The application of mathematical models to the prediction of the performance of automotive catalytic converters is gaining increasing interest, both for gasoline and diesel engine vehicles. This article addresses converter modeling in the transient state under realistic experimental conditions. The model employed in this study relies on Langmuir-Hinshelwood kinetics, and a number of apparent kinetic parameters must be tuned to match the behavior of each different catalyst formulation. The previously applied procedure of manually tuning kinetics parameters requires significant manpower. This article presents a methodology for kinetic parameter estimation that is based on standard optimization methods. The methodology is being applied in the exploitation of synthetic gas experiments and legislated driving cycle tests and the assessment of the quality of information contained in the test results. Although the optimization technique employed for parameter estimation is well known, the development of the specific parameter estimation methodology that employs the results of the available types of experiments is novel and required significant development. Application of this refined tuning methodology increases the quality and reliability of prediction and also greatly reduces the required manpower, which is important in the specific engineering design process. The parameter estimation procedure is applied to the example of modeling of a diesel catalytic converter with adsorption capabilities, based on laboratory experiments and vehicle driving cycle tests.

**Keywords:** Automotive catalytic converters; Reaction kinetics; Mathematical modeling

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INTRODUCTION

Research on chemical kinetics of complex heterogeneous catalytic reactions of industrial importance often requires the estimation of rate (or even equilibrium) coefficients by nonlinear regression (Froment, 1987). A variety of methods are applied to solve practical problems in parameter optimization, starting from traditional calculus methods and ranging to the so-called “evolutionary algorithms” (Park and Froment, 1998). These methodologies have been applied during the past two decades to the modeling of steady-state industrial processes (Watson et al., 1996; Moros et al., 1996; Felis et al., 1999; Wolf and Moros, 1997). However, modeling of catalytic reactors with transient prevailing behavior has been only recently supported by such methodologies. On the other hand, the increasingly stringent emission standards introduced by legislation forces automotive and catalyst manufacturers to develop and apply a large number of catalytic exhaust after-treatment systems. The catalytic converter has been the crucial component in the majority of such systems (Koltsakis and Stamatelos, 1997). The design of catalytic converter systems is increasingly supported today by mathematical modeling. In a catalytic converter, there is strong interaction between physical processes (species mass transfer to and from the washcoat and heat transfer between the exhaust gas and the monolith) and chemical processes (heterogeneous catalytic reactions taking place on the noble metals of the washcoat and, under certain conditions, adsorption, storage, and desorption of chemical species in the washcoat).

Heat and mass transport in catalytic converters (reactor submodel) have been modeled with variable detail and scope, ranging from the assumption of adiabatic monoliths in uniform inlet flow distribution, e.g., Young and Finlayson (1976) and Heck and Wei (1976), as well as simplified control-oriented models (Glielmo et al., 2000), to more complex models that take into account heat exchange with the monolith’s canning and the surrounding air and nonuniform distribution at the converter’s inlet (Flytzani-Stefanopoulos et al., 1986; Chen et al., 1988). However, the cornerstone of each catalytic converter model is the chemical kinetics submodel. The exact reaction scheme depends on the kind of catalytic converter under study but for every reaction taken into account by the model, a reaction rate must be provided. The reaction rates are different for each washcoat formulation and cannot be determined a priori. This is due to several reasons (Schmidt, 1998):

- First, all reactions occurring in a catalytic converter proceed heterogeneously on the noble metal surface. The exact reaction path involves multiple reactions and intermediate steps, thus it is not known. Besides,
the reaction path depends on the possible presence of species in the real exhaust gas that are not present in an experimental setup.

- Second, the reactions kinetics are very sensitive to the washcoat formulation. Noble metal loading and its dispersion in the washcoat, washcoat porosity, etc., may affect the reaction rates. Impurities that may be present may promote one rate over the others.

- Last but not least, catalytic processes suffer from aging and deactivation, and these depend on the conditions under which the catalyst is aged. Two catalytic converters with identical washcoat formulations behave quite differently after aging under different operating conditions.

To summarize, reaction kinetics in a catalytic converter are sensitive to the input gas formulation, the washcoat formulation, and its history. To circumvent the above difficulties, especially in the study of real-world catalyst performance on-vehicle, a class of simplified models, using Langmuir-Hinshelwood (LH) kinetics, is increasingly applied as engineering tools. This category of models uses empirical reaction rate expressions, which involve tunable parameters (Siemund et al., 1996; Koltsakis and Stamatelos, 1998). All phenomena that are not explicitly accounted for by the model are lumped into the values of these tunable parameters.

The kinetics expressions following the Langmuir-Hinshelwood formalism are of the type:

$$r_{rea} = \frac{Ae^{-E/R_T}T^{x_A}x_B}{G_1}, \quad \text{where } G = G(T, x_A, x_B, \ldots, x_N, K_1, K_2, \ldots, K_n)$$

The Langmuir-Hinshelwood expressions predict an exponential (Arrhenius-type) dependence on temperature, while $G$ is an inhibition term, a function of temperature and concentrations $x$ 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 term $G$ are considered tunable parameters. The effect of different washcoat formulations and the interaction between different species are lumped into these parameters. Consequently, the resulting reaction rates can be considered as fitting laws.

Traditionally, the lumped parameters were manually tuned to compromise between the accurate fitting of the results of several experiments and tests. In this paper, a model already tested in diesel catalytic converter design optimization (Pontikakis et al., 2000) was linked to a computer-aided procedure for tuning kinetic parameters, based on experimental data from both the laboratory and vehicle driving cycle tests.
SYSTEM DESCRIPTION

Balance Equations and Chemical Processes

A diesel oxidation catalyst modeling case is employed in this study, because diesel catalyst modeling is simpler and does not require the complex NOx reduction kinetics around stoichiometry that a three-way catalyst does. A short description of the modeling approach follows.

**Mass Balances.** The mass balance calculations in the catalytic converter are employed for one monolith channel. The mass transfer of reactants and products to and from the catalytic surface correspondingly is computed with the aid of a “film model” approach. According to this approximation, the species from each channel’s bulk gas flow diffuse down to a hypothetical catalyst’s solid-gas interface, through the gas flow boundary layer and the adsorbing washcoat. At the chemically active solid-gas interface species may react or adsorb and desorb to and from the washcoat. Reaction products and desorbing species diffuse back to the bulk gas flow.

A mean bulk value $x_j$ is employed for the gas phase concentration of each species. Likewise, a value $x_{s,j}$ is considered for the concentration of each species at the active interface. Thus, the mass balance for the gas phase is the following:

$$-\rho_g u \frac{\partial x_j}{\partial z} = \rho_g k_{m,j} S(x_j - x_{s,j})$$

A mass transfer coefficient $k_{m,j}$ is employed for the species diffusion through the flow boundary layer and the washcoat. The mass transfer coefficients are given as functions of the Nusselt and Sherwood dimensionless numbers for the monolith’s channels.

A separate mass balance must be applied for gas-phase components in the washcoat:

$$\frac{\rho_g}{M_g} k_{m,j} S(x_j - x_{j,s}) = R_{rea,j} + R_{srp,j}$$

The rates $R_{rea,j}$ and $R_{srp,j}$ refer to the production or consumption of species at the solid-gas interface due to reaction and adsorption-desorption respectively. For $N_R$ reactions, each taking place with a rate $r_k$, the rate of consumption or production of a species $j$ is

$$R_{rea,j} = \sum_{k=1}^{N_R} a_{j,k} r_k$$
where \( a_{j,k} \) is the stoichiometric coefficient of species \( j \) in reaction \( k \). Finally, the sorption (adsorption-desorption) rate \( R_{srp,j} \) of species \( j \) is directly proportional to the rate at which the species’ mass is stored in the adsorbing medium or released from it.

\[
R_{srp,j} = \frac{\varepsilon}{M_j} \frac{d\theta_j}{dt}
\]

(4)

In the above relationship, \( \varepsilon \) is the volume of the adsorbing micropores per unit volume catalytic converter (void fraction of micropores).

**Energy Balances.** The energy balances in the catalytic converter are also employed for one monolith channel, but the heat losses to the surroundings are also taken into account. The “film model” approach is used for the energy calculations as well. Similarly to the above, a mean bulk value \( T_g \) is used for the exhaust gas temperature, and a solid phase temperature \( T_s \) is introduced for the monolith and the solid-gas interface. Energy is transferred to and from the exhaust gas only due to convection with the channel walls. Thus, the energy balance for the gas phase becomes

\[
\rho_s c_p u_z \frac{\partial T_g}{\partial z} = hS(T_s - T_g)
\]

(5)

The temperature field in the converter (1-D in the \( z \)-direction, considered as adiabatic in this study) is described by the equation of transient heat conduction with heat sources.

\[
\rho_s c_p s \frac{\partial T_s}{\partial t} = k_{s,z} \frac{\partial^2 T_s}{\partial z^2} + hS(T_g - T_s) + \sum_{k=1}^{N_R} \left(-\Delta H_k^{rea}\right) r_k + \sum_{j=1}^{N_{AS}} \left(-\Delta H_j^{srp}\right) R_{srp,j}
\]

(6)

The source terms of the above energy balance include heat exchanged with the exhaust gas flow due to convection and energy released due to chemical reactions and adsorption or absorbed due to desorption.

**Reactions and Sorption Kinetics Submodel.** The activation energies, the pre-exponential factors, and the inhibition factors of the LH expression for each reaction are fitted in order to match the experimental results. Here, attention is focused on the catalyst performance as regards carbon monoxide (CO) and hydrocarbon (HC) conversion. A typical reaction scheme is that of Table I. H\(_2\) oxidation is also taken into account in the
reaction scheme, since it may contribute significantly in the overall reaction exothermy.

More than one HC species is taken into account in the reaction scheme because the real exhaust gas contains a very complicated mixture of hydrocarbons. Every hydrocarbon species is oxidized at different temperatures. In practice, the diversity of the HC mixture is usually taken into account by considering two kinds of hydrocarbons being present in the exhaust gas: an easily oxidizing HC ("fast" HC), represented by propene, and a less easily oxidizing HC ("slow" HC), represented by propane. Hydrocarbon adsorption desorption behavior plays an important role in diesel oxidation catalyst performance. Long-chain and aromatic HC species are much keener to adsorb in the washcoat compared to smaller molecule species. Therefore, apart from the "slow" and "fast" HC species, a third, absorbable HC species is taken into account in the reaction scheme; it is represented by decane.

The following equation (Dubinin-Radushkevich isotherm) gives (for each adsorbable species) the adsorbed mass at equilibrium per unit volume of void in the washcoat $\theta_{eq,j}$ as a function of temperature and partial pressure of the hydrocarbon (Thomas and Thomas, 1997):

$$\theta_{eq,j} = \rho_{liq,j} - \exp \left( D \left[ \ln \left( \frac{P_0}{P} \right) \right]^2 \right), \quad D = A \left( \frac{R_g T}{\beta} \right)^2$$

Factor $\beta$ is an affinity coefficient depending only on the adsorbate, and $A$ is characteristic of the pore size distribution of the catalyst. The sorption rate is assumed to be a linear function of the difference between the mass of the adsorbed species $\theta_j$ and the corresponding equilibrium mass $\theta_{eq,j}$ calculated by the above equation:

$$r_{srp} = \frac{d\theta_j}{dt} = k_{srp}(\theta_{eq,j} - \theta_j)$$

### Table I  Reaction scheme and rate expressions used in the model

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Rate expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO + 1/2O$_2$ $\rightarrow$ CO$_2$</td>
<td>$r_{rea,1} = \frac{A_1 e^{-E_1/RT}}{G_1}$</td>
</tr>
<tr>
<td>H$_2$ + 1/2O$_2$ $\rightarrow$ H$_2$O</td>
<td>$r_{rea,2} = \frac{A_2 e^{-E_2/RT}}{G_1}$</td>
</tr>
<tr>
<td>C$_i$H$_j$ + (x + 0.25y)O$_2$ $\rightarrow$ xCO$_2$ + 0.5yH$_2$O</td>
<td>$r_{rea,i} = \frac{A_i e^{-E_i/RT}}{G_i}$, $i = 3 \ldots 5$</td>
</tr>
<tr>
<td>$i = 3$:C$_3$H$_6$, $i = 4$:C$<em>3$H$<em>8$, $i = 5$:C$</em>{10}$H$</em>{22}$</td>
<td></td>
</tr>
</tbody>
</table>

Inhibition term:

$G_1 = T(1 + K_1_{CO} + K_2_{xC,H_i})^2(1 + K_3_{xCO}x_{C,H_i}y_{C,H_i})(1 + K_4x_{NO}^{0.7})$

$K_i = K_0_i \exp(-E_i/R_gT)$
Here, $k_{srp}$ is a sorption rate, which is constant in the case of adsorption since adsorption is a non-activated process (Kaerger and Ruthven, 1992):

$$k_{srp} = k_{ads} = \text{const}, \quad \theta_j < \theta_{eq,j}$$  \hspace{1cm} (9)

Desorption is an activated process (Kaerger and Ruthven, 1992), thus the sorption rate exhibits exponential temperature dependence in this case:

$$k_{srp,j} = k_{des,j} = k_{des,j}^0 \exp\left(\frac{-E_{D,j}}{R_g T}\right), \quad \theta_j > \theta_{eq,j}$$  \hspace{1cm} (10)

More details about the introduction of the additional absorbing hydrocarbon and the role of the adsorption submodel, along with additional information about modeling details and justification, can be found in Pontikakis et al. (2000).

**Numerical Solution Procedure and Simulation Duration Data.** The balance equations are discretized along the axial direction, and for each node, the Newton-Raphson method is employed to solve the nonlinear system of equations that results from the application of Equation (2) for all reacting species. To achieve this, the rates of species production or consumption due to reaction ($R_{rea}$) and adsorption-desorption ($R_{srp}$) are needed. Although the calculation of the rates of reactions is straightforward from Equation (3), the calculation of the adsorption/desorption rate from Equation (4) is more complicated. It implies a series of equilibrium steps that are taken to calculate the mass of adsorbed species from Equation (8). The solution gives the vector of species concentrations ($x_i$) at the gas-solid interface of the catalyst. This is used to solve numerically the coupled mass and energy balances using a finite-difference scheme and thus to get the axial distribution of concentrations and temperatures. A typical run of the full new European driving cycle (NEDC) using a Pentium III 1000 MHz PC takes less than five minutes, that is, CATRAN software runs the simulation of the catalytic converter faster than real time.

**Tunable Parameters**

The use of apparent kinetics for the reaction and the sorption submodels introduces a number of model parameters that must be estimated based on the results of suitable experiments. The tunable parameters are the pre-exponential factors and the activation energies for the oxidation of CO and each of the HC species. For the tunable parameters contained in the inhibition term ($G_1$), the values specified in Koltsakis and Stamatelos (1998) that are adapted from the work of Voltz et al. (1973) are
<table>
<thead>
<tr>
<th>Model equations and tunable parameter</th>
<th>Model equations</th>
<th>Equation number</th>
<th>Tunable parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass transfer</strong></td>
<td><strong>Balance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equation</td>
<td>( \rho_{g} \frac{\partial x_j}{\partial t} + \rho_{g} u_z \frac{\partial x_j}{\partial z} = \rho_{g} k_{m,j} S(x_j - x_{j,s}) )</td>
<td>(1)</td>
<td></td>
</tr>
<tr>
<td><strong>Boundary condition</strong></td>
<td>( \frac{\rho_{g}}{M_g} k_{m,j} S(x_j - x_{j,s}) = R_{rea,j} + R_{sop,j} )</td>
<td>(2)</td>
<td></td>
</tr>
<tr>
<td><strong>Heat transfer</strong></td>
<td><strong>Balance</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>equation (gas phase)</td>
<td>( \rho_{s} c_{p,s} \frac{\partial T_s}{\partial z} = hS(T_s - T_g) )</td>
<td>(5)</td>
<td></td>
</tr>
<tr>
<td>equation (solid phase)</td>
<td>( \rho_{s} c_{p,s} \frac{\partial T_s}{\partial r} = k_{s,s} \frac{\partial^2 T}{\partial z^2} + k_{s,j} \frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial T}{\partial r} \right) )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>[ + hS(T_g - T_s) \sum_{k=1}^{N_s} (-\Delta H_k^{rea}) r_k + \sum_{j=1}^{N_m} (-\Delta H_j^{mp}) R_{sop,j} ]</td>
<td>(6)</td>
<td></td>
</tr>
<tr>
<td><strong>Boundary conditions</strong></td>
<td>( k_s \frac{\partial T_s}{\partial r} = h_{amb} (T_s - T_{amb}) + \varepsilon \sigma (T_s^4 - T_{amb}^4) ) at ( r = R_{man} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( \frac{\partial T_s}{\partial r} = 0 ) at ( r = 0 )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reactions rates</td>
<td>Equilibrium</td>
<td>Sorption rates</td>
<td></td>
</tr>
<tr>
<td>-----------------</td>
<td>-------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>( R_{\text{obs},j} = \sum_{K=2}^{N} A_k \exp \left( \frac{R_g T}{k_{\text{ads},j}} \right) )</td>
<td>( \theta_{\text{eq},j} = \mu_{\text{eq},j} - \exp \left( \frac{R_g T}{k_{\text{ads},j}} \right) )</td>
<td>( R_{\text{sr},j} = k_{\text{ads},j} \exp \left( \frac{R_g T}{k_{\text{ads},j}} \right) )</td>
<td></td>
</tr>
<tr>
<td>( k_{\text{ads},j} = k_{\text{des},j} = \text{const} )</td>
<td>( \theta_{\text{eq},j} &lt; \theta_{\text{eq},i} )</td>
<td>( \theta_{\text{eq},j} &gt; \theta_{\text{eq},i} )</td>
<td></td>
</tr>
</tbody>
</table>
employed. No adjustment of $G_1$ terms is attempted at this stage. Also, based on usual practice, the pre-exponential factor and activation energy for $H_2$ oxidation are assumed to be equal to the ones for CO oxidation and are not separately tuned.

The adsorption-desorption submodel also introduces tunable parameters for each adsorbable species, namely the affinity coefficient $\beta$, the adsorption rate $k_{ads}$, and the desorption pre-exponential factor $k_{des}$ and activation energy $E_D$. The pore size distribution factor $A$ in Equation (7) and the void fraction of the micropores $\varepsilon$ in Equation (4) are characteristics of the catalyst. In our case, their values are $A = 10^{-9} \text{[mol/J]}$ and $\varepsilon = 7 \times 10^{-3} \text{[m}^3/\text{m}^3\text{]}$.

The equations of the model and the tunable parameters each equation introduces are summarized in Table II.

**TUNING PROCEDURE**

**Current Tuning Practice**

Although the use of tunable parameter catalytic converter models is more than 20 years old, not much work has been carried out in the direction of computer-aided tuning. In most cases, kinetic tuning is done in an empirical manner. For the inhibition terms of the reaction rates, the kinetics provided in the historical work of Voltz et al. are popular even today in this class of models. The order of magnitude of the apparent activation energies is approximately known for most reactions and could be used as a starting point. Then, one would manually try to adjust the pre-exponential factor and, to a much lesser extent, the activation energy, in order to adequately fit the computed curves to the experimental ones.

Montreuil et al. (1992) were the first to present a systematic attempt for the tuning of the parameters of their steady-state three-way catalytic converter model. They compiled an experimental database of steady-state efficiencies for two catalyst formulations and fitted the parameters of their model according to the database. This was done by defining a merit function of the tunable parameters as the square differences between experimental and computed values and minimizing it with the aid of the conjugate gradients method. The chemical reactions submodel contained 95 parameters. By grouping the tunable parameters according to each kinetic subsystem, they progressively tuned all model parameters in a semi-empirical way.

Dubien and Schweich (1997) also published a methodology to determine the frequency factor and the activation energy of simple rate expressions from light-off experiments. They used theoretical calculations to provide an initial approximation of the tunable parameters and then optimized the parameters similar to the method of Montreuil et al., i.e.,
defining a merit function and using the downhill simplex method to 
minimize it. Their approach was successful but of limited practical value 
because it was applicable only to noncompeting reactions. It was there-
fore restricted to the study of simple mixtures of reactants and could not 
be used to fit parameters of a realistic reaction scheme.

In this work, the diesel catalytic converter model is tuned based on 
the results of routine experiments. The merit function approach is also 
used here and, in order to minimize it, the method of conjugate gradients 
is employed.

**Tuning Experiments**

In order to evaluate the tunable parameters of the model of the diesel 
oxidation catalyst, we employed the published performance of a catalyst 
by means of the results of

- synthetic gas bench (SGB) experiments with mini-catalysts and
- vehicle driving cycle experiments with full-scale catalysts in real engine 
  exhaust (Pontikakis et al., 2000).

The SGB tests presented in the aforementioned work lie in two 
categories: sorption and light-off tests. They are used in this work to tune 
the adsorption-desorption and reaction submodels respectively. In par-
allel, an independent assessment of the tunable parameter values was 
accomplished using the data from driving cycle tests.

Sorption tests aimed at isolating the hydrocarbons’ adsorption-
desorption process. Therefore the gas used in the sorption tests contained 
only hydrocarbon (decane). The inlet mixture was balanced by nitrogen. 
The catalyst was initially clean (i.e., it did not contain any adsorbed 
hydrocarbons); gas was supplied at constant temperature and flow rate 
and hydrocarbon adsorption occurred. When the process reached equi-
librium (i.e., inlet and outlet hydrocarbon concentrations were equili-
brated), hydrocarbon supply was zeroed; temperature was ramped at a 
constant rate of 1 K/s and the adsorbed hydrocarbon gradually desorbed 
(Pontikakis et al., 2000). Light-off tests were conducted under constant 
gas hourly space velocity (GHSV) and composition. O₂, CO₂, CO, NO, 
SO₂, and H₂O were included in the gas mixture in order to resemble real 
exhaust gas conditions. The catalysts of the experiments were initially 
clean. Temperature was ramped at 1 K/s as soon as the experiment began.

The inlet gas composition of the sorption and light-off tests is given 
in Table III.

SGB tests can be considered as only a simplification of the full-scale 
tests with real exhaust gas, which is a very complex mixture containing a 
lot of hydrocarbons and also oxygenates in the case of diesel exhaust.
Therefore, physical and chemical phenomena may take place during the catalyst operation with real exhaust that are absent from SGB tests. The model does not account for these side effects explicitly, but they are lumped into the values of the model’s tunable parameters.

The experience gained from previous applications of mathematical models in real converter design case studies showed that the estimation of kinetics parameters by SGB tests is not very successful for the prediction of catalyst performance with real exhaust. On the other hand, simple SGB experiments are important for the identification of the most prominent phenomena, the preliminary assessment of a new model, and the initial evaluation of the tunable parameters’ respective ranges.

According to experience, before routine use of a model of the above described type in real-world applications, the tunable parameter values have to be fine-tuned using full-scale engine bench or chassis dynamometer driving cycle tests with real exhaust gas.

For the above reason, catalyst performance results on a legislated new European driving cycle (NEDC) test that were available from the above-mentioned publication were employed in fine-tuning the kinetics and sorption parameters in this case study (Pontikakis et al., 2000), which comprises an underfloor diesel catalyst mounted on a two liter engine car.

### Optimization Procedure

Several different experiments may be available to facilitate model tuning, and for each experiment, among other important variables as such as model input, selected exhaust species concentrations are recorded, both at converter inlet and exit. When the mathematical model is applied to simulate the specific tuning experiment, for each species concentration computed and experimental curves are compared. Consistent model tuning means finding the set of tunable parameters that minimizes the error between computation and tuning experiment results. In order to tune the parameters of the model, the problem is formulated so that a standard mathematical procedure is applicable.

Let \( \mathbf{x} \) be the vector of tunable parameters, \( P(t, \mathbf{x}) \) be the matrix of computed species concentrations at selected points along the catalyst coinciding with the measurement locations, and \( \hat{P}(t) \) be the

<table>
<thead>
<tr>
<th>Test type</th>
<th>HC</th>
<th>NO</th>
<th>O(_2)</th>
<th>CO</th>
<th>CO(_2)</th>
<th>H(_2)O</th>
<th>SO(_2)</th>
<th>GSHV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sorption</td>
<td>2700 ppm</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>0%</td>
<td>70000 h(^{-1})</td>
</tr>
<tr>
<td>Light-off</td>
<td>100 ppm</td>
<td>300 ppm</td>
<td>10%</td>
<td>500 ppm</td>
<td>10%</td>
<td>10%</td>
<td>20 ppm</td>
<td>70000 h(^{-1})</td>
</tr>
</tbody>
</table>
corresponding matrix of measured concentrations. The error between the experimental and computed variables is, for each element in the matrix,

\[ e_{i,r}(t, \mathbf{x}) = \hat{P}_{i,r}(t) - P_{i,r}(t, \mathbf{x}) \]  

(11)

where \( P_{i,r} \) is the \( i \)th measured concentration of species \( i \) from the \( r \)th experiment.

The performance measure is taken to be a weighted average of the individual errors, over time, over all variables and over all experiments, where the variables \( P_i, r \) are considered at times \( t = k\Delta t \), with \( \Delta t \) being the discretization interval. The resulting performance measure is

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

(12)

which is essentially an overall measure of the relative error between experimental \((\hat{P}_{t}, t = 1 \ldots T)\) and computed \((P_t, t = 1 \ldots T)\) data over all experiments. The weights \( w_{i,r} \) scale the contribution of each error quantity \( e_{i,r} \) in the performance measure.

In this work, the penalty method (Pierre, 1965) is employed to properly account for constraints. These constraints limit the acceptable values of the tunable parameters within specified bounds. Thus, model tuning reduces to solving the following problem:

\[
\text{minimize } f(\mathbf{x})
\]

where \( f(\mathbf{x}) = \begin{cases} s(\mathbf{x}) & \mathbf{c}(\mathbf{x}) > 0 \\ s(\mathbf{x}) + W \cdot \sum(c(\mathbf{x}))^2 & \mathbf{c}(\mathbf{x}) < 0 \end{cases} \)  

(13)

and \( \mathbf{c}(\mathbf{x}) = [c_1(\mathbf{x}), c_2(\mathbf{x}), \ldots, c_n(\mathbf{x})]^T \)  

(14)

where \( f(\mathbf{x}) \) is the new merit function, \( \mathbf{x} = [x_1, x_2, \ldots, x_n]^T \) is the vector of tunable parameters, and \( \mathbf{c}(\mathbf{x}) \) is the constraints vector.

The penalty term \( W \cdot \sum(c(\mathbf{x}))^2 \) increases the value of the merit function beyond the performance measure in case one or more constraints are violated. \( W \) is a constant that has a very big value compared to the merit function value. Here, the value of \( W \) was set as \( W = 10^6 \).

The constraints are introduced because the tunable parameters represent physical properties and, thus, may not have values that contradict their physical meaning.
In this work, the merit function $f(x)$ is minimized by use of the conjugate gradients method. The conjugate gradients minimization algorithm performs successive line minimizations along the directions $h_i$, which are set to be

$$h_{i+1} = g_{i+1} + \gamma_i h_i,$$

where $g_i = -\nabla f(x)$,

$$\gamma_i = \frac{g_{i+1} \cdot g_{i+1}}{g_i \cdot g_i}$$

and $h_0 = g_0$.

It has been proved (Press et al., 1988) that the vectors $h_i$ (along which we perform the minimizations) satisfy the conjugancy condition:

$$h_i \cdot H \cdot h_j = 0, \quad j < i$$

where $H$ is the Hessian matrix of the function $f$ at point P:

$$[H]_{ij} = \left. \frac{\partial^2 f}{\partial x_i \partial x_j} \right|_p$$

Minimizing along a direction $h_{i+1}$, which is conjugate to the previous direction $h_i$, means that the gradient along the direction $h_{i+1}$ is perpendicular to the direction $h_i$. Thus, minimization along $h_{i+1}$ will not spoil the previous minimization along $h_i$. If the merit function $f$ is an exact quadratic form, $n$ line minimizations (where $n$ is number of components of vector $x$) along the conjugate directions $h_i$ will lead to the minimum. Practically, our merit function is not an exact quadratic form, therefore the repetition of the $n$ line minimizations is needed in order to converge to the minimum.

In this work, a FORTRAN-77 implementation of the conjugate gradients algorithm that is given by Press et al. (1988) was employed. The derivatives of the merit function were computed numerically by discretizing on the tunable parameters space, since analytical expressions of the derivatives are not readily obtainable. The details of the numerical derivatives estimation are also given in the book by Press et al. (1988). In the case that the pre-exponential factor $A$ and the oxidation energy $E$ of an oxidation reaction were tuned simultaneously, convergence problems occurred in the search for the optimum point. This was due partly to the
several orders-of-magnitude difference between the values of $A$ and $E$, roughly varying in the range $10^{10} < A < 10^{25}$ and $50000 < E < 150000$ and partly to the several orders-of-magnitude difference between the values of the sensitivity of the merit function with respect to $A$ and $E$. This insensitivity of the merit function along certain directions in the parameter space, along with the errors involved in the numerical estimation of the derivatives of the merit function with respect to these parameters, contributed to the poor convergence of the optimization algorithm. This problem was overcome using the following reparameterization:

$$A = 10^\bar{A} \Rightarrow \bar{A} = \log A$$

$$E = 10^4 \bar{E} \Rightarrow \bar{E} = 10^{-4} E$$

where $\bar{A}$ and $\bar{E}$ are the new parameters. The values of $\bar{A}$ and $\bar{E}$ vary within ranges of the same order of magnitude, $10 < \bar{A} < 25$ and $5 < \bar{E} < 15$, and the sensitivities are of the same order of magnitude. With the above formulation of the tunable parameters, the convergence problems were eliminated.

RESULTS

Adsorption-Desorption Tuning

Initially, the adsorption phase parameters of the model were tuned using the available SGB adsorption-desorption tests. Specifically, the adsorption phase ($0–500$ s) of two sorption experiments, conducted at different inlet gas temperatures (106 and 127°C) but with the same inlet composition (2000 ppm decane), was employed. These experimental data are shown in Figures 1–2. Table IV presents the optimal estimates of the affinity coefficient $\beta$ and the hydrocarbon adsorption rate $k_{ads}$ for decane, along with the initial estimates used in the algorithm and the lower & upper limits of the parameter values. The computed versus measured output hydrocarbon concentrations that result using the optimum values of $k_{ads}$ and $A$ are given in Figures 1–2 for $T = 106°C$ and $T = 127°C$ respectively. It is observed that the results are quite satisfactory.

Moreover, an attempt was made to tune pre-exponential factor $k_{des}$ and activation energy $E_{des}$ involved in the rate of desorption, using the desorption phase of the experiments $(500–800$ s). The optimization algorithm failed to converge to a single solution—for different initial values the algorithm converged to different optimum points. Figure 3 shows a plot of the merit function in respect to $k_{des}$ and $E_{des}$. It became apparent that the merit function has no single minimum but a plateau of
minima. The simulation is not sensitive to the rate of desorption. This could imply that the process is controlled by the adsorption-desorption equilibrium. In other words, the simulated system behavior seems not to depend on the rate that the system reacts against the shift of the equilibrium point but on the rate the equilibrium shifts (due to the gradual inlet temperature increase).

Thus, the tunable parameters cannot be determined unambiguously from the specific data. As shown in the next section, full-scale vehicle tests were finally employed for this task.

Inserting any one of the “optimum” pairs of $k_{des}$ and $E_{des}$ values to model the adsorption-desorption experiments, the curves shown in Figure 1 ($T = 106^\circ C$) and ($T = 127^\circ C$) are generated. Thus, the experiments are not suitable for the determination of the values of $k_{des}$ and $E_{des}$. In order to achieve this, the experiments should be conducted again with a faster temperature rise during the desorption phase.

**Oxidation Tuning using SGB Light-Off Experiments**

The next step of the tuning exercise was to evaluate the tunable parameters for the oxidation of CO and HC. For each species, there are two tunable parameters, namely the pre-exponential factor $A$ and the
activation energy $E$. A first attempt was made to determine the pre-exponential factor $A_{CO}$ and the activation energy $E_{CO}$ of the CO oxidation based on the results of routine light-off tests.

The experimental CO light-off curve shown in Figure 4 was employed in this process. It must be noted that the input gas in this test also contained hydrocarbon, which is oxidized in the experiment’s temperature range. In order to focus only on the simultaneous determination of $A_{CO}$ and $E_{CO}$, the kinetics for hydrocarbon oxidation were adopted from previous experience.

The algorithm converged to different optimum points, depending on the starting point of the optimization procedure. To better present this situation, the merit function was plotted against the two tunable parameters, and the results are visualized in Figure 5. From any starting

Table IV Tunning of the adsorption phase parameters

<table>
<thead>
<tr>
<th>Tunable parameter</th>
<th>Initial value</th>
<th>Optimum value</th>
<th>Lower limit</th>
<th>Upper limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta$</td>
<td>0.3</td>
<td>0.91</td>
<td>0.01</td>
<td>2</td>
</tr>
<tr>
<td>$k_{ads,decane}$</td>
<td>0.1</td>
<td>0.021</td>
<td>0</td>
<td>5</td>
</tr>
</tbody>
</table>
Figure 3. Merit function vs. $k_{dec}$ and $E_{dec}$ for desorption phase tuning.

Figure 4. Computed vs. experimental CO light-off curves.
point, the algorithm easily finds its way to the long narrow valley but fails
to optimize along it. This is due to the fact that the gradient of the merit
function along the direction of the long narrow valley, shown in Figure 5,
is negligible. Such incidents are well known from the published experi-
ence with this class of optimization routines in a variety of applications
(Pierre, 1965).

To further investigate this behavior of the algorithm, three light-off
curves were computed with different pairs of $A_{CO}$ and $E_{CO}$. Their values
were obtained by fixing the value of the activation energy and optimizing
for the pre-exponential factor. The optimum values for these three cases
are shown in Table V. The corresponding computed curves are compared
with the experimental one in Figure 4. It seems that it is possible to tune
the pre-exponential factor $A$ so as to obtain quite satisfactory results
regardless of the value of the activation energy $E_{CO}$. However, values for
activation energies for the various reactions are more or less known for
each different catalyst and do not vary significantly between catalysts.
Thus, the main tuning effort is directed to the pre-exponential factors.
From the results of Figure 5 and Table V it may be observed that the
merit function is not sensitive to the large variation of the values of $A_{CO}$
and $E_{CO}$ along a certain direction of the parameter space. This direction
is the principal direction of the Hessian of the merit function, which
corresponds to the lowest eigenvalue. To further illustrate this, the

![Figure 5. Merit function vs. $A_{CO}$ and $E_{CO}$ for light-off tests tuning.](image_url)
The eigenvalues and the eigenvectors of the Hessian matrix of the merit function are shown in Table V for each case. The eigenvalues, which measure the curvature of the merit function at the optimal point along the principal directions, are also indicative of the relative uncertainty in the parameter estimates along these principal directions. The large uncertainty observed along one direction indicates that the available experimental data were no adequate for the reliable estimation of these parameters.

Thus, SGB light-off tests alone cannot be used for the determination of CO oxidation parameters. The same applies for the HC oxidation, since the light-off behavior of hydrocarbons is similar to that of CO and, furthermore, the rate expressions for CO and HC oxidation are of the same type.

**Oxidation Tuning Using a Driving Cycle**

As a final step, a vehicle driving cycle test was employed in order to successfully tune the model. The driving cycle test is a complex transient test where all physical and chemical phenomena taking place in the catalyst are coupled. Therefore, one cannot isolate the chemical reaction and tune for the corresponding parameters separately. Instead, it is required to tune all parameters simultaneously.

The complicated mixture of exhaust gas hydrocarbons was simulated in the above-described model with three hydrocarbons: a fast-oxidizing HC, represented by propene, a slow-oxidizing HC, represented by propane, and an adsorbable HC, represented by decane. Thus, it was

<table>
<thead>
<tr>
<th>Point</th>
<th>ACO and ECO at each point</th>
<th>Merit function value</th>
<th>Eigenvalue of Hessian matrix</th>
<th>Eigenvectors of Hessian matrix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5 \times 10^{17} 80000</td>
<td>2.13 \times 10^{-3}</td>
<td>\lambda_1 = 155.7 \quad \lambda_2 = -3.4</td>
<td>v_1 = \begin{bmatrix} -0.874 \ 0.486 \end{bmatrix}, \quad v_2 = \begin{bmatrix} 0.486 \ 0.874 \end{bmatrix}</td>
</tr>
<tr>
<td>2</td>
<td>2.6 \times 10^{18} 90000</td>
<td>2.19 \times 10^{-3}</td>
<td>\lambda_1 = 159.6 \quad \lambda_2 = 3.8</td>
<td>v_1 = \begin{bmatrix} -0.863 \ 0.51 \end{bmatrix}, \quad v_2 = \begin{bmatrix} 0.51 \ 0.863 \end{bmatrix}</td>
</tr>
<tr>
<td>3</td>
<td>6.0 \times 10^{20} 110000</td>
<td>2.72 \times 10^{-3}</td>
<td>\lambda_1 = 164.283 \quad \lambda_2 = 5.864</td>
<td>v_1 = \begin{bmatrix} -0.848 \ 0.53 \end{bmatrix}, \quad v_2 = \begin{bmatrix} -0.53 \ 0.848 \end{bmatrix}</td>
</tr>
</tbody>
</table>
attempted to minimize the error between computed and measured outlet concentration of CO and HC by tuning:

- CO activation energy $E_{CO}$ and pre-exponential factor $A_{CO}$
- HC activation energy $E_{HC,j}$ and pre-exponential factor $A_{HC,j}$ for each of the three hydrocarbons
- Four tunable parameters involved in the absorption-desorption model for the adsorbable HC, i.e., the affinity coefficient $\beta$ and the adsorption-desorption rate parameters $k_{ads}$, $k_{des}$, and $E_{des}$.

In total, 12 tunable parameters must be determined. Two experimentally determined catalyst outlet concentration curves available for CO and HC were employed in the process of optimal fitting of the above 12 parameters. Because two experimental curves are used, the weights in Equation (12) must be properly set. To facilitate that, we computed the average of the measured outlet concentration for CO and for HC. Their ratio is

$$\frac{\text{average measured CO outlet concentration}}{\text{average measured HC outlet concentration}} \cong 5$$

Thus, in order for the contribution of each experimental data set to be of the same order of magnitude, the weight for HC was set five times greater that the corresponding weight for CO: $w_{HC} = 5$, $w_{CO} = 1$.

The initial and optimum values for each parameter are given in Table VI. The computed versus measured outlet concentration curves for CO, HC emissions, and computed versus measured temperatures at the converter

<table>
<thead>
<tr>
<th>Tunable parameter</th>
<th>Initial value</th>
<th>Minimum value</th>
<th>Maximum value</th>
<th>Optimum value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{CO}$</td>
<td>$10^{21}$</td>
<td>$10^{10}$</td>
<td>$10^{30}$</td>
<td>$1.6 \cdot 10^{15}$</td>
</tr>
<tr>
<td>$E_{CO}$</td>
<td>110000</td>
<td>50000</td>
<td>130000</td>
<td>66290</td>
</tr>
<tr>
<td>$A_{propene}$</td>
<td>$10^{20}$</td>
<td>$10^{10}$</td>
<td>$10^{30}$</td>
<td>$1.1 \cdot 10^{21}$</td>
</tr>
<tr>
<td>$E_{propene}$</td>
<td>90000</td>
<td>50000</td>
<td>100000</td>
<td>84260</td>
</tr>
<tr>
<td>$A_{propane}$</td>
<td>$10^{20}$</td>
<td>$10^{10}$</td>
<td>$10^{30}$</td>
<td>$4.9 \cdot 10^{17}$</td>
</tr>
<tr>
<td>$E_{propane}$</td>
<td>120000</td>
<td>100000</td>
<td>150000</td>
<td>130150</td>
</tr>
<tr>
<td>$A_{decane}$</td>
<td>$10^{20}$</td>
<td>$10^{10}$</td>
<td>$10^{30}$</td>
<td>$6.1 \cdot 10^{14}$</td>
</tr>
<tr>
<td>$E_{decane}$</td>
<td>90000</td>
<td>50000</td>
<td>100000</td>
<td>56140</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.2</td>
<td>0.01</td>
<td>5</td>
<td>0.47</td>
</tr>
<tr>
<td>$k_{ads}$</td>
<td>0.02</td>
<td>0</td>
<td>10</td>
<td>$2.5 \cdot 10^{-3}$</td>
</tr>
<tr>
<td>$k_{des}$</td>
<td>10</td>
<td>0</td>
<td>$10^5$</td>
<td>8.7</td>
</tr>
<tr>
<td>$E_{des}$</td>
<td>20000</td>
<td>1000</td>
<td>50000</td>
<td>22930</td>
</tr>
</tbody>
</table>
exit are presented in Figures 6–10. For the sake of clarity, focus is made on different parts of the cycle.

The determination of the tunable parameters seems to be quite successful, since the computed curves are very close to the measured ones,

Figure 6. Computed vs. measured CO concentrations at outlet, 0–400 s.

Figure 7. Computed vs. measured CO concentrations at outlet, 400–800 s.
Figure 8. Computed vs. measured HC concentrations at outlet, 0–400 s.

Figure 9. Computed vs. measured temperature evolution at converter exit during the full driving cycle. Inlet temperature is also shown in the figure.
especially for CO concentration. Computed temperature evolution at the converter exit is also quite successful. The most discrepancies between experiment and computation can be observed for the HC curve, especially in the first 400 s of the driving cycle test. During this period, the adsorption-desorption phenomena are more intense, and their influence on the measured HC concentration curve is prominent. As seen in Figure 9, this problem also affects the converter exit temperature prediction accuracy. Overall, the attainable accuracy of optimization is comparable, and possibly superior, to the optimization presented in the previous section (based on the SGB tests). More important, the process converged to a single set of kinetics parameters values. This could be attributed to the presence of an ensemble comprising multiple operational modes inside the legislated cycle. This allows for a more reliable parameter optimization. A more profound understanding of the quality of information contributed by different operational modes present in a driving cycle could lead to the definition of custom driving cycles for improved estimation efficiency. This is a subject that deserves further treatment.

Of course, the specific type of algorithm employed (conjugate gradients) is apt to be trapped in local minima, and one must always have this in mind in using the above-deduced sets of tunable kinetics. However, the fact is that even this standard procedure, when used with the necessary care, significantly enhances the applicability of the model described and the associated software (University of Thessaly, 2001) in real-world case studies. An important reduction in the necessary
man-hours devoted to kinetic tuning is already achieved, and improved simulation accuracy is observed.

This promising step in the application of standard optimization techniques in computer-aided tuning of transient catalytic converter models employed as engineering tools in real design tasks sets the stage for further work in the improvement and validation of optimization procedures and the correlation of kinetics determined from SGB versus real vehicle or engine bench-test results. Extension to kinetic tuning for three-way catalytic converter modeling is already underway (Pontikakis and Stamatelos, 2001). The case of three-way catalytic converters requires a more complex reaction scheme and also poses more difficulties to the optimization procedure due to its redox sensitivity. The next step in this process is the application of global optimization procedures like genetic algorithms, following the directions set up in (Glielmo and Santini, 2001). This is expected to partially relieve us from the tendency of the current method to be trapped in local minima by significantly increasing the CPU time required for kinetic parameter estimation.

CONCLUSIONS

The application of mathematical models for the prediction of catalytic converter operation with Langmuir-Hinshelwood type kinetics has been traditionally based on manual kinetic parameter fitting. This fact limited the practical value of the application of such models in complex real-world catalytic converter design.

Previous attempts in the direction of computer-aided kinetic parameter fitting in this field were scarce and limited to the modeling of simple laboratory experiments with synthetic exhaust gas or to simple control-oriented models with real driving cycle data.

In this article, a computational methodology is applied to the kinetic tuning of a mathematical model of transient operation of a diesel catalytic converter with real exhaust gas. Based on employing a standard optimization procedure (conjugate gradients), it was possible to employ the computer in tuning the kinetic parameters of the model based on the results not only of SGB tests but also of real vehicle tests in legislated cycles.

Application of the computer-aided tuning methodology significantly reduces the required manpower for model tuning and allows faster assessment of model predictive ability, leading to suggestions for possible improvement of the experimental protocols and also of the simplified apparent kinetics submodel.

Extension of the methodology developed towards the modeling of other types of catalytic converters, and especially the three-way catalytic converter, is under way. Also, the application of other, more global
optimization procedures, like genetic algorithms, is currently being tested as a means of relieving the tendency of the optimization method to be trapped in local minima.

**NOMENCLATURE**

- \( a_{j,k} \): mass action coefficient of species \( j \) in reaction \( k \)
- \( A \): constant, characteristic of the pore size distribution, \( \text{mol/J} \)
- \( A_k \): pre-exponential factor of reaction rate expression, \( \text{mol} \cdot \text{K}/(\text{m}^3\text{s}) \)
- \( c_p \): specific heat capacity, \( \text{J/(kg \cdot K)} \)
- \( c \): constraints vector
- \( D \): quantity defined in Equation (7) as: \( D = A(R_gT/\beta)^2 \), \( \text{kg/m}^3 \)
- \( e \): error between measurement and computation
- \( E \): activation energy of reaction rate expression, \( \text{J} \)
- \( G \): inhibition term (Table I)
- \( H \): Hessian matrix
- \( h \): convection coefficient, \( \text{W/(m}^2\text{s)} \)
- \( k \): thermal conductivity, \( \text{W/(mK)} \)
- \( k_{srp} \): sorption rate, \( 1/\text{s} \)
- \( k_m \): mass transfer coefficient, \( \text{m/s} \)
- \( K \): inhibition term (Table I)
- \( M \): molecular mass, \( \text{kg/mol} \)
- \( N_{AS} \): number of species that can be adsorbed
- \( N_R \): number of reactions
- \( p \): partial pressure of the adsorbate, \( \text{Pa} \)
- \( p_0 \): saturation pressure of the adsorbate, \( \text{Pa} \)
- \( r \): radial distance from monolith’s axis, \( \text{m} \)
- \( r_k \): rate of reaction \( k \), \( \text{mol/m}^3\text{s} \)
- \( P \): computed quantity
- \( \bar{P} \): measured quantity
- \( R_g \): universal gas constant, \( 8.314 \text{ J/(mol} \cdot \text{K)} \)
- \( R_{rea} \): reaction rate, \( \text{m/s} \)
- \( R_{srp} \): sorption rate, \( \text{m/s} \)
- \( S \): geometric specific surface, \( \text{m}^2/\text{m}^3 \)
- \( t \): Time, \( \text{s} \)
- \( T \): temperature, \( \text{K} \)
- \( u_z \): exhaust gas velocity, \( \text{m/s} \)
- \( v \): eigenvector of Hessian matrix
- \( w \): weight factor, in Equation (12)
- \( x \): concentration in the gas phase
- \( x_{tg} \): concentration in the gas phase at solid-gas interface
- \( x_{t} \): tunable parameters vector
- \( z \): distance from the monolith inlet, \( \text{m} \)

**Greek letters**

- \( \beta \): affinity coefficient
- \( \varepsilon \): volume of micropores per unit volume catalytic converter, \( \text{m}^3/\text{m}^3 \)
- \( \varepsilon \): emissivity factor (radiation)
- \( \theta \): mass of adsorbed species at washcoat, \( \text{kg/m}^2 \)
- \( \lambda \): eigenvalue of Hessian matrix
- \( \sigma \): Stefan-Boltzmann constant, \( \text{W/(m}^2\text{T}^4) \)
Subscripts

ads adsorption
des desorption
eq equilibrium
g gas
liq liquid
r radial direction
rea reaction
s 1. solid, 2. solid-gas interface
srp sorption
tot total
j species j
k reaction k
z axial direction

REFERENCES


