

1D Thermo-Fluid Dynamic Modeling of Reacting Flows inside Three-Way Catalytic Converters

G. Montenegro and A. Onorati
Politecnico di Milano

Copyright © 2009 SAE International

ABSTRACT

In this work a detailed model to simulate the transient behavior of catalytic converters is presented. The model is able to predict the unsteady and reacting flows in the exhaust ducts, by solving the system of conservation equations of mass, momentum, energy and transport of reacting chemical species. The engine and the intake system have not been included in the simulation, imposing the measured values of mass flow, gas temperature and chemical composition as a boundary condition at the inlet of the exhaust system. A detailed analysis of the diffusion stage triggering is proposed along with simplifications of the physics, finalized to the reduction of the calculation time. Submodels for water condensation and its following evaporation on the monolith surface have been taken into account as well as oxygen storage promoted by ceria oxides. Moreover, the interaction between the gas and the deposited water film has been modelled to simulate the effect of water dragging inside the monolith channel. The validation of the model has been carried out on the basis of experimental measurements during hot and cold start at fixed engine operating conditions.

INTRODUCTION

The reduction of air pollution is an issue of the utmost importance in the field of automotive powertrain. Exhaust gases containing compounds such as carbon oxide, nitric oxides and unburned hydrocarbons are subjected to regulations imposing their conversion to harmless compounds before being discharged into

the atmosphere. To comply with these limits the solution which allows the conversion of pollutants at low energy requirements, resulting in cost effective systems, is the adoption of catalysts in the engine exhaust system. The use of the correct catalyst is of primary importance, since the abatement efficiency depends on the thermal and chemical behavior of that device. Moreover, the presence of the catalyst along the exhaust system causes an increase of the back pressure which penalizes the fuel consumption. It is therefore mandatory to carefully optimize the position of the catalytic converter inside the exhaust system, in order to find a good balance between quick chemical activation, low thermal stress and low fuel consumption penalty. In this scenario, car manufacturers are nowadays experiencing the usage of simulation tools to study the interaction between the engine and the after-treatment devices. As a matter of fact the adoption of simulation tools is particularly useful during the design phase, since it permits to simulate different exhaust configurations without the need of building the system itself, resulting in time and cost savings. There are several levels of accuracy which can be reached during the optimization of the exhaust system, namely 0D, 1D and multiD. Zero dimensional approaches allow to study the system on the basis of the mean exhaust gas mass flow, reducing the reacting device to an element which operates the chemical conversion according to kinetic parameters given as input. On the other hand the most complex approach, the 3D one, is typically addressed whenever an issue concerning the flow distribution needs to be studied. This kind of analysis is usually steady state, and can recur to different levels of detail, from the microscale

approach [1] to the macroscale [2] one, however all of them are characterized by a considerable computational time. This drawback confines the usage of CFD codes to simulate steady state points, associated to a specific operating condition. In between these two approaches, stays the 1D level of approximation, which allows to perform the simulation of the chemical and thermo-fluid dynamic behavior of the whole exhaust system during both unsteady and steady state operating condition, relying on provided kinetic parameters. The simulation of the thermo-fluid dynamic behavior of the complete exhaust system during a Driving Cycle (NEDC or FTP), for example, is more practicable when using a 1D simulation code, as it requires a computation of at least 1180 seconds of successive operating conditions [3, 4]. The possibility of simulating a complete driving cycle becomes fundamental when the purpose is the optimization of the exhaust thermal transient, finalized to the quickest activation of the catalyst and consequently to the reduction of the pollutant emissions. Therefore, the 1D numerical simulation allows, with a reasonable effort, to study the influence on the light-off time of specific devices, such as small catalysts, insulated ducts, flanges or dented pipes [5].

This paper describes a method to calculate the warm-up of the exhaust after-treatment system of a S.I. engine during specific test cycles, taking into account the effect of the chemical reactions occurring in the catalytic converters. The code used for the simulations has been developed in-house by the authors at the Politecnico di Milano [6, 7]. The model is able to predict the unsteady and reacting flows in the exhaust ducts, by solving the system of conservation equations of mass, momentum, energy and transport of reacting chemical species. The engine and the intake system have not been included in the simulation, imposing the measured values of mass flow, gas temperature and chemical composition as a boundary condition at the inlet of the exhaust system. The imposed properties of the gas are then transported along the duct system, taking into account the instantaneous heat transfer between the gas and the pipe walls and the chemical reactions occurring in the catalyst. The model takes into account also the effects of moisture condensation onto the catalyst walls, and its subsequent evaporation. This process gives rise to a flat temperature profile during the heat up of the catalyst, causing a delay in the chemical activation of the converter. To validate the predictive capability of the heat transfer model an experimental campaign has been carried out at IFP (Institut Francais du Petrole) labs considering two different type of catalyst: one with a ceramic substrate and another one with a metallic substrate.

FLUID DYNAMIC MODEL FOR UNSTEADY REACTING FLOWS

The code used in this work is GASDYN, a 1D thermo-fluid dynamic model that is being continuously developed and enhanced by the authors at the Politecnico di Milano; the main features of the numerical code have already been fully described in previous works [6, 8]. The model has been developed for the simulation of internal combustion engines coupled to their intake and exhaust systems. This allows for a detailed analysis of the fluid dynamic, thermal and chemical behaviors of the whole system. The differential equations expressing the mass, the momentum and the energy conservation for each computational node are written as [9]:

$$\frac{\partial(\rho F)}{\partial t} + \frac{\partial(\rho u F)}{\partial x} = 0 \quad (1)$$

$$\frac{\partial(\rho u F)}{\partial t} + \frac{\partial(\rho u^2 F + p F)}{\partial x} = p \frac{\partial F}{\partial x} - \frac{2}{D} \rho u |u| f_w F \quad (2)$$

$$\frac{\partial(\rho e_0 F)}{\partial t} + \frac{\partial(\rho e_0 u F + u p F)}{\partial x} = \rho (q_{re} + q) F \quad (3)$$

The source term q_{re} in the energy equation is the heat released by the chemical reactions occurring in the gas phase (per unit mass per unit time) and q is the sum of the convective and radiative heat transferred from the gas to the pipe walls. The information concerning the varying chemical composition along the system is accounted for by solving the mass conservation equation for each chemical specie considered:

$$\frac{\partial(\rho Y_i F)}{\partial t} + \frac{\partial(\rho u Y_i F)}{\partial x} = \rho \dot{Y}_i F \quad (4)$$

where $Y_j = m_j/m$ is the mass fraction in the control volume for the j -th specie and $\dot{Y}_j$ is the rate of variation of mass fraction due to chemical reactions involving the j -th specie. The internal energy for the j -th specie of the mixture is expressed by means of polynomial relationships, hence the specific heat depends on both gas the temperature and chemical composition. The system of conservation equations represents a quasi-linear hyperbolic problem which can be solved by means of shock-capturing numerical methods: in the performed simulations, symmetric finite difference techniques with second order accuracy, such as the MacCormack predictor-corrector method and the two-step Lax-Wendroff method (with the addition of flux-limiting techniques) have been used.

THE THREE WAY CATALYST MODEL

The computational model developed allows the simulation of chemical converters such as the Three Way Catalyst and the Diesel Oxidation Catalyst, both on

chemical and fluid dynamic point of view [10]. In particular, the typical honeycomb geometry of the monolith is represented by means of a single tiny channel whose dimensions are calculated on the basis of standard descriptive parameters such as cell density, wall thickness, open frontal area, monolith diameter and length. The system of equations (Eq.1-3) is thus applied to a single channel and the solution extended to all the channels constituting the monolith. A specific boundary condition is used to split the flow from the upstream pipe to the vast number of channels of the monolith, accounting for the concentrated pressure losses at the inlet and outlet. This work is mainly focused on the simulation of different types of three way catalysts; the chemistry proposed, therefore, takes into account various reactions, involving the main chemical species contained in the exhaust gas [11]:

- 1) $CO + \frac{1}{2}O_2 \rightarrow CO_2$
- 2) $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$
- 3) $C_3H_6 + \frac{4}{5}O_2 \rightarrow 3CO_2 + 3H_2O$
- 4) $C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
- 5) $CO + NO \rightarrow CO_2 + \frac{1}{2}N_2$
- 6) $C_3H_6 + 3H_2O \rightarrow 3CO + 6H_2$
- 7) $C_3H_8 + 3H_2O \rightarrow 3CO + 7H_2$
- 8) $CO + H_2O \rightarrow CO_2 + H_2$
- 9) $NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O$
- 10) $C_3H_6 + 9NO \rightarrow 3CO_2 + 3H_2O + 4.5N_2$
- 11) $C_3H_8 + 10NO \rightarrow 3CO_2 + 4H_2O + 5N_2$
- 12) $Ce_2O_3 + \frac{1}{2}O_2 \rightarrow 2CeO_2$
- 13) $Ce_2O_3 + NO \rightarrow 2CeO_2 + \frac{1}{2}N_2$
- 14) $CO + 2CeO_2 \rightarrow Ce_2O_3 + CO_2$
- 15) $H_2 + 2CeO_2 \rightarrow Ce_2O_3 + H_2O$
- 16) $C_3H_6 + 12CeO_2 \rightarrow 6Ce_2O_3 + 3CO + 3H_2O$
- 17) $C_3H_8 + 14CeO_2 \rightarrow 7Ce_2O_3 + 3CO + 4H_2O$

The model takes into account the oxidation of CO, H₂, C₃H₆ and C₃H₈ (representatives of fast and slow oxidizing hydrocarbons, reactions 1-4), the NO reduction (reaction 5), two steam reforming reactions (reactions 6, 7), the water gas shift reaction (reaction 8), the reaction between the H₂ generated by the steam reforming reactions and the NO (reaction 9) and the reaction between hydrocarbons and NO (reactions 10 and 11) [12]. The oxygen storage and release process promoted by the Ceria oxides contained in the

wash-coat (reactions 12-17) is also considered in the model.

The internal surface of the monolith channels is coated with a porous substrate of alumina. Typically

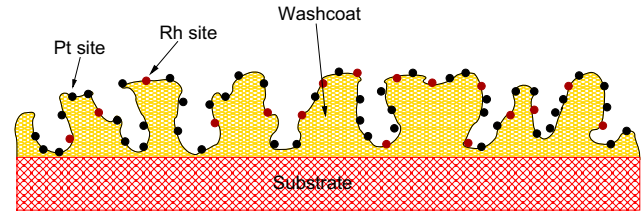


Figure 1: Longitudinal section of the monolith channel showing the washcoat layer deposited onto the substrate material.

the amount of washcoat deposited onto the monolith walls is provided as a specification of the catalyst in terms of washcoat loading per unit volume of the catalyst (γ). The main feature of the washcoat is the high specific surface (α) as a consequence of its high porosity. This property is indicated as m² of surface per grams of substance. The deposition of the washcoat onto the substrate increases the surface available for the chemical reactions, giving rise to the so called physical surface (S_{phys}):

$$S_{phys} = \alpha \gamma V_{cat} \quad (5)$$

The precious metals, used as catalytic substances, are deposited over this surface. In Figure 1 it is shown a section of the catalyst tiny channel with the noble metals (Platinum and Rhodium for simplicity sake) deposited onto the washcoat. The surface available for the reactions (the active surface) is therefore represented by the PGM sites, whose mass is around 0.1% (θ_w) in weight of the washcoat. This area is lower than the physical one and the ratio between the two can be calculated on the basis of the PGM loading and of an average Pt and Rh particle size Φ_{site} . For Platinum sites this ratio can be estimated as follows:

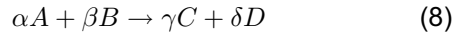
$$\phi_{Pt} = \frac{A_{pt}}{S_{phys}}. \quad (6)$$

A_{pt} depends on the number of active sites, which is calculated from the weight fraction of Pt and Rh and their molecular weight

$$A_{Pt} = \frac{\gamma V_{cat} \theta_w \Phi_{Pt}}{M_{w,Pt}} \quad (7)$$

The conversion of reactants into products involves convective mass transfer of reactants through the wash-coat, towards the catalytic surfaces, as well as adsorption of reactants and desorption of products at the active sites. To account for the competition of the chemical species in activating on the active sites, the

Langmuir-Hinshelwood theory has been adopted. For a generic reaction:



the reaction rate can be expressed as follows:

$$r_i = \gamma \alpha V_{cat} \phi_{Pt,Rh} \cdot k_i \frac{C_{s,a} C_{s,b}}{G_i} E_{q_i} \quad (9)$$

where:

$$E_{q_i} = 1 - \frac{C_{s,c}^\delta \cdot C_{s,d}^\gamma}{C_a^\alpha \cdot C_b^\beta K_p(T)} \quad (10)$$

The term G_i is the inhibition factor, it takes into account the impact, on the overall kinetics, of the adsorption and desorption of reactants and products on the active sites. This term is directly proportional to the wash-coat temperature T_w and to the concentration of the reactants involved in the reactions:

$$G_i = T_s (1 + K_1 C_{s,CO} + K_2 C_{s,CHC})^2 (1 + K_3 C_{s,CO}^2 C_{s,CHC}^2) \quad (11)$$

$$(1 + K_4 C_{s,NO}^{0.7}) \quad (12)$$

The terms k_i and K_i are Arrhenius type kinetic constants, which regulate the reaction and adsorption mechanisms and depend on the substrate temperature, the activation energy and the pre-exponential factors A_i and $A_{ad,i}$:

$$k_i = A_i \exp\left(-\frac{E_i}{RT_w}\right) \quad (13)$$

$$K_i = A_{ad,i} \exp\left(-\frac{E_{ad,i}}{RT_w}\right). \quad (14)$$

Depending on the typology of the chemical converter to be studied, a suitable reaction scheme has to be considered in order to reproduce the behavior of the converter under different operating conditions. It is also important to give reasonable values of the pre-exponential factors, which can be used as tunable factors to fit the specific catalyst that has to be simulated [13].

OXYGEN STORAGE MODEL

Cerium dioxide is a standard component of the Three Way Catalyst wash-coat that is usually present in quantities of up to 25%. It is used for different purposes such as the need of alumina stabilization. It also promotes the steam reforming reactions, the noble metal dispersion and noble metal reduction. However, an important function of ceria in the TWC is the oxygen storage, which is possible through a transition cycle between two different states of oxidation Ce^{4+} and Ce^{3+} [14]. The effect of the oxygen storage is evident when the engine operating conditions vary alternately from lean to rich mixture conditions and vice-versa. Therefore, during lean operating conditions,

reactions 9 and 10 are responsible for the oxidation of the ceria contained in the wash-coat. In particular, reaction 10 becomes more important during the first period of the cold start transient due to the high oxidation capacity of the nitrogen monoxide. Reactions 12-17 are responsible for exploiting the stored oxygen to oxidize the unburned hydrocarbons, hydrogen and carbon monoxide during rich operating conditions. The rate of each reaction is proportional to the concentration of the gaseous species involved in the reaction, as shown in the following equations [15]:

$$r_{12} = k_{12} C_{s,O_2} (1 - \psi) \quad (15)$$

$$r_{13} = k_{13} C_{s,NO} (1 - \psi) \quad (16)$$

$$r_{14} = k_{14} C_{s,CO} \psi \quad (17)$$

$$r_{15} = k_{15} C_{s,H_2} \psi \quad (18)$$

$$r_{16} = k_{16} C_{s,C_3H_6} \psi \quad (19)$$

$$r_{17} = k_{17} C_{s,C_3H_8} \psi \quad (20)$$

where the variable ψ expresses the oxidation state of the wash-coat, given by the balance between the activity of the storage and release reactions:

$$\frac{\partial \psi}{\partial t} = r_{12} + r_{13} - (r_{14} + r_{15} + r_{16} + r_{17}). \quad (21)$$

ψ is evaluated as the ratio between the oxidized ceria Ce_2O_3 and the total moles of ceria in the wash-coat [16]:

$$\psi = \frac{\text{moles } CeO_2}{\text{moles } CeO_2 + 2 \text{ moles } Ce_2O_3}. \quad (22)$$

The chemical model considers the local oxidation state of the wash-coat for every calculation node. In this way the different parts of the catalyst are governed by the different chemical activity. The values of the pre-exponential factors of the Arrhenius terms can be determined from experimental measurements carried out on catalyst samples. In this work values available in the literature have been considered [15].

MASS TRANSFER MODEL

The study of the thermal transient of the exhaust system cannot be carried out on the basis of a simple kinetic approach. The temperatures reached inside the catalyst during the NEDC cycle range from the cold start value up to approximately 1100 K in the extra urban phase of the test. In particular, during the first 50 seconds of the driving cycle the substrate temperatures are so low that the kinetics is dominant in comparison to the mass diffusion processes. On the other hand, at temperatures around 600-700 K the kinetics is sustained by the high temperature, while the diffusion of the reactants through the solid phase represents a bottleneck for the whole process [17]. For this reason a specific submodel is used for the diffusion of the reactants through the wash-coat, to calculate

the concentrations of the reactants in the solid phase. These concentrations are different from those in the gas phase and can be calculated once the number of moles of each chemical component that diffuses to the wash-coat pores is known. Since these quantities are function of the specie concentration gradient, the equation that has to be solved is implicit, therefore an iterative algorithm has been adopted. To simplify this calculation, it has been assumed that there is no accumulation of mass inside the wash-coat. It means that all the chemical compounds that diffuse into the pores are supposed to react on the active sites of the catalyst. The system of equations (one for each chemical component considered in the model) can be summarized as follows [18]:

$$\frac{\rho_g}{M_g} S k_{m,i} (C_{g,i} - C_{s,i}) = r_i \quad (23)$$

where $k_{m,i}$, which is the mass transfer coefficient of the i -th chemical compound, is calculated by means of the heat-mass transfer analogy [19]:

$$k_{m,i} = \frac{\mathcal{D}_i}{D} S_{lim} \left(1 + 0.095 \frac{D \cdot Re \cdot S_c}{A} \right). \quad (24)$$

The expression of the mass transfer coefficient described in Eq. 24 is a function of the Schmidt number ($S_c = \mu/\rho\mathcal{D}$), of the Reynolds number, of the hydraulic diameter D , of the components diffusion coefficient and of the active catalytic surface A . The S_{lim} is the limiting Sherwood number, which is equal to 3,236 in case of square section. The diffusion coefficient for one component in a mixture of n components is given by the following equation [19]:

$$\mathcal{D}_i = \frac{1 - C_i}{\sum_{j=2}^{N_s} \left(\frac{C_j}{\mathcal{D}_{ij}} \right)} \quad (25)$$

where the binary gas diffusion $\mathcal{D}_{ij}$ coefficient for the i -th gas diffusing through a mixture of gases i and j is calculated by means of the Chapman-Enskog equation [19]:

$$\mathcal{D}_{ij} = 1.85 \cdot 10^{-3} \frac{T^{1.5} \left(\frac{1}{M_i} + \frac{1}{M_j} \right)^{0.5}}{P \left(\frac{\sigma_i + \sigma_j}{2} \right)^2 \Omega_D}. \quad (26)$$

The expression of the binary gas diffusion coefficient reveals a dependence of the diffusivity on the power of 1.5 of the gas temperature, pointing out the higher influence it has on the global kinetics of the reactions at high temperature levels. The diffusivity is also a function of the molar weight (M_i), of the collision integral (Ω_D), evaluated on the basis of the Lennard-Jones potentials (ϵ_0), and of the collision diameter (σ_i) as suggested in the literature [19]. Approximated formulas can be also used to express the value of the

collision integral, rather than exploiting tabulated values valid within certain ranges of temperature. The authors used the following correlation during the calculations:

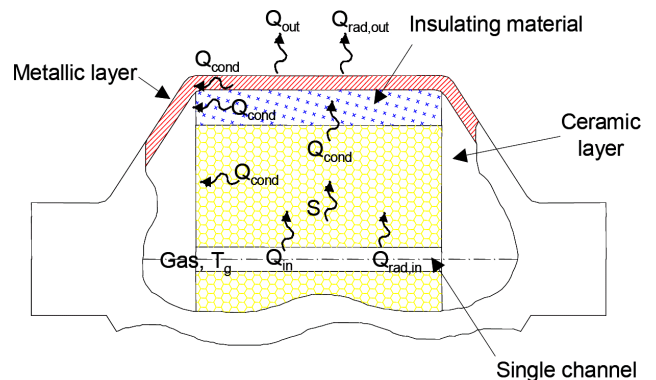
$$\begin{aligned} \Omega_D = & \left(\frac{1.06036}{\frac{kT}{\epsilon_0} 0.15610} \right) + \left(\frac{0.19300}{e^{0.47635 * \frac{kT}{\epsilon_0}}} \right) \\ & + \left(\frac{1.03587}{e^{1.52996 * \frac{kT}{\epsilon_0}}} \right) + \left(\frac{1.76474}{e^{3.89411 * \frac{kT}{\epsilon_0}}} \right) \end{aligned} \quad (27)$$

The iterative procedure to calculate the solid concentration of the reactants may be computationally demanding if the simulation of a long real time period is addressed. To achieve a reduction of the computational time, a simplified approach was developed on the basis of the Baruah's theory [19]. The main assumption is that when the global kinetics becomes controlled by the mass transfer process, all the reactants diffusing into the washcoat are going to react on the active sites and consequently their concentration in the solid phase can be considered small. This means that the concentration gradient between the gas phase and the solid phase of the reactants can be approximated to the gas phase concentration itself. Therefore, the reaction rate will be given by the minimum value between the reaction rate expressed by the Arrhenius expression (Eq. 9) and the rate of mole transfer of the reactants from the gas to the solid phase. The mole transfer rate is expressed as follows:

$$\dot{K}_{m,i} = K_{m,i} \frac{\rho Y_i}{M_{w,i}} S. \quad (28)$$

It expresses the number of moles per unit time of the i -th specie diffusing from the gas into the solid phase through the surface S .

HEAT TRANSFER MODEL



The prediction of the thermal transient of the exhaust system can be carried out considering the heat transferred between the gas and the walls in the energy balance of the gas, as a source term in Eq. 3 and in