Mathematical modelling of catalytic exhaust systems for EURO-3 and EURO-4 emissions standards

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Abstract: The application of computer simulation in the development of catalytic exhaust aftertreatment systems for cars is over thirty years old. However, ever-increasingly stringent exhaust emissions legislation requires an ever-increasing degree of accuracy and complexity in the mathematical models applied. Traditionally, the Langmuir–Hinshelwood kinetics were applied in the majority of the models available, with a small number of representative chemical reactions. In this paper it is proved, by means of typical case studies, that the above modelling approach, with the necessary refining, can be brought to the level of accurately predicting the behaviour of advanced catalyst systems employed in EURO-3 and EURO-4 emissions homologation. An essential characteristic that was introduced to this end is the computer-aided selection (best fit) of the tunable parameters representing the apparent chemical kinetics and oxygen storage and release properties of each different catalyst–washcoat combination. Other modelling improvements are also discussed in the present paper, setting the scene for high accuracy simulations in view of the current and future emissions standards for spark-ignited, diesel and gasoline direct injection (GDI)-engined vehicles. These include the modelling of the aged catalyst, as well as taking into account the effect of precious metal loading variation on the apparent kinetics.

Keywords: automotive exhaust emissions, emissions standards, three-way catalytic converters, mathematical modelling, parameter estimation

NOTATION

\[ r \] radial distance from monolith’s axis (m)  
\[ r_k \] rate of reaction \( k \) (mol/m\(^3\) s)  
\[ P \] computed response  
\[ P_m \] measured response  
\[ R \] reaction rate (m/s)  
\[ R_g \] universal gas constant \( = 8.314 \text{ J/mol K} \)  
\[ S \] geometric specific surface (m\(^2\)/m\(^3\))  
\[ t \] time (s)  
\[ T \] temperature (K)  
\[ u_z \] exhaust gas velocity (m/s)  
\[ w \] weight factor  
\[ x \] concentration in the gas phase  
\[ x_s \] concentration in the gas phase at solid–gas interface  
\[ z \] distance from the monolith inlet (m)  
\[ \alpha \] number of carbon atoms in hydrocarbon molecule  
\[ \beta \] number of hydrogen atoms in hydrogen molecule  
\[ \varepsilon \] emissivity factor (radiation)  
\[ \theta \] tunable parameters vector  
\[ \sigma \] Stefan–Boltzmann constant (W/m\(^2\) K\(^4\))  
\[ \tau \] duration of an experiment [equation (2)] (s)  
\[ q \] transformed tunable parameter vector

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Subscripts

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
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<tbody>
<tr>
<td>g</td>
<td>gas</td>
</tr>
<tr>
<td>( j )</td>
<td>species ( j )</td>
</tr>
<tr>
<td>( k )</td>
<td>reaction ( k )</td>
</tr>
<tr>
<td>( r )</td>
<td>radial direction</td>
</tr>
<tr>
<td>( s )</td>
<td>1, solid; 2, solid–gas interface</td>
</tr>
<tr>
<td>( z )</td>
<td>axial direction</td>
</tr>
</tbody>
</table>

1 INTRODUCTION

Since the introduction of automotive emission standards in the USA and Europe, legislation is becoming increasingly stringent, following the ever-increasing need to control automobile air pollution in urban areas. This trend requires the manufacturers of exhaust systems to improve their components and systems design constantly in order to conform to the emissions standards. Mathematical modelling of the various parts and components of an exhaust system is usually employed as a tool for efficient system design and development. Of foremost importance is the modelling of the catalytic converter, the latter being the most crucial part of the exhaust system with regard to the emissions behaviour.

As emission standards diminish the allowable CO, HC and NO\(_x\) tailpipe emissions, catalytic converter technology is pushed to its limits and the gap between feasible and legislated emission levels narrows. Increased accuracy of mathematical modelling is therefore needed, in order to enable reliable prediction of the catalyst’s efficiency. Through the years, many models have appeared in the literature; focusing, with varying detail or complexity, on the physical and chemical phenomena involved in catalytic converter operation.

Early modelling work concentrated mainly on the heat and mass transfer phenomena in the catalytic converter. The models basically aimed to predict the point that the catalyst’s light-off occurs. Therefore, only simplified oxidation reaction schemes were incorporated in these models. Young and Finlayson [1] developed a two-dimensional channel model for a monolith and discussed in detail the applicability of the quasi-static assumption for the gas phase or transient catalyst operation. Heck et al. [2] showed that a one-dimensional model is adequate for the prediction of monolith behaviour. Chen et al. [3] presented a three-dimensional model of monolithic catalytic converters, again including only oxidation reactions.

The introduction of EURO-1 emission standards motivated the inclusion of more complicated reaction schemes in the models. Pattas et al. [4] were the first to provide a comparison between measurement and computation for a three-way catalytic converter (3WCC) under driving cycle operating conditions. Their model featured an early form of an oxygen storage submodel.

Later, Siemund et al. [5] published a well-documented 3WCC model based on the kinetics of Voltz et al. [6] for the oxidation reactions and on that of Subramanian and Varma [7] for NO reduction kinetics and compared it with engine bench experiments. This model lacked an oxygen storage submodel, however, and this was also true for the subsequent model of Dubien et al. [8]. At this stage of development, it was adequate for the models to predict cumulative driving cycle emissions satisfactorily, even if they failed to simulate instantaneous emissions within an acceptable level of accuracy [9].

Exhaust system design for EURO-2 emission standards called for more accurate model predictions. Focus was shifted to the instantaneous emissions of the catalytic converter, especially regarding the CO and hydrocarbons (HCs). NO\(_x\) emissions continued to be difficult to model. The two-dimensional model presented by Koltaksis et al. [10, 11], featuring an oxygen storage submodel and incorporating steam-reforming reactions, was linked to a transient heat transfer model for the exhaust manifold and piping [12]. This was the first time that a unified computer-aided engineering methodology [13–15] had been targeted to the design and optimization of exhaust systems comprising exhaust piping, start and main catalysts, as well as possible catalyst fast light-off techniques [16].

Regardless of the particular model or catalytic converter under study, a reaction rate must be provided for every reaction taken into account in the model. All the above-mentioned models are lumped-parameter models that employ rate expressions based on the Langmuir–Hinselwood formalism. This approach lumps into the tunable parameters all phenomena (washcoat formulation, catalyst ageing and deactivation, inhibition effects, etc.) that are not explicitly taken into account by the model.

Practically, in order to assess and model the behaviour of a catalytic converter, only the pre-exponential factor \( A \) and the activation energy \( E \) of the rate expression are tuned. For the inhibition terms, expressions from the literature are used without or with minor modifications. Although this greatly simplifies the problem of parameter estimation, it is still difficult to tune the model reliably. Moreover, the model’s tunable parameters must be estimated using data from an engine bench test or a driving cycle test. Synthetic gas bench experiments are useful for the preliminary assessment of a catalyst but cannot be used to simulate a catalyst’s operation under realistic conditions, owing to the complexity of the real exhaust gas. Thus, the reactions cannot be decoupled and it is necessary to tune for all parameters simultaneously.

The situation is further complicated for the case of the 3WCC, because there is not enough experience either with the CO–NO reaction or with oxygen storage modelling [10, 11]. Although the effects of different rate expressions for CO and HC oxidation reactions have
been reported in the literature [17], no such comparisons have been published for the CO–NO reaction. The oxygen concentration of the exhaust gas mixture constantly fluctuates around stoichiometry, and the CO–NO reaction is strongly dependent on this behaviour, making the determination of a successful rate expression even more difficult. Similarly, the correct estimation of the oxygen storage submodel is crucial for successful modelling, and only a few quantitative works have been published.

Today, EURO-3 level emission standards have to be met, posing a new challenge for catalytic converter modelling. Good prediction of instantaneous emissions, including NO\textsubscript{x}, is necessary if the model is to be exploited in modern exhaust system design optimization. Therefore, parameter estimation has to be done more precisely, and the need for a well-defined procedure for parameter estimation is emerging. To achieve this, computer-aided parameter estimation is desirable, possibly coupled with customized engine bench tests.

EURO-4 emission standards will probably render the above methodologies absolutely necessary. Moreover, for the efficient utilization of modelling in exhaust systems design, even more complicated issues must be addressed, such as catalyst ageing and deactivation and the effect of precious metal loading.

In this work, an attempt is made to address the problem of precise model tuning, in view of the EURO-3 legislation, now effective in Europe. Focus is laid on the prediction of NO\textsubscript{x} emissions, which is the weak point of most 3WCC models. Tuning of the model parameters is done directly on the basis of the measured results in an FTP-75 test. To perform the tuning, a conjugate gradients optimization scheme is employed, aiming at minimization of the error between computation and measurement. A comparison of the simulation results with the corresponding results of the manual tuning procedure is discussed and some plausible explanations are attempted for the observed differences.

## 2 MODEL DESCRIPTION

### 2.1 Modelling of physical and chemical phenomena

The 3WCC model employed in this work is a one-dimensional, single-channel model [11]. Models of this type are widely employed today in the design of automotive exhaust aftertreatment systems. This includes 3WCC, diesel oxidation catalysts, NO\textsubscript{x} traps or even diesel particulate filters.

The physical phenomena (heat and mass transfer in both gaseous and solid phases) are described by a system of balance equations. A detailed presentation of the system of equations has been given elsewhere [10, 11, 14]. Here, they are summarized in Table 1. The present work focuses on the reaction scheme for the 3WCC.

A limited number of apparent kinetic rate expressions have appeared in the literature for this type of reactor. Probably the most acclaimed kinetics are those determined by Voltz et al. [6] for the oxidation of CO and HCs on pellet-type Pt catalysts. They have been successfully used for the modelling of monolithic catalytic

### Table 1  Model equations and tunable parameters

<table>
<thead>
<tr>
<th>Model equations</th>
<th>Tunable parameters</th>
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<tbody>
<tr>
<td><strong>Mass transfer</strong></td>
<td></td>
</tr>
<tr>
<td>Balance equation</td>
<td>$\rho_k \frac{\partial X_j}{\partial t} + \rho_k u_j \frac{\partial X_j}{\partial z} = \rho_k k_{n,j} S(x_j - x_{s,j})$</td>
</tr>
<tr>
<td>Boundary condition</td>
<td>$\frac{\rho_k}{M_k} k_{n,j} S(x_j - x_{s,j}) = R_j$</td>
</tr>
<tr>
<td><strong>Heat transfer</strong></td>
<td></td>
</tr>
<tr>
<td>Balance equation (gas phase)</td>
<td>$\rho_s c_p u_j \frac{\partial T_j}{\partial z} = hS(T_j - T_s)$</td>
</tr>
<tr>
<td>Balance equation (solid phase)</td>
<td>$\rho_s c_p, k_{n,j} S \frac{\partial T_j}{\partial t} + k_{n,j} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T_j}{\partial r} \right) + hS(T_j - T_s) + \sum_{k=1}^{N_R} (-\Delta H_k) r_k$</td>
</tr>
<tr>
<td>Boundary conditions</td>
<td>$k_r \frac{\partial T_s}{\partial r} = h_{amb}(T_s - T_{amb}) + \epsilon \alpha (T_s - T_{amb})$, at $r = R_{mon}$</td>
</tr>
<tr>
<td>Reactions</td>
<td></td>
</tr>
<tr>
<td>Reaction rates</td>
<td>$R_j = \sum_{k=1}^{N_R} a_{j,k} r_k$, $r_{rea,k} = \frac{A_x e^{-E_k/k_B T_s X_s X_B}}{G_1}$</td>
</tr>
</tbody>
</table>
converters with more complicated washcoat formulations. For the 3WCC, Subramanian and Varma [7] provided the first expression for the CO–NO reaction. Pattas et al. [4] also mention an empirical rate expression for the CO–NO reaction, with variable order of reaction. Montreuil et al. [18] also presented an extended reaction scheme for the modelling of Pt–Rh and Pd–Rh catalysts.

In the present model, the oxidation reaction rates of CO, H2 and HCs are based on the expressions by Voltz et al. [6]. Two HC species are accounted for in the reaction scheme, because the real exhaust gas contains a very complicated mixture of hydrocarbons. Every hydrocarbon species is oxidized at a different temperature. In practice, the diversity of the HC mixture is usually taken into account by considering two kinds of HCs being present in the exhaust gas, an easily oxidizing HC ('fast' HC), and a less easily oxidizing HC ('slow' HC) [10]. This practice usually allows for sufficient degrees of freedom to simulate real exhaust behaviour. Hydrogen oxidation is also included in the model, because of its significant exothermy. CO, H2 and HC oxidation reactions along with their rate expressions are given in Table 2.

Most catalysts contain an oxygen storage component in their washcoat, i.e. a component that can undergo successive reductions and oxidations, depending on the prevailing conditions in the gas–catalyst interface. The most important component that plays such a role is ceria, usually combined with zirconia. Under net oxidizing conditions, three-valent Ce oxide (Ce2O3) may react with O2, NO or H2O and oxidize to its four-valent state (CeO2). Under net reducing conditions, CeO2 may function as an oxidizing agent for CO, HC and H2. The model allows for Ce2O3 oxidation by O2 and CeO2 reduction by CO and HCs (reactions 5, 6 and 7 in Table 2). The auxiliary quantity ψ along with its rate of variation, which is also defined in Table 2, express the fractional extent of oxidation of the oxygen storage component.

### Table 2 Reaction scheme and rate expressions

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidation reactions</td>
<td>$r_1 = \frac{A_1 \exp(-E_1/R_T \cdot T \cdot \alpha \cdot CO \cdot V \cdot O_2)}{G}$</td>
</tr>
<tr>
<td>1 CO + 1/2 O2 → CO2</td>
<td>$r_2 = \frac{A_2 \exp(-E_2/R_T \cdot T \cdot \beta \cdot O_2)}{G}$</td>
</tr>
<tr>
<td>2 H2 + 1/2 O2 → H2O</td>
<td>$r_3 = \frac{A_3 \exp(-E_3/R_T \cdot T \cdot \gamma \cdot CO \cdot V \cdot O_2)}{G}$, $k = 3, 4$</td>
</tr>
<tr>
<td>Oxygen storage</td>
<td>$r_5 = A_5 \exp(-E_5/R_T \cdot T \cdot \delta \cdot NO \cdot \frac{1}{V \cdot O_2})$</td>
</tr>
<tr>
<td>5 Ce2O3 + 1/2 O2 → 2CeO2</td>
<td>$r_6 = A_6 \exp(-E_6/R_T \cdot T \cdot \epsilon \cdot NO \cdot \delta \cdot \frac{1}{V \cdot O_2})$</td>
</tr>
<tr>
<td>6 2CeO2 + CO → Ce2O4 + CO2</td>
<td>$r_7 = A_7 \exp(-E_7/R_T \cdot T \cdot \zeta \cdot CO \cdot V \cdot O_2)$</td>
</tr>
<tr>
<td>7 CuH3 + (α + 0.25β)O2 → αCO2 + 0.5βH2O</td>
<td>$r_8 = A_8 \exp(-E_8/R_T \cdot T \cdot \beta \cdot NO \cdot \delta \cdot \frac{1}{V \cdot O_2})$</td>
</tr>
<tr>
<td>NO reduction and steam reforming</td>
<td>$r_9 = A_9 \exp(-E_9/R_T \cdot T \cdot \alpha \cdot CO \cdot V \cdot O_2)$</td>
</tr>
<tr>
<td>8 2CO + 2NO → 2CO2 + N2</td>
<td>$r_{10} = A_{10} \exp(-E_{10}/R_T \cdot T \cdot \alpha \cdot CO \cdot V \cdot O_2)$</td>
</tr>
<tr>
<td>Auxiliary quantities</td>
<td>$\psi = \frac{2 \times \text{moles CeO}_2}{2 \times \text{moles CeO}_2 + \text{moles Ce}<em>2\text{O}<em>3}$, $\frac{d\psi}{dt} = - \frac{r_5}{\psi</em>{\text{cap}}} + \frac{r_6}{\psi</em>{\text{cap}}}$</td>
</tr>
<tr>
<td>Inhibition term</td>
<td>$E_{\text{cap}} = \frac{X_{\text{CO}} \cdot \alpha \cdot V \cdot O_2}{X_{\text{CeO}<em>2} \cdot \psi</em>{\text{cap}} \cdot K_{\gamma}(T)}$, if $E_{\text{cap}} &gt; 1$ then $r_3 = 0$</td>
</tr>
</tbody>
</table>
The reduction of NO is mainly accomplished via reaction with CO, although other species may contribute to NO conversion (e.g. H$_2$ or HCs). In this work, the reaction between CO and NO is modelled using an empirical reaction rate adopted from Pattas et al. [4], which predicts a variable order of reaction for the CO oxidation from NO, depending on CO concentration. The expression is qualitatively consistent with the results of Koberstein and Wannemacher [19], which predict that the reaction order for CO in the CO–NO reaction tends to unity as the reactants’ concentrations tend to vanish.

The high HC conversion efficiency observed in fresh catalysts during operation in rich conditions has been attributed to the steam-reforming reaction [20]. This reaction, also promoted by CeO$_2$, generates H$_2$ which may reduce NO to N$_2$ [21]. Thus, steam reforming for the hydrocarbons should also be incorporated in the model (reactions 9 and 10 of Table 2). In the rate expression for the steam-reforming reaction, the same inhibition factor as in the oxidation reactions is used, because of the absence of further kinetic data. A factor $E_q$ is introduced into the rate expression to allow for the chemical equilibrium of the steam-reforming reaction. A detailed discussion of the solution procedure and the model kinetics is given in reference [22].

### 2.2 Tunable parameters

As is evident from Table 1, the heat and mass transfer balance equations do not contain any tunable parameters. All tunable parameters are introduced by the chemical description of the catalyst, because this type of modelling relies on simplified rate expressions for apparent chemical kinetics.

The parameters of the inhibition term $G$ are also not allowed to vary. Instead, the values specified in the work of Voltz et al. [6] are used and are given in Table 2. Thus, every reaction $j$ introduces only two tunable parameters, its pre-exponential factor $A_j$ and its activation energy $E_j$. It must be noted that the H$_2$ oxidation is not tuned. The values for $A_2$ and $E_2$ are set equal to those for CO oxidation ($A_1$ and $E_1$, respectively).

As a general remark, it may be stated that the number of tunable parameters is kept to the minimum figure that is capable of supplying the degrees of freedom recognized in real-world catalytic converter operation.

### 3 MODEL TUNING

#### 3.1 Current tuning practice

Although lumped-parameter models have been extensively used for the prediction of catalytic converter efficiency, not much work has been done on correct tunable parameter estimation. The usual practice has been the manual tuning of the parameters, using a starting point suggested by previous experience and adjusting the pre-exponential factor of each reaction and, to a lesser extent, the activation energy.

Montreuil et al. [18] were the first to present a systematic attempt for the tuning of the parameters of their steady state 3WCC model. They proceeded with a compilation of an experimental database of steady state efficiencies for two catalyst formulations. Then, they fitted the parameters of their model against these data. In their work, they adjusted not only the pre-exponential factor and activation energy terms but tunable parameters contained in the inhibition terms as well.

Dubien and Schweich [23] also published a methodology to determine the pre-exponential factor and the activation energy of simple rate expressions from light-off experiments. They provided an initial estimation of the tunable parameters using theoretical calculations. Their approach was successful but of limited practical value, because it was applicable only to non-competing reactions. Thus, the methodology reported could not be used for the parameter estimation of a realistic reaction scheme using data from engine exhaust gas emissions measurements.

In this work, tuning of the 3WCC model was based on the results of an FTP 75 test (mainly bag 1 emissions). The procedure followed in order to tune the model is detailed below. Then, the simulation results are presented and compared with previous manual tuning results.

#### 3.2 Formulation of the optimization problem

In order to tune the parameters of the model, one or more different experiments or tests available may be employed. Moreover, for each experiment or test, there are usually multiple measurements (responses), e.g. measurements of various species’ concentrations at the catalyst’s outlet, temperature at several points of the monolithic converter, etc. Model tuning requires the estimation of all tunable parameters in order to minimize the error between available measurements and the computations.

Thus, a performance measure has to be defined which assesses the quality of the parameter estimation, i.e. it assesses the error between measured and computed responses. Let $x$ be the vector of tunable parameters. Let also $\hat{P}(t)$ be the matrix of the measured responses for each experimental run as a function of time and $P(t, x)$ be the corresponding matrix of computed responses—which is a function of both $t$ and $x$. Then, the residual error between measurement and computation for the $i$th response from the $r$th experiment may be expressed as follows:

$$Z_{i,r}(x, t) = P_{i,r}(x, t) - \hat{P}_{i,r}(t)$$

A performance measure may be defined as the weighted
sum of the squared individual errors, over time, over all responses and over all experiments, in the form of the following expression:

\[ s(x) = \frac{\sum_{r=1}^{N_{\text{exp}}} \sum_{i=1}^{N_{\text{res}}} \sum_{t=1}^{N_{\text{rt}}-1} w_{i,t,r} (P_{i,t,r} - \hat{P}_{i,t,r})^2}{\sum_{r=1}^{N_{\text{exp}}} \sum_{i=1}^{N_{\text{res}}} \sum_{t=1}^{N_{\text{rt}}-1} w_{i,t,r} P_{i,t,r}^2} \]  

(2)

The weights \( w_{i,t,r} \) scale the contribution of each residual error \( Z_{i,t,r} \) in the performance measure. The responses \( P_{i,t,r} \) and \( \hat{P}_{i,t,r} \) are considered at times \( t = k \Delta t \), with \( \Delta t \) being a discretization interval.

The tunable parameters of the model cannot be allowed to vary without limits. They have to be restricted to regions that make sense scientifically. If a parameter \( \theta \) must be restricted between a minimum and a maximum value \( (\theta_{\text{min}} \text{ and } \theta_{\text{max}} \text{ respectively}) \), then, following Bates and Watts [24], a logistic transformation of the parameter \( \theta \), of the form

\[ \theta = \theta_{\text{min}} + \frac{\theta_{\text{max}} - \theta_{\text{min}}}{1 + e^{-\varphi}} \]  

(3)

is performed or, equivalently,

\[ \varphi = \ln \left( \frac{\theta - \theta_{\text{min}}}{\theta_{\text{max}} - \theta} \right) \]  

(4)

The problem of parameter vector \( \theta \) estimation can now be expressed as the following problem of unconstrained function minimization:

Minimize \( s(q) \), \( q \in \mathbb{R}^n \) \n
(5)

where the elements of the transformed parameters vector \( q \) are defined by the transformation (4) (given the constraint vectors \( \theta_{\text{min}} \) and \( \theta_{\text{max}} \)).

It must be noted that, using equation (4), a constrained minimization problem has been transformed into an unconstrained minimization problem. This work employs the implementation of the conjugate gradients algorithm that is given in the book of Press et al. [25] to solve the unconstrained minimization problem. The algorithm is slightly modified according to Lueneberger [26] to include algorithm restarts.

### 3.3 Tuning procedure

In order to support the tuning procedure, test results for a close-coupled converter of 0.75 l volume installed on a EURO-3 homologated, 1.8 l engine, according to the FTP-75 test procedure, were employed. The results comprised a second-by-second recording of exhaust gas mass flowrate, exhaust temperature at converter inlet, exhaust pollutant concentration (dry CO, NO\textsubscript{x} emissions, wet THC emissions) at catalytic converter inlet and exit, CO\textsubscript{2} and O\textsubscript{2} emissions as well as A/F as measured by an UEGO sensor, at catalytic converter inlet.

In all stages of the tuning procedure, optimization was performed against data from the first 505 s of the FTP cycle, which corresponds to the cold start phase of the cycle. Data from the rest of the cycle are not used in this case study, owing to the excessive computational time needed for the full FTP cycle optimization. The validity of this approach was tested by comparing the measured and computed results for the hot start phase of the FTP cycle after the determination of the tunable parameters.

Initially, CO and NO\textsubscript{x} measurements were used to optimize the parameters corresponding to reactions 1, 5, 6 and 8 (Table 2). This was done to investigate the sensitivity of the model to the tunable parameters and to identify the interrelation between the CO consumption by O\textsubscript{2} and by NO. The simulations were satisfactory for both the CO and the NO\textsubscript{x} measurements, implying that the model is capable of good NO\textsubscript{x} prediction, provided that it is tuned correctly.

Subsequently, the model was tuned only against the CO and HC measurements. At this stage, the parameters of reactions 1, 3–5, 7, 9 and 10 were tuned, while the CO–NO reaction was disabled (14 parameters in total). The optimizations revealed a lack of sensitivity to the parameters corresponding to the steam-reforming reactions and to ‘slow’ hydrocarbon oxidation. The relative lack of sensitivity to the steam-reforming kinetics was attributed to the specific tuning of the exhaust gas air–fuel ratio characteristics. As regards the ‘slow’ hydrocarbon kinetics insensitivity, this is attributed to the relatively low exhaust gas temperatures during this part of the cycle, that do not fully activate slow HC oxidation. On the basis of the observed behaviour, the kinetics of these reactions were not further adjusted but set to previously known values.

### 3.4 Simultaneous tuning of all parameters

The next step was made with the simultaneous tuning of all parameters involved in the reactions 1, 3, 5, 6, 7 and 8, simultaneously using the measurements of CO, HC and NO\textsubscript{x}. Here, another issue appeared: the optimization algorithm converged to local minima of the performance measure, which gave a very bad fit especially for the NO\textsubscript{x} curve.

This behaviour can be attributed to the type of optimization algorithm employed. The family of descent directions algorithms (such as quasi-Newton or conjugate gradients) may be deceived by a strong local minimum of the minimized function. The behaviour depends on the initial guess supplied. In order to circumvent the problem, another algorithm could be employed, such as a simulated annealing or a genetic algorithm.

In the present case study, this difficulty was bypassed by fixing the activation energy of CO oxidation at a constant value and then tuning the rest of the parameters. This was repeated for several values of the activation energy of CO oxidation. In this way, convergence problems were eliminated. Comparing the results for
each case, the simulations were shown to be optimum for \( E_1 = 90,000 \).

### 4 RESULTS AND DISCUSSION

The computed instantaneous CO, HC and NO\(_x\) concentrations at catalyst exit are compared with their measured counterparts in Figs 1 to 3 respectively for the first 200 s (CO), 250 s (HC) and 500 s (NO\(_x\)) of the FTP 75 cycle. It is evident that there is very good agreement between measurement and computation for all curves, compared with what has been previously published for analogous cases. The improved quality of computational results allows specific points of significant difference between experiment and computation to be spotted, e.g. the computed CO spike at 25 s or the characteristic hydrocarbon adsorption–desorption pattern during the first 25 s (this phenomenon is not included in the specific reaction scheme), and further improvement in the prediction to be tried or possibly errors in the experiment to be found. Similarly, there are only a few points of disagreement between computation and experiment regarding NO\(_x\) emissions, with the model over-predicting at about 30, 60, 200 and 270 s and under-predicting at about 70 and 350 s.

In order to check whether the parameter estimation was valid for other regions of the FTP cycle, the estimated parameters based on the first 505 s were employed to simulate catalyst performance over the whole FTP 75 cycle. Figures 4 to 6 show the calculation for the hot start phase. These figures indicate a certain over-prediction for CO and HC emissions overall, with (at least) the latter being attributed to the lack of optimization of the ‘slow’ hydrocarbon kinetics mentioned in Section 3.3. As regards the NO\(_x\) emissions, a closer look reveals some (minor) events at 2070, 2200, 2250 and 2380 s that are predicted by the model but not measured, whereas at 2090, 2160 and 2320 s the model appears to miss some clearly observable events. As previously mentioned, it is not, at present, possible to explain these minor discrepancies, but the continuous development of model and experimental quality control is expected to improve future predictions further. Again, the overall computation quality can be judged as satisfactory, particularly since the model was tuned based on information from the cold start phase only.

It is interesting to compare the results of the computer aided tuning procedure with those obtained by the previously applied manual tuning procedure. In Figs 7 to 9, the outlet concentrations of CO, HC and NO\(_x\) that correspond to manual model tuning are presented. Again, the results refer to the cold start phase of the FTP 75 cycle. It is obvious that the manual tuning of the model fails to simulate correctly the NO\(_x\) emissions of the catalyst, although the CO and HC predictions are sufficiently accurate. In specific parts of the cycle, for example in the period from 50 to 100 s, and also between 70 and 200 s, the manually tuned model performed better, presumably because the manual tuning has been implicitly aimed at good cold start HC prediction with a higher weight factor.

The reason for the superior overall performance of the computer aided tuning model is highlighted by a comparison of the manually tuned values of the parameters with those calculated by the above optimization procedure. The values are given in Table 3. Apparently, the direct oxidation of CO by O\(_2\) is overestimated. In contrast, the optimized parameter estimation sets a much lower pre-exponential factor to this reaction, allowing for more CO oxidation by stored O\(_2\) and by NO. The CO–NO reaction is responsible for the consumption of a larger percentage of the available CO and the fluctuations in the NO\(_x\) computation are avoided.

The above comparison may explain why sometimes the mathematical modelling with manual parameter estimation failed to produce accurate results to support real exhaust system design optimization.

Obviously, the specific set of tunable parameter values
be produced if the set of parameters that are allowed to vary during the optimization procedure is changed. This is an important area of future research that will further enhance the applicability of this type of computational tool.

Once the model is tuned to represent the measured test cycle behaviour of Figs 1 to 3, it may be employed to support optimization of the exhaust system by predicting system performance for the following design modifications:

(a) converter size;
(b) converter position;
(c) combination with an underfloor converter for further emissions reduction;
(d) change of precious metal loading;
(e) change of washcoat loading;
(f) change of substrate (shift to thin-walled substrates or metallic substrates).

Although in this type of model it is not possible to simulate the effect of precious metal loading directly (because catalytic activity is not expressed per catalyst loading as happens with true kinetic modelling), it is possible to predict the variation in activity, as expressed by a variation in the frequency factors $A_i$, on the basis of a semi-empirical relation that has been successfully tested in a number of case studies [22]. This further enhances the model’s capacity to study tailpipe emissions optimization by the use of different versions of thin-walled substrates. The fundamental capacity of the model to study thin-walled substrate effects has already been demonstrated in the past [27].

Catalyst ageing is another important issue that can only indirectly be addressed by modelling in general. As regards ageing, the specific class of tunable parameter models is superior to any other category of models, since they may be readily tuned to represent the phenomenological behaviour of an aged catalytic converter with reduced oxidation, reduction or storage activity [22]. Naturally, significant refining of the computer aided
parameter estimation procedure presented in this paper will be necessary in order to finalize a reliable computational tool that will not require exceptional skills and experience from its user. Only when this has been done will it be possible to employ the model in a simple and straightforward way by regular users in exhaust system design optimization.

However, the results shown in Figs 4 to 6 demonstrate that high accuracy can be attained by this type of modeling in matching and predicting real-world catalytic converter operation. Such an accuracy level is sufficient to support the design of catalytic exhaust systems, not only for EURO-3 but also for EURO-4 emissions standards.

5 CONCLUSIONS

Current and oncoming automotive exhaust emissions legislation sets a quite demanding situation for the catalytic converter, with overall conversion efficiency exceeding 95 per cent for all three main pollutants.

Under these circumstances, very accurate mathematical modelling of transient catalytic converter operation is necessary in order for the modelling to continue to play a role in the design optimization of real exhaust aftertreatment systems.

This paper has demonstrated the capabilities of a popular class of mathematical models with tunable parameters, which are based on the Langmuir–Hinshelwood kinetics assumptions.

In order to attain the maximum possible accuracy, a computer-aided parameter estimation methodology was developed that is demonstrated to determine the apparent kinetics parameters efficiently, exploiting second-by-second results from routine emissions testing.

An application case study is employed in this paper to demonstrate the high accuracy attainable with such a methodology and compared with typical accuracy levels obtainable with previously applied, manual tuning procedures.

Finally, focusing on the maximization of model applicability, an integrated methodology that also takes into account precious metal loading variation and catalyst ageing is discussed.

The modelling methodology presented is already being
applied in design optimization of exhaust systems for EURO-3 homologation and is also capable of being applied in EURO-4 systems versions.

REFERENCES


