)
C _x H _y + (2x+y/2) NO ₂ → x CO ₂ + y/2 H ₂ O + (2x+y/2) NO	(c)
C _x H _y + (2x+y/2) NO → x CO ₂ + y/2 H ₂ O + (x+y/4) N ₂	(d)
NO + 1/2 O ₂ → NO ₂	(e)
NO ₂ → NO + 1/2 O ₂	(f)
CO + NO ₂ → CO ₂ + NO	(g)

In real diesel exhaust gas, a large number of different hydrocarbon species exists. These hydrocarbons present different chemical activity [13]. To deal with this issue, hydrocarbons are grouped in 2 groups to account for the individual oxidation and adsorption properties of the different HC species in the exhaust gas. C₃H₆ and C₁₂H₂₆ were assumed to simulate the behavior of each group more accurately respectively and were therefore used in the SGB experiments.

Together with the oxidation reactions, adsorption phenomena may also play an important role during the warm-up phase of the catalyst. These phenomena may affect both the species availability and the temperature response of the monolith. Therefore, competitive species adsorption are modeled using the validated Dubinin and Radushkevich adsorption isotherm and appropriate adsorption/desorption rates [25]. According to this approach, the adsorbate in intimate contact with the solid is assumed to be in liquid form. The equation of the D-R isotherm gives the adsorbed mass at equilibrium x_{eq} as function of temperature and partial pressure:

$$\ln x = \ln(w_0 \rho) - D \left[\ln \left(\frac{p_{HC}}{p_{sat,HC}} \right) \right]^2 \quad (1)$$

$$D = A \left(\frac{RT}{\beta} \right)^2 \quad (2)$$

where W_0 is the total volume of all micropores, A is a constant characteristic of the pore size distribution (both depend on the properties of the solid). β is the affinity coefficient, which depends on the adsorbate, ρ is the liquid phase density, p_{sat} is the saturation pressure and p_{HC} is the partial pressure of the adsorbate at the gas-solid interface. The above equations imply that the mass of hydrocarbon that can be adsorbed at equilibrium conditions is a function of the local gas phase concentration, the local temperature and the saturation pressure, which in turn is also a function of temperature [25].