Identification of catalytic converter kinetic model using a genetic algorithm approach

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Abstract: The need to deliver fast-in-market and right-first-time design for ultra-low-emission vehicles at a reasonable cost is driving the automotive industries to invest significant manpower in computer-aided design and optimization of exhaust after-treatment systems. To serve the above goals, an already developed engineering model for the three-way catalytic converter kinetic behaviour is linked with a genetic algorithm optimization procedure, for fast and accurate estimation of the set of tuneable kinetic parameters that describe the chemical behaviour of each specific washcoat formulation. The genetic-algorithm-based optimization procedure utilizes a purpose-designed performance measure that allows an objective assessment of model prediction accuracy against a set of experimental data that represent the behaviour of the specific washcoat formulation over a typical legislated test procedure.

The identification methodology is tested on a demanding case study, and the best-fit parameters demonstrate high accuracy in matching the measured test data. The results are definitely more accurate than those usually obtained by manual or gradient-based tuning of the parameters. Moreover, the set of parameters identified by the genetic algorithm methodology is proven to describe in a valid way the chemical kinetic behaviour of the specific catalyst, and this is tested by the successful prediction of the performance of a smaller-size converter.

The parameter estimation methodology developed fits in an integrated computer-aided engineering methodology assisting the design optimization of catalytic exhaust systems that extends all the way through from model development to parameter estimation, and quality assurance of test data.

Keywords: catalytic converter kinetic model, genetic algorithm, catalytic exhaust systems

NOTATION

- $\Delta H$: molar heat of reaction (J/mol)
- $h$: convection coefficient (W/m$^2$ s)
- $k$: thermal conductivity (W/m K)
- $k_m$: mass transfer coefficient (m/s)
- $K$: inhibition term (Table 2) (—)
- $m$: exhaust gas mass flowrate (kg/s)
- $M$: molecular mass (kg/mol)
- $N$: number of time intervals for evaluation of performance function $=t/\Delta t$
- $Q_{amb}$: heat transferred between converter and ambient air (J/m$^3$ s)
- $r$: rate of reaction (mol/m$^3$ s)
- $R_g$: universal gas constant $=8.314$ J/mol K
- $R$: rate of species production/depletion per unit reactor volume (mol/m$^3$ s)
- $S$: geometric surface area per unit reactor volume (m$^2$/m$^3$)
- $t$: time (s)
- $T$: temperature (K)
- $u_z$: exhaust gas velocity (m/s)
- $z$: distance from the monolith inlet (m)

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\[\gamma \] catalytic surface area per unit washcoat volume (m\(^2\)/m\(^3\) washcoat)
\[\delta\] washcoat thickness (m)
\[\varepsilon\] emissivity factor (radiation) (m\(^{-1}\))
\[\Theta\] tuneable parameters vector
\[\rho\] density (kg/m\(^3\))
\[\sigma\] Stefan–Boltzmann constant (W/m\(^2\) T\(^4\))
\[\tau\] duration of an experiment (s)
\[\psi\] fractional extent of the oxygen storage component (—)
\[\psi_{cap}\] washcoat capacity of the oxygen storage component (mol/m\(^3\))

Subscripts

amb ambient
g gas
(i) parameter index
(j) species index
(k) reaction index
mon monolith
(n) time index
in inlet
s solid or solid–gas interface
(z) axial direction

1 INTRODUCTION

Catalytic converters have been in use for the past 30 years as an efficient and economic solution for the reduction of pollutants emitted by passenger car engines. Ever-decreasing legislated emission levels trigger the development of high-efficiency exhaust after-treatment systems, which involve optimization of the engine, catalytic converter, exhaust piping and control for each application. Catalytic converter modelling tools significantly assist this development process. Modern modelling methodologies have demonstrated their capacity to be successfully incorporated in the process of exhaust after-treatment systems design [1–5]. Among the plethora of catalytic converter models that have been published in the literature, kinetic models with reduced reaction schemes and semi-empirical rate expressions appear to be better suited to the requirements and constraints of the automotive engineer [6]. They have been proven able to match the accuracy levels required in the prediction of catalyst performance in legislated driving cycle tests and thus to provide the engineer with reliable, fast and versatile tools that may significantly decrease the cost and development time of new exhaust lines.

Reduced reaction scheme models employ a limited number of phenomenological reactions that contain only initial reactants and final products instead of elementary reactions on the catalyst active sites. The complexity and details of the reaction path are lumped into the kinetic rate expressions of these models. Rate expressions usually follow the Langmuir–Hinselwood formalism, modified by empirical terms. Generally, the form of the rate expressions of such models for the reaction between two species a and b is

\[ r = \frac{A e^{-E/RT}}{G(c_a, c_b; K_1, K_2, \ldots)} \]

Thus, the Langmuir–Hinselwood rate expressions determine an exponential (Arrhenius-type) dependence on temperature while G is an inhibition term, a function of temperature and concentrations c of various species that may inhibit the reaction. In the above expression, factors A and E (the pre-exponential factor or frequency factor and the activation energy) as well as factors K included in the inhibition term G are considered as fitting (tuneable) parameters. The effects of all phenomena not included explicitly into the model are lumped in these terms. Therefore, their values are dependent on the chemical composition of the catalyst’s washcoat and must be estimated by fitting the model to a set of experimental data, which represent the behaviour of the catalyst in typical operating cycles.

The identification process of the model’s tuneable parameters is commonly referred to as model tuning. Applicability of the lumped-parameter models is significantly affected by the successful identification of their tuneable parameters. Once accurate parameter identification is successful, the model may be used subsequently for the prediction of the catalytic converter efficiency for different geometrical and design characteristics or under different operation conditions.

Traditionally, fitting of lumped-parameter catalytic converter models was accomplished manually, a process which is highly empirical, requires experience and does not guarantee the success of the undertaking over a wide range of operating conditions (i.e. full legislated cycles with significant variation of reactor conditions). To circumvent these drawbacks, several efforts have been made towards a systematic methodology for model tuning. All of these are based on the transformation of the tuning problem into an optimization problem, where a quantity that indicates goodness of fit is optimized for the tuneable parameters of the model. The goodness-of-fit quantity may be viewed as a performance measure of the model, since it indicates the performance of the model compared with the experimental data.

Montreuil et al. [7] were the first to present a systematic attempt to tune their steady state three-way catalytic converter model, using a conjugate gradients optimization procedure. Dubien and Schweich [8] presented a conceptually similar methodology to determine the kinetics of simple rate expressions from light-off experiments, employing the downhill simplex method. Pontikakis and Stamatelos [9] used the conjugate-gradients technique to determine kinetic parameters of a transient three-way catalytic converter model from driving cycle tests.
Glielmo and Santini [10] presented a simplified control-oriented three-way catalytic converter model that was tuned using a genetic algorithm. All the above efforts used performance measures based on the least-squares error [11] between measured and computed results. The work of Glielmo and Santini must be distinguished because of its optimization aspects, as it uses a multi-objective optimization procedure for the identification of the model. The genetic algorithm has a potential to avoid local optima in the optimization space and thus to fit the model to the experimental data with higher accuracy.

The combination of a catalytic converter model with an optimization procedure for the identification of the model’s parameters is only a first step towards a complete computer-aided methodology for catalytic converter design and optimization, which is under continuous development at the authors’ laboratory during the last decade. The complete methodology is based on the following fourfold framework:

(a) catalytic converter model and software based on tuneable Langmuir–Hinselwood kinetics approach;
(b) kinetic parameter estimation software based on a properly adapted optimization procedure;
(c) emissions measurements quality assurance methodology and software;
(d) design and implementation of critical experiments

This work is a continuation of the work presented in reference [9] and addresses the interaction of the first two of the above issues. It is based on the CATRAN three-way catalytic converter model, which is continuously developed and validated against real-world case studies [12–15]. The performance measure and the optimization algorithm of the procedure are updated, in an attempt to approach the problem of computer-aided identification of the kinetic model more systematically. Specifically, a performance measure is first formulated that is suited to the problem of catalytic converter model tuning in driving cycle tests. Then, a purpose-designed genetic algorithm is used to extract a set of tuneable parameters that optimizes the performance measure to obtain a good fit of the model to the experimental data.

### 2 MODEL DESCRIPTION

The catalytic converter model used in this study is briefly described below. The model’s underlying concept is the minimization of degrees of freedom and the elimination of any superfluous complexity in general. A more detailed description of the model and its design concept has been given in references [6] and [15].

The prevailing physical phenomena that occur in the catalytic converter are heat and mass transfer in both gaseous and solid phases. They are described by a system of balance equations, which is summarized in Table 1. The model has the following features:

(a) transient, one-dimensional heat transfer calculations for the solid phase of the converter;
(b) quasi-steady one-dimensional calculations of temperature and concentration axial distributions for the gaseous phase;
(c) simplified reaction scheme featuring a minimum set of Langmuir–Hinselwood-type reduction–oxidation (redox) reactions and an oxygen storage submodel for three-way catalytic converter washcoats.

Heat transfer in the solid phase involves a fully transient calculation. Nevertheless, quasi-steady heat and

<table>
<thead>
<tr>
<th>Mass balances</th>
<th>Gas phase (channel)</th>
<th>$\rho \frac{\partial T_g(z)}{\partial z} = hS[T_g(z) - T_{\text{in}}(z)]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid phase</td>
<td>(washcoat)</td>
<td>$\rho \frac{\partial c}{\partial z} = \rho \frac{\partial k}{\partial z}S[c(z) - c_{\text{in}}(z)]$</td>
</tr>
<tr>
<td>Heat balances</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas phase (channel)</td>
<td>$\rho \frac{\partial T_g(z)}{\partial z} = k_s \frac{\partial T_s(z)}{\partial z} + hS[T_s(z) - T_{\text{in}}(z)]$</td>
<td></td>
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<tr>
<td>Solid phase</td>
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<td>$\rho \frac{\partial c}{\partial z} = \rho \frac{\partial k}{\partial z}S[c(z) - c_{\text{in}}(z)]$</td>
</tr>
<tr>
<td>Reaction rates</td>
<td>$R_i = \delta g \sum_{k=1}^{9} (a_{k,s} r_k)$</td>
<td></td>
</tr>
<tr>
<td>Boundary conditions</td>
<td>$Q_{\text{amb}} = h_{\text{amb}}(T_g - T_{\text{amb}}) + e\alpha(T_g - T_{\text{amb}})$</td>
<td></td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Tuneable parameters</th>
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<tbody>
<tr>
<td>$A_k, k = 1, \ldots, 9$</td>
</tr>
</tbody>
</table>

Table 1  Model equations and tuneable parameters
mass balances are employed for the gas phase, since the heat and mass accumulation terms in the gas phase are neglected, which is a realistic assumption [16, 17].

2.1 Washcoat level modelling

A ‘film model’ approach (see, for example, references [12] and [18]) approximates the washcoat (usually about 50 μm thickness) with a solid–gas interface, where it is assumed that all reactions occur. This approximation essentially neglects diffusion effects in the pore system of the washcoat and assumes that all catalytically active sites are directly available to gaseous-phase species at this solid–gas interface [18, 19]:

$$\frac{\rho k_m(\epsilon_j - \epsilon_{j,0})}{M_g} = R_j$$

(2)

On the right-hand side of equation (2), the rate $R_j$ refers to the production or consumption of each species at the solid–gas interface. For $N_k$ reactions, each taking place with a rate $r_k$, the rate of consumption or production of a species $j$ is

$$R_{\text{rea},j} = \delta \gamma S \sum_{k=1}^{N_k} (a_{j,k} r_k)$$

(3)

where $a_{j,k}$ is the stoichiometric coefficient of species $j$ in reaction $k$, $\delta$ is the washcoat thickness and $\gamma$ is the specific catalyst area, i.e. catalytically active area per washcoat volume. Thus, any washcoat diffusion effects are lumped in the kinetics expressions.

The two primary categories of heterogeneous catalytic reactions occurring in the washcoat are redox reactions and oxygen storage reactions (see reaction scheme in Table 2). Oxygen storage phenomena play a principal role in the efficiency of the modern three-way catalytic converter, as they supply the lack of oxygen under reducing environment. Oxygen storage occurs mainly on the ceria surface. Ceria (together with zirconia which has analogous activity) are contained in large quantities in the catalyst’s washcoat (order of 30 wt %). Under net

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>Rate expression</th>
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<tbody>
<tr>
<td>Oxidation reactions</td>
<td></td>
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</tr>
<tr>
<td>1</td>
<td>CO + 0.5O₂ → CO₂</td>
<td>$r_1 = A_1 e^{-r_1 j T c_{CO} c_{O}} G$</td>
</tr>
<tr>
<td>2</td>
<td>H₂ + 0.5O₂ → H₂O</td>
<td>$r_2 = A_2 e^{-r_2 j T c_{H2} c_{O}} G$</td>
</tr>
<tr>
<td>3</td>
<td>CH₃,fast + 1.45O₂ → CO₂ + 0.9H₂O</td>
<td>$r_3 = A_3 e^{-r_3 j T c_{CH3,fast} c_{O}} G$</td>
</tr>
<tr>
<td>4</td>
<td>CH₃,slow + 1.45O₂ → CO₂ + 0.9H₂O</td>
<td>$r_4 = A_4 e^{-r_4 j T c_{CH3,slow} c_{O}} G$</td>
</tr>
<tr>
<td>NO reduction</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>2CO + 2NO → 2CO₂ + N₂</td>
<td>$r_5 = A_5 e^{-r_5 j T c_{CO} c_{NO}} G$</td>
</tr>
<tr>
<td>Oxygen storage</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>CeO₂, + 0.5O₂ → 2CeO₂</td>
<td>$r_6 = A_6 e^{-r_6 j T c_{CeO2} c_{O}} (1 - \psi)$</td>
</tr>
<tr>
<td>7</td>
<td>CeO₂, + NO → 2CeO₂ + 0.5N₂</td>
<td>$r_7 = A_7 e^{-r_7 j T c_{CeO2} c_{NO}} (1 - \psi)$</td>
</tr>
<tr>
<td>8</td>
<td>2CeO₂ + CO → Ce₂O₃ + CO₂</td>
<td>$r_8 = A_8 e^{-r_8 j T c_{CeO2} c_{CO}} \psi$</td>
</tr>
<tr>
<td>9</td>
<td>CH₃,fast + 3.8CeO₂ → 1.9Ce₂O₃ + CO₂ + 0.9H₂O</td>
<td>$r_9 = A_9 e^{-r_9 j T c_{CH3,fast} (c_{CeO2} + c_{CeO2}) \psi}$</td>
</tr>
<tr>
<td>10</td>
<td>CH₃,slow + 3.8CeO₂ → 1.9Ce₂O₃ + CO₂ + 0.9H₂O</td>
<td>$r_{10} = A_{10} e^{-r_{10} j T c_{CH3,slow} (c_{CeO2} + c_{CeO2}) \psi}$</td>
</tr>
</tbody>
</table>

The inhibition term is

$$G = T(1 + K_{i,c}_{CO} + K_{2,c}_{THC})^2(1 + K_{i,c}_{CeO2}^2)/(1 + K_{i,c}_{NO})$$

where

$$K_{i,c} = A_i e^{-r_i j T}, \quad i = 1, \ldots, 4,$$

with

$$A_1 = 65.5, \quad A_2 = 2080, \quad A_3 = 3.98, \quad A_4 = 4.79 \times 10^5$$

$$E_1 = -7990, \quad E_2 = -3000, \quad E_3 = -96534, \quad E_4 = 31036$$

and where

$$c_{THC} = c_{CeO2} + c_{CeO2}$$

The auxiliary quantities are

$$\psi = \frac{2 \times \text{mol CeO}₂}{2 \times \text{mol CeO}₂ + \text{mol CeO}₂}$$

$$\frac{d\psi}{dt} = \frac{r_6 + r_7 - r_8 + r_9 + r_{10}}{\psi_{\text{cap}}}$$

Table 2 Reaction schemes and rate expressions of the model
oxidizing conditions, three-valent cerium oxide (Ce\(_2\)O\(_3\)) may react with O\(_2\) or NO and oxidize to its four-valent state (CeO\(_2\)). Under net reducing conditions, CeO\(_2\) may function as an oxidizing agent for CO, hydrocarbons (HC) and H\(_2\).

The model uses the auxiliary quantity \(\psi\) to express the fractional extent of oxidation of the oxygen storage component [12]. Specifically, the oxidation rate of the oxygen storage component is assumed proportional to the active sites of Ce\(_2\)O\(_3\), i.e. to \(\Psi_{\text{cap}}(1 - \psi)\). On the other hand, the oxidation rate of CO and HC by CeO\(_2\) is assumed proportional to \(\Psi_{\text{cap}}\psi\). Moreover, the rates of these reactions should be linearly dependent on the local concentration of the corresponding gaseous-phase reactant. The extent of oxidation, \(\psi\), is continuously changing during transient converter operation. Its value is affected by the relative reaction rates of reactions 6 to 10 in Table 2. The rates of reactions are expected to be linear functions of \(\psi\) for CeO\(_2\) reduction and 1 - \(\psi\) for Ce\(_2\)O\(_3\) oxidation. The rate of variation in \(\psi\) is the difference between the rate that Ce\(_2\)O\(_3\) is oxidized and reduced:

\[
\frac{d\psi}{dt} = \frac{r_6 + r_7}{\Psi_{\text{cap}}} - \frac{r_8 + r_9 + r_{10}}{\Psi_{\text{cap}}} \tag{4}
\]

The above equation is solved analytically for \(\psi\) at each node (typically 15–30 nodes are employed to model the full channel length), along the catalyst channels. The quantity \(\Psi_{\text{cap}}\) is the total oxygen storage capacity and its value may be estimated by the content of ceria in the washcoat.

### 2.2 Channel-level modelling

For the formulation of the channel-level model, two usual simplifications are employed: firstly, the axial diffusion of mass and heat in the gas phase is negligible and, secondly, the mass and heat accumulation in the gas phase is negligible. (This includes the assumption for the quasi-steady state nature of the problem.)

Using the quasi-steady state approximation and neglecting diffusion and accumulation terms, the mass balance for the gas phase becomes

\[
\rho_g \mu_z \frac{\partial c_i}{\partial z} = \rho_g k_{m,i} [c_i(z) - c_{s,i}(z)] \tag{5}
\]

where \(c_i\) is a mean bulk value employed for the gas-phase concentration of each species and \(c_{s,i}\) the corresponding value at the solid–gas interface. Energy is transferred to and from the exhaust gas only due to convection with the channel walls (gas-phase energy balance):

\[
\rho_g c_p \mu_z \frac{\partial T_g}{\partial z} = hS[T_s(z) - T_g(z)] \tag{6}
\]

Similarly to the above, a mean bulk value \(T_s\) is used for the exhaust gas temperature, and a solid-phase temperature \(T_s\) is introduced for the monolith and the solid–gas interface. The parameter \(h\) is the heat transfer coefficient and is calculated as a function of the Nusselt number. Finally, the boundary conditions for the temperature, mass flowrate and concentrations are given from measurement at the converter’s inlet.

### 2.3 Reactor-level modelling

The reactor model presented in this work is a one-dimensional heat transfer model for the transient heat conduction in the monolith. Heat losses to the environment via convection and radiation are also taken into account. The model’s primary assumptions are the following.

The temperature field in the converter is described by the equation of transient heat conduction in one dimension, with heat sources being convection from the exhaust gas, the enthalpy released from the reactions and convection to ambient air:

\[
\rho_s c_p, s \frac{\partial T_s}{\partial t} = k_{s,z} \frac{\partial^2 T_s}{\partial z^2} + hS(T_g - T_s) + \sum_{k=1}^{N} (-\Delta H_k) r_k + Q_{\text{amb}} \tag{7}
\]

Finally, the boundary condition needed for the solution of the heat conduction equation refers to the heat losses to ambient air:

\[
Q_{\text{amb}} = S_{\text{mon}} [h_{\text{amb}}(T_s - T_{\text{amb}}) + \varepsilon \sigma (T_s^4 - T_{\text{amb}}^4)] \tag{8}
\]

The one-dimensional approximation of the converter neglects any non-uniformity of inlet flow profiles [20]. Two- or three-dimensional model versions exist [12]; however, it would be unrealistic to require such huge amount of input data (time series of inlet flow profiles) in order to predict the performance of a catalytic converter on a car.

For the formulation of the reaction scheme, two types of heterogeneous catalytic reaction are considered: redox reactions and oxygen storage reactions. The complete reaction scheme of the model, together with the rate expression for each reaction, is summarized in Table 2. The constants for the inhibition term are taken from references [19] and [21]. Below, the features of the reaction scheme are examined in some more detail.

Redox reactions take place on the precious metal loading of the washcoat (a combination of platinum (Pt) palladium (Pd) and rhodium (Rh) depending on the formulation) and involve oxidation of CO, H\(_2\) and a complex mixture of HC compounds in the exhaust gas, as well as reduction of nitrous oxides (NO\(_x\)) to N\(_2\). Oxygen storage reactions proceed on the ceria component of the washcoat, where three-valent cerium oxide (Ce\(_2\)O\(_3\)) is oxidized by O\(_2\) and also by NO (see also references [22] and [23]) to its four-valent counterpart (CeO\(_2\)). In turn, CeO\(_2\) is reduced by CO and HC to Ce\(_2\)O\(_3\).
In the present model, the oxidation reactions rates of CO and HC are based on the expressions obtained by Voltz et al. [24], which were originally developed for a Pt oxidation catalyst but, interestingly enough, they proved successful, with certain improvements made by other researchers [19, 21], in describing the performance of Pt : Rh, Pd, Pd : Rh and even trimetal catalyst wash-coats. Of course, a search for further improvements in the inhibition expressions and parameters can be undertaken in the future with the assistance of the genetic algorithm optimization tool described here. However, this will require dedicated high-accuracy experiments, and the improved expressions will be valid for the specific washcoats. The philosophy here is to fit the needs of the automotive manufacturer to the models of global validity and minimized requirement in specialized experiments.

Another simplification is made regarding the modelling of the HC reactions. In practice, flame ionization detector analysers measure only the total hydrocarbon content of the exhaust gas and make no distinction of the separate HC species. Therefore, for modelling purposes, the total HC content of the exhaust gas is divided into two broad categories: easily oxidized HC (‘fast’ HC), and less easily oxidized HC (‘slow’ HC). Throughout this work, it is assumed that the exhaust hydrocarbon consisted of 85 per cent fast HC and 15 per cent slow HC. This is a rough approximation introduced because of lack of more accurate data. According to our experience, it gives satisfactory results [9, 12]. The same practice has been employed by other researchers in the field. Both fast HC and slow HC are represented as CH$_{1.8}$, since the average ratio of hydrogen to carbon atoms in the exhaust gas is 1.8. Thus, the two HC compounds are distinguished in the model only by the difference in the kinetic parameters.

### 4 TUNING PROCEDURE

#### 4.1 General comments

The reaction rate expressions introduce into the catalytic converter model a set of parameters that has to be estimated with reference to a set of experimental data. In the present model, the set of tuneable parameters is formed by the pre-exponential factors $A_k$ that are included in the reaction rates $r_k$. Our objective is to fit them against experimental data from a routine driving cycle test.

In concept, the activation energy $E_k$ of each reaction and the set of terms $K_i$, included in the Voltz inhibition term $G$, may also be considered as tuneable parameters, but no attempts are made to tune them for simplicity and better control of the set of tuneable parameters. Indicative activation energy values for each reaction are known from previous experience and published work [19, 21, 24]. Their variation over different washcoat formulations is not very significant. Of course, here apparent kinetics and not real kinetics are being considered. Owing to the complexity of the reaction scheme and the characteristic range of conditions of the specific reactor, differences in apparent activation energies between different washcoats can be usually accommodated by the tuning of the pre-exponential factors reported above. Furthermore, the Voltz inhibition factor without modification in its term has been found to give consistently satisfactory results for a wide range of washcoats. Of course, there exists the possibility to tune activation energies together with the pre-exponential factors. This alternative has also been tested and the genetic algorithm usually resulted in values that are close to those originally known.

Additionally, the kinetic constants of H$_2$ oxidation are also not tuned in this work. The H$_2$ content of the exhaust gas is typically of the order of one-third of the CO content (due to the thermodynamics of the water–gas shift reaction in the exhaust gas [25]). It is not routinely measured in exhaust emissions testing. In this work the kinetics of H$_2$ oxidation are assumed to be equal to those of CO oxidation. A justification for this assumption is that in presence of CO the oxidation rate of hydrogen is inhibited by CO to approximately the same extent as the oxidation of CO itself [26]. Also, this practice was suggested from experience with computer-aided parameter estimation, where it was noticed that the genetic algorithm does not converge for the specific reaction. Thus, there are nine tuneable parameters in total, one for each reaction except for the reaction of H$_2$.

Since the problem of model tuning is a parameter-fitting problem, it may be tackled as an optimization problem. This involves the development of two components:

(a) a performance measure, which qualitatively assesses the goodness of fit of the model for each possible set of parameter values;
(b) an optimization procedure, which finds a set of tuneable parameters giving an optimum value for the performance measure, i.e. yields in modelling results that are as close to the measured results as possible.

The most usual performance measure used is based on the least-squares error between measured and computed instantaneous concentrations of pollutants at the converter’s outlet. Here, a new performance measure is modified that is more beneficial for optimization purposes and may also be used independently as an objective generic measure to compare the performance of different models.

The performance measure was optimized using a genetic algorithm, because previous experience has shown that the problem of model parameter estimation is multi-modal and the genetic algorithm is a powerful technique for multi-modal optimization. The genetic algorithm was
properly adapted to the problem at hand. The details of the performance measure and genetic algorithm formulation are presented below.

4.2 Formulation of the performance measure

The performance measure that is formulated below exploits information on the measurement of species concentrations at the inlet and the outlet of the catalytic converter. Specifically, it is based on the conversion efficiency \( E_i \) for a pollutant \( j \). Herein, the three legislated pollutants are taken into account; thus \( j = \text{CO}, \text{HC} \) or \( \text{NO}_x \).

To account for the goodness of computation results compared with a measurement that spans over a certain time horizon \( t \), an error \( e \) for each time instance must be defined. The latter should give the deviation between computation and measurement for the conversion efficiency \( E \). Summation over time should then be performed to calculate an overall error value for the whole extent of the measurement. Here, the error is defined as

\[
|e| = |E - \hat{E}|
\]  

(9)

Absolute values are taken to ensure error positiveness. This error definition also ensures that \( 0 \leq |e| \leq 1 \), since it is based on conversion efficiency.

The error between computation and measurement is a function of time and the tuneable parameter vector: \( e = e(t; \vartheta) \), where \( \vartheta \) is formed by the pre-exponential factor of each reaction of the model:

\[
\vartheta = [A_1, A_2, \ldots, A_{N_p}]^T
\]  

(10)

The performance function \( f(t; \vartheta) = f(e(t; \vartheta)) \) is a function of the error \( e \), which is subsequently summed over some time horizon \( t \) to give the performance measure \( F \). Here, the performance function is defined as

\[
f(t_n; \vartheta) = \frac{|e(t_n; \vartheta)|}{e_{\text{max}}(t_n)}
\]  

(11)

Time \( t \) take discrete values, \( t_n = n \Delta t \), with \( \Delta t \) being the discretization interval which corresponds to the frequency that data is measured. The quantity \( e_{\text{max}} \) is the maximum error between computation and measurement, and it is defined as

\[
e_{\text{max}}(t_n) = \max[\hat{E}(t_n), 1 - \hat{E}(t_n)]
\]  

(12)

The performance measure can be subsequently formed using some function of the sum of the performance function over time:

\[
F(\vartheta) = F\left(\sum_{n=0}^{N} f(t_n; \vartheta)\right), \quad N = \frac{t}{\Delta t}
\]  

(13)

In this work, the performance measure \( F \) is defined as the mean value of the performance function over the time period of interest:

\[
F(\vartheta) = \frac{1}{N} \sum_{n=0}^{N} f(t_n; \vartheta) = \frac{1}{N} \sum_{n=0}^{N} \frac{|e(t_n; \vartheta)|}{e_{\text{max}}(t_n)}
\]  

(14)

The performance measure defined in equation (13) is used for the assessment of the performance of each of the three pollutants \( \text{CO}, \text{HC} \) and \( \text{NO}_x \). The total performance measure is computed as the mean of these three values:

\[
F = \frac{F_{\text{CO}} + F_{\text{HC}} + F_{\text{NO}_x}}{3}
\]  

(15)

The above performance measure presents advantageous features compared with the classical least-squares performance measure:

1. It ranges between two, previously known finite extreme values. Extremes correspond to zero and maximum deviation between calculation and experiment.
2. The extrema of the performance measure are the same for all physical quantities that may be used and all different measurements where the performance measure may be applied; i.e. the performance measure is normalized so that its extrema do not depend on either the measured quantities or the experimental protocol.

It should be noted here that, because of the above properties, this performance measure may be used as a general measure to compare the model’s performance under different case studies or to compare alternative models for a single case study; i.e. it is a generic quantitative measure to assess the model’s performance. This should be contrasted with the usual practice for model assessment, which is simply based on inspection. Although a visualization procedure is necessary to gain insight to the model’s results, it is a subjective criterion. A least-squares performance measure, on the other hand, depends on the measurement at hand and is not helpful for comparison purposes. A normalized performance measure such as that defined above eliminates this problem and should provide more insight to model assessment.

From the optimization point of view, normalization of the performance measure is required because the total performance measure \( F \) is computed as the mean of \( F_{\text{CO}}, F_{\text{HC}} \) and \( F_{\text{NO}_x} \). If each of the individual performance measures was not normalized by definition, they would take values of different points of magnitude. Then, arbitrary scaling factors (weights) would be necessary before taking the average to compute \( F \). With the current performance measure definition, this is avoided.

4.3 Optimization procedure

Having defined the performance measure for the model, the problem of tuneable parameter estimation reduces in finding a tuneable parameter vector \( \vartheta \) that minimizes \( F \).
Owing to the multimodal character of the problem, a genetic algorithm has been employed for the task. Since genetic algorithms are maximization procedures, the problem is converted into a maximization problem for $F'$, defined as $F' = 1 - F$.

Summarizing the above, the mission of the genetic algorithm is to solve the following problem:

Maximize $F'(\mathbf{g}) = 1 - F(\mathbf{g})$

$$= \frac{1}{3N} \sum_{j=1}^{3} \sum_{i=1}^{3} \sum_{n=0}^{N} |e_j(t_n; \mathbf{g})|$$

This is a constraint maximization problem, since the components of the vector $\mathbf{g}$ are allowed to vary between two extreme values, i.e. $\mathbf{g}_{i,\text{min}} \leq \mathbf{g}_i \leq \mathbf{g}_{i,\text{max}}$.

The genetic algorithm is a kind of artificial evolution, where a population of solutions evolves similarly to nature’s paradigm: individual solutions are born, reproduce, are mutated and die in a stochastic fashion that is nevertheless biased in favour of the fittest individuals [27]. The implementation of the algorithm that has been developed in this work takes the following steps.

**Step 1: Initialization.** A set of points in the optimization space is chosen at random. This is the initial population of the genetic algorithm, with each point (each vector of tuneable parameters) corresponding to an individual of the population.

**Step 2: Fitness calculation.** The fitness of each individual in the population is computed using equation (16). It should be noted that the fitness calculation requires that the model be called for each individual, i.e. as many times as the population size.

**Step 3: Selection.** Random pairs of individuals are subject to tournament, i.e. mutual comparison of their fitnesses [28]. Tournament winners are promoted for recombination.

**Step 4: Recombination (mating).** The simulated binary crossover (SBX) operator [29] is applied to the couples of individuals that are selected for recombination (parents). The resulting chromosomes are inserted in the children population.

**Step 5: Mutation.** A small part of the population is randomly mutated; i.e. random parameters of the chromosomes change value in a random fashion [30].

**Step 6:** The original parent population is discarded; the children population becomes the parent population.

**Step 7:** Steps 3 to 6 are repeated for a fixed number of generations or until an acceptably fit individual has been produced.

Genetic algorithms are not black-box optimization techniques. On the contrary, a genetic algorithm should be adapted by the user to the target problem [28]. There are a number of design decisions and parameters that influence the operation, efficiency and speed of the genetic algorithm. The present implementation is summarized in Table 3. The genetic algorithm is a real-coded genetic algorithm and uses the SBX [29] for the mating and recombination of individuals.

The SBX operator works directly on the real-parameter vector that represents each individual, thus eliminating the need for a real-to-binary encoding–decoding required in binary encoded genetic algorithm. The SBX operator also works on arbitrary precision, which should be contrasted with the finite precision of binary encodings.

The randomized nature of the genetic algorithm enables it to avoid local extrema of the parameter space and converge towards the optimum or a near-optimum solution. It should be noted, however, that this feature does not guarantee convergence to the global optimum. This behaviour is common to all multimodal optimization techniques and not a specific genetic algorithm characteristic.

The above-described genetic algorithm optimization procedure forms the basis of software with the general flow chart in Fig. 1.

### 5 Application Case Study

The validity of the approach that is described above is assessed in a real-world application case. Manual tuning of the model is originally performed, and the results are subsequently compared with the identification results produced by the genetic algorithm. It is found that the genetic algorithm manages to find a set of tuneable parameters that fits the experimental data with much higher accuracy than the manual efforts. In order to check the useability of the genetic-algorithm-tuned model, it is applied to a second set of driving cycle data, obtained with a catalyst with significantly reduced size. It is found that the model is able to predict the efficiency of the second catalyst successfully.

Specifically, in this application example, a set of measurements of emissions upstream and downstream of a Pt:Rh (5:1) catalyst installed on a 1.8 l gasoline engine, tested according to a simulated new European driving cycle (NEDC) test on the computer-controlled engine bench, is employed. The washcoat thickness is about 50 μm. The precious metal loading is 50 g/ft². The

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**Table 3 Parameters of the genetic algorithm**

<table>
<thead>
<tr>
<th>Encoding type</th>
<th>Real parameter encoding</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algorithm type</td>
<td>Generational</td>
</tr>
<tr>
<td>Selection scheme</td>
<td>Deterministic tournament</td>
</tr>
<tr>
<td>Crossover operator</td>
<td>(SBX)</td>
</tr>
<tr>
<td>Mutation operator</td>
<td>Random mutation</td>
</tr>
<tr>
<td>Population size</td>
<td>100</td>
</tr>
<tr>
<td>Crossover probability</td>
<td>0.6</td>
</tr>
<tr>
<td>Mutation probability</td>
<td>0.02</td>
</tr>
<tr>
<td>Parameter range</td>
<td>$10^5 &lt; A &lt; 10^{25}$</td>
</tr>
</tbody>
</table>
catalytic converter has a circular cross-section of 127 mm diameter and it consists of two beds with a total length of 203 mm. CO, HC NOx, O₂ and CO₂ analysers measure the exhaust gas content upstream and downstream of the catalyst. Data acquisition is made at 1 Hz frequency and the analysers’ response time constants range from 0.1 to 0.5 s. Figure 2 presents an overview of the emissions measurements set-up.

Figure 3 presents a summary of the measured results after preprocessing with the data consistence and error checking routines [31]. Evidently, the catalytic converter light-off occurs at about 50 s after the beginning of the measurement. After light-off, and up to about 800 s, emissions are almost zeroed. The first 800 s correspond to the urban phase of the driving cycle. During this phase, only few emission breakthroughs occur. Comparatively more pollutants are emitted in the period from 800 to 1180 s (which corresponds to the extra-urban phase of the NEDC), because of the higher space velocity of the exhaust gas.

It is important to note that, because of the very low emission standards, it does not suffice to predict the light-off point of the catalyst. Increased accuracy is demanded during the whole extent of the cycle test. The low levels of concentrations at the catalyst exit, compared with the corresponding concentrations at the inlet, further complicate the undertaking. Its success is thus heavily dependent on both the careful model formulation and the accurate tuneable parameter identification.

Proceeding to the model identification, Table 4 presents the set of kinetics parameters of the model and their values tuned manually and by the genetic algorithm. In principle, the kinetic parameters are 21 in total: one parameter for the oxygen storage capacity, and ten pairs of parameters A and E for the 10 reactions incorporated in the reaction scheme.

As previously discussed, not all kinetic parameters are tuned. The activation energies are more or less known from previous experience [21]. They could be varied a little, but this is not necessary since the rate depends on both A and E and any small difference can be compensated by respective modification of A. The oxygen storage capacity is also not tuned, since its approximate magnitude is estimated on the basis of the washcoat composition (Ce and Zr) [32] and is also checked by its emptying behaviour at characteristic parts of the cycle.

Finally, the H₂ oxidation kinetics are assumed to be approximately equal to those of CO oxidation. Thus, nine pre-exponential factors are left to be tuned: four reactions of gaseous phase species on the Pt surface, and another five reactions on the ceria–zirconia components of the washcoat. The manual tuning that was initially performed gives the results that are illustrated in Figs 4 and 5. Manual tuning was performed following a trial-and-error procedure and was mainly aided by previous experience with similar catalysts. Figure 4 gives the cumulative emissions for all pollutants. Although the computed total mass of pollutants matches the measurements, at least regarding CO and NO, the computation loses accuracy in several parts of the cycle. For example, the error in the prediction of cumulative CO emissions.
in Fig. 4 approaches 20 per cent at about 800 s from start. Much higher errors are reported in the prediction of instantaneous emissions. For example, error in the prediction of instantaneous CO emissions (Fig. 5) sometimes exceeds 500 per cent. The situation presented in Fig. 5 can be described as some kind of qualitative fit of the computed instantaneous CO concentrations at the converter’s outlet.

The model’s accuracy concerning instantaneous emissions is significantly improved when the model is fitted using the genetic algorithm. The comparison of computed versus measured cumulative emissions is illustrated in Fig. 6. The form of the curves for all three pollutants matches the measured data much more closely (maximum error in cumulative emissions is of the order of 5 per cent, which indicates that also the instantaneous emissions of the model are fitted with good accuracy. This becomes obvious in the comparison of computed and measured instantaneous emissions for CO, HC and NOx in Figs 7, 8 and 9 respectively. Here it could be also said that there is a good quantitative fit of the instantaneous emissions in a real cycle. Maximum error can reach even 100 per cent in certain cases (e.g. HC emissions between 800 and 1050 s in Fig. 8), but these are exceptions that hint at specific problems (possibly with the storage submodel and the data quality), to be investigated in the future.

It must be noted that the fit of the model is more successful for the CO and HC curves than for the NOx curve. This is mainly attributed to the Voltz inhibition

Table 4 Values of activation energy, tuneable pre-exponential factors (manual estimates versus values determined by the genetic algorithm) and oxygen storage capacity value inserted in the model

<table>
<thead>
<tr>
<th>Reaction number</th>
<th>Reaction</th>
<th>( E ) (fixed value)</th>
<th>Manual tuning</th>
<th>Genetic tuning</th>
<th>( \psi^{\text{cap}} ) (fixed value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( \text{CO} + 0.5\text{O}_2 \rightarrow \text{CO}_2 )</td>
<td>90 000</td>
<td>( 1 \times 10^{19} )</td>
<td>( 4.89 \times 10^{20} )</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \text{H}_2 + 0.5\text{O}_2 \rightarrow \text{H}_2\text{O} )</td>
<td>90 000</td>
<td>( 1 \times 10^{19} )</td>
<td>( 4.89 \times 10^{20} )</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>( \text{CH}_4\text{(fast)} + 1.45\text{O}_2 \rightarrow \text{CO}_2 + 0.9\text{H}_2\text{O} )</td>
<td>95 000</td>
<td>( 2 \times 10^{19} )</td>
<td>( 3.61 \times 10^{20} )</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>( \text{CH}_4\text{(slow)} + 1.45\text{O}_2 \rightarrow \text{CO}_2 + 0.9\text{H}_2\text{O} )</td>
<td>120 000</td>
<td>( 5 \times 10^{19} )</td>
<td>( 1.83 \times 10^{21} )</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>( 2\text{CO} + 2\text{NO} \rightarrow 2\text{CO}_2 + \text{N}_2 )</td>
<td>90 000</td>
<td>( 4 \times 10^{14} )</td>
<td>( 1.54 \times 10^{17} )</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>( \text{Ce}_2\text{O}_3 + 0.5\text{O}_2 \rightarrow 2\text{CeO}_2 )</td>
<td>90 000</td>
<td>( 2 \times 10^{10} )</td>
<td>( 2.94 \times 10^{19} )</td>
<td>600</td>
</tr>
<tr>
<td>7</td>
<td>( \text{Ce}_2\text{O}_3 + \text{NO} \rightarrow 2\text{CeO}_2 + 0.5\text{N}_2 )</td>
<td>90 000</td>
<td>( 3 \times 10^{10} )</td>
<td>( 4.68 \times 10^{19} )</td>
<td>600</td>
</tr>
<tr>
<td>8</td>
<td>( 2\text{Ce}_2\text{O}_3 + \text{CO} \rightarrow 2\text{CeO}_2 + \text{CO}_2 )</td>
<td>85 000</td>
<td>( 2 \times 10^{10} )</td>
<td>( 7.85 \times 10^{19} )</td>
<td>600</td>
</tr>
<tr>
<td>9</td>
<td>( \text{CH}_4\text{(fast)} + 3.8\text{CeO}_2 \rightarrow 1.9\text{Ce}_2\text{O}_3 + \text{CO}_2 + 0.9\text{H}_2\text{O} )</td>
<td>85 000</td>
<td>( 9 \times 10^{10} )</td>
<td>( 1.35 \times 10^{20} )</td>
<td>600</td>
</tr>
<tr>
<td>10</td>
<td>( \text{CH}_4\text{(slow)} + 3.8\text{CeO}_2 \rightarrow 1.9\text{Ce}_2\text{O}_3 + \text{CO}_2 + 0.9\text{H}_2\text{O} )</td>
<td>85 000</td>
<td>( 1 \times 10^{10} )</td>
<td>( 2.43 \times 10^{19} )</td>
<td>600</td>
</tr>
</tbody>
</table>
Fig. 4  Manual tuning: comparison of computed versus measured cumulative emissions for CO, HC and NO\textsubscript{x} (full-size converter)

The evolution of the genetic algorithm population of solutions is indicative of the problem difficulty and explains the limited success of manual tuning or tuning that uses gradient-based methods. To illustrate the evolution process, a graph of the evolution of maximum and average fitness of the population is presented in Fig. 10. The genetic algorithm quickly improves the maximum performance measure solution at the beginning of the run. Then, evolution is slower and, after some point, it completely stalls. This indicates that the genetic algorithm
population has converged to a specific attraction basin of the optimization space and not much improvement may be achieved. At this point, the algorithm is stopped. The specific computation required about 72 h on a 2.4 GHz Pentium 4 computer.

It may be noted that the absolute value of the performance measure does not vary much during the genetic algorithm run. This is a property of the performance measure formulation but also indicates the multimodality of the problem, since it appears that many combinations of kinetic parameters lead to the same overall performance of the model.

The spreads of individuals in the 20th, the 45th and the last (135th) generation are given in Figs 11, 12 and 13 respectively. The individuals are sorted in descending order according to their performance measure.

Figure 11 visualizes the spread of the kinetic parameters in the population of the genetic algorithm near the beginning of the procedure. The kinetic parameters are allowed to vary in certain intervals that are induced on the basis of previous experience and are consistent with their physical role in the respective reactions. The different kinetic parameters pertaining to reactions that occur on the three distinct catalytic components of the
washcoat (in our example, Pt, Rh and Ce) fall in three distinct intervals.

Figure 12 gives the spread of individual solutions in the 45th generation of the population. Apparently, the population has started to converge for the pre-exponential factors of some reactions. This indicates that the kinetics of these reactions influence the quality of the model fit (and thus the performance measure value) much more significantly than the rest of the reactions.

Figure 13 presents the last population of the genetic algorithm run. It is evident that the parameters for the oxidation of slow HC with oxygen on Pt or with stored oxygen do not converge, whereas the rest of the parameters show clear signs of convergence. This could be attributed to the fact that the slow HC are only 15 percent of the total HC content and thus influence the total HC efficiency of the catalyst much less than the fast HC. The same absence of convergence is noticed for the kinetics of CO + NO reaction, whereas the complementary reaction of ceria + NO shows clear signs of convergence. This fact suggests a lack of sensitivity of the model regarding the above three reactions. It should not be deduced at this early investigation point that these reactions are less important than the rest to the model’s
accuracy and predictive ability. Experience shows that further reduction in the number of reactions leads to an observable deterioration of the model-fitting ability.

For comparison purposes, the best set of kinetic parameters values derived in the three characteristic generations of the genetic algorithm evolution is presented, together with the manually derived set, in Fig. 14.

The above discussion should make apparent that the parameter identification methodology developed gives significant feedback also to the reaction modelling. This is a subject of continuing investigation.

As a next step in the evaluation of the parameter identification methodology, the kinetic parameters derived by the genetic algorithm for the full-scale converter are applied in the prediction of the behaviour of a reduced size converter with the same washcoat formulation and loading. This is a demanding exercise for any model of this type. The model’s prediction is checked against experimental results obtained with a cylindrical converter of 120 mm diameter and 60 mm length. The results are presented in Fig. 15 in the form of cumulative CO, HC and NO\textsubscript{x} emissions.

The results, which are considered good with the exception of HC emissions, are indicative of the predictive ability of the one-dimensional model for typical quality test data. To check further the model’s performance regarding HC, the computed instantaneous

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**Fig. 10** Evolution of the genetic algorithm: maximum and average population fitness during the first 135 generations

**Fig. 11** Spread of genetic algorithm population at the 20th generation (HC\textsubscript{f}, HC\textsubscript{fast}; HCs, HC\textsubscript{slow})
HC emissions are compared with the experimental values in Fig. 16. A certain degree of discrepancy is observed, which could be attributed to the enhanced three-dimensional effects introduced by the very small length-to-diameter ratio of the reduced-size catalytic converter. Overall, it should be stressed that the model prediction continues to stay close to the experimental data, both qualitatively and quantitatively, which further supports the validity of the kinetic model approach.

6 CONCLUSIONS

1. A genetic algorithm methodology was developed for the identification of the kinetic submodel of a previously developed three-way catalytic converter model. This is a one-dimensional model for the heat and mass transfer in the catalytic converter that features a reduced kinetics scheme.

2. This scheme involves rate expressions which contain a limited number of apparent kinetic parameters that may be viewed as fitting parameters. Their values are identified in order to fit a set of experimental data that represents the behaviour of the specific washcoat formulation over a typical test procedure.

3. In this paper, a complete identification methodology for the above problem is formulated in two steps. Firstly, a performance measure is defined that is suitable for the assessment of the model’s performance in fitting the data. Secondly, a genetic algorithm is
Fig. 14 Comparison of manually derived kinetics and kinetics identified at the 20th, 45th and 135th generations of the genetic algorithm run

Fig. 15 Application of the kinetic parameters identified by the genetic algorithm for the full-size converter, to predict the behaviour of the reduced-size converter: comparison of computed versus measured cumulative emissions for CO, HC and NOx.

employed that uses the performance measure as an objective function. The genetic algorithm searches the parameter space to find the optimal set of parameters producing the best fit to the data.

4. The identification methodology is tested on a characteristic case study, and the best-fit parameters produced demonstrate a high accuracy in matching the test data describing the behaviour of a specific catalyst installed on a 1.8 l passenger car engine tested according to the NEDC procedure. The results are far more accurate than those that may be obtained by manual or gradient-based tuning of the parameters, because the search space is highly multi-modal, which causes non-stochastic search procedures to become trapped to local optima.

5. Moreover, the set of parameters identified by the genetic algorithm methodology is found to describe in a valid way the chemical kinetic behaviour of the specific catalyst. This is confirmed by applying the specific set of kinetic parameters to predict the behaviour of a reduced-size converter with the same catalyst formulation. The prediction accuracy is remarkable if the statistical variation in the performance of such a complex system is taken into account.
6. The parameter estimation methodology developed is completing a previously developed systematic computer aided engineering methodology assisting the design optimization of catalytic exhaust systems.

REFERENCES


13 CATRAN Catalytic Converter Modeling Software. User’s Guide. Version 1.4r2, December 2002 (Laboratory of Thermodynamics and Thermal Engines (LTTE), University of Thessaly, Volos).


