



ATI 2015 - 70th Conference of the ATI Engineering Association

## Numerical simulation of the flow field and chemical reactions within a NSC diesel catalyst

Francesco Fornarelli\*, Sergio Camporeale, Ruggiero Dadduzio, Bernardo Fortunato, Marco Torresi

*Politecnico di Bari, Dipartimento di Meccanica, Matematica e Management  
Via Edoardo Orabona 4, 70125 Bari, Italy*

---

### Abstract

In the present work three-dimensional steady and unsteady numerical simulations of the flow field and chemical reactions within aNO<sub>x</sub> Storage Converter (NSC) diesel catalyst have been made. In the first part of the paper, only the flow characteristics within a catalyst have been investigated by mean of a steady three-dimensional Reynolds-Averaged Navier-Stokes approach and a transport equation for each of the incoming chemical species. For flow simulations, the catalyst volume has been split in three zones: inlet, catalytic monolith, treated as porous media, and outlet, medium. The results have been reported in three different working points. Evidences on how the non-uniform flow distribution affects the catalyst efficiency have been described. In the second part, the fluid-dynamic solver has been coupled with a chemical reaction mechanism in order to catch the chemical surface reaction within a NSC catalyst. This coupled model has been validated according to the literature. Volumetric and superficial species concentration have been calculated imposing the site density and the kinetic of the reactions on a substrate Ba/Al<sub>2</sub>O<sub>3</sub>. NO<sub>x</sub> spatial distributions within the catalyst during a dsorption phase are reported. The model represent a reliable tool to investigate in detail the complex flow/chemistry interaction within the modern diesel engine catalysts.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of the Scientific Committee of ATI 2015

*Keywords:* catalyst; NO<sub>x</sub> storage; CFD; kinetic modeling

---

\* Corresponding author. Tel.: +390805963627; fax: +39 080 596 3411.

*E-mail address:* francesco.fornarelli@poliba.it.

## 1. Introduction

Stringent air pollution regulations for vehicular emission of diesel engines push scientists and engineers to develop efficient exhaust gas after-treatment techniques for NO<sub>x</sub> abatement. Selective Catalytic Reduction (SCR), Nitrogen oxide Storage-reduction Catalyst (NSC) are devices able to efficiently reduce the final NO<sub>x</sub> emissions in lean-burn diesel engines. Several experimental and numerical works have been focused on modeling the chemical reactions involved in NO<sub>x</sub> storage and reduction processes [1,2]. Although accurate chemical models can be found in the literature, usually several empirical parameters have to be set in order the model findings to match and the experimental measurements. Conventionally, a NSC catalyst is made of an inflow diffuser, a ceramic monolith and an outlet nozzle. The ceramic monolith consists of several channels, whose walls are coated with a thin wash coat. Experimental and numerical works show that the catalyst geometry can heavily affect its efficiency [3,4]. This evidence suggests that the three-dimensional flow field plays a key role in the catalyst performance. Indeed, in three-dimensional complex geometries, the flow field may induce a non-uniform flow distribution in the porous media where the chemical reactions take place [5]. Ideally, in a converter the flow at the inlet of the monolith should be uniform in order to equally distribute the flow in all the channels. Therefore, inlet pipe curvature, inlet diffuser cone angle and unsteadiness of inflow coming from engine exhaust, affect the fluid flow and can induce boundary layer separation from the diffuser wall [6]. It causes higher flow velocity in the central channels with respect to the peripheral ones.

NSC catalyst works under alternating lean or rich condition in order to trigger storage or reduction phase, respectively. These features of the NSC catalysts are managed by active control of the combustion process. Actually, regeneration periods need to be controlled through an estimation of the catalyst performance. Therefore a realistic estimation of the catalyst saturation curve of NO<sub>x</sub> adsorption is necessary in order to evaluate the regeneration time interval. In order to develop a reliable model to describe the chemical behavior of NSC catalyst, several reaction mechanisms have been proposed and tested [7, 8, 9]. The chemical behavior of a NSC catalyst can be described with a four steps mechanism: (I) oxidation of NO to NO<sub>2</sub> on Pt, (II) NO<sub>2</sub> storage on BaO, (III) NO<sub>x</sub> release, and (IV) NO<sub>x</sub> release to N<sub>2</sub>. The comparison of the 0/1D models with experimental test cases leads to an accurate reconstruction of the kinetic model parameters. In order to make richer the numerical analysis of the flow within an NSC catalyst a complex chemical mechanisms has been implemented and coupled with the flow solver. The model has been validated reproducing the experiments of Olsson et al. [7]. Here the preliminary results of this model applied to the real catalyst geometry in a working point are reported.

### Nomenclature

$\rho$	mixture density
$\vec{v}$	velocity vector
$p$	static pressure
$\bar{\tau}$	viscous stresses
$k$	turbulent kinetic energy
$\varepsilon$	turbulent dissipation
$G_i$	gas phase species
$S_i$	surface adsorbed species

$N_g$ and $N_s$	total number of gas and surface species
$g'_{i,r}, s'_{i,r}, g''_{i,r}, s''_{i,r}$	stoichiometric coefficients
$\mathcal{R}_r$	reaction rate for the $r^{\text{th}}$ reaction
$k_{f,r}$ and $k_{b,r}$	forward and backward rate constant for the $r^{\text{th}}$ reaction
$\Gamma$	site density
$\varepsilon_o$	efficiency uniformity rate

## 2. Numerical Modeling

### 2.1. Flow numerical model

The computational domain of the catalytic converter geometry used has been obtained reproducing an existing commercial device. By mean of three-dimensional graphic techniques a reverse engineering of the device has been performed. In figure 1 the three dimensional model of the catalyst has been reported and the main dimensions are listed in table 1.

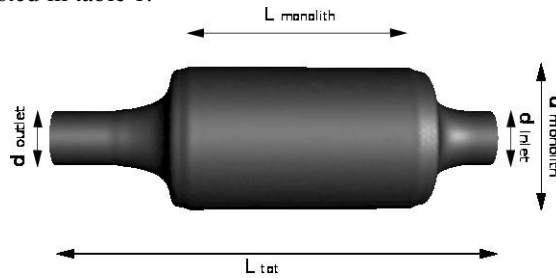


Figure 1 Three-dimensional model of the catalytic converter. The main dimensions are reported.

Table 1. Main dimensions of the catalytic converter.

$L_{tot}$	486 mm
$L_{monolith}$	221 mm
$d_{inlet}$	59 mm
$d_{outlet}$	57 mm
$d_{monolith}$	152 mm

The steady flow within the inlet diffuser and the outlet nozzle has been numerically simulated by means of the Reynolds Averaged Navier-Stokes equations. The gas mixture is assumed ideal and incompressible, being the Mach number lower than 0.1. Density and viscosity variations due to the mixture composition and temperature are taken into account in the model. The governing equations read:

$$\nabla \cdot (\rho \vec{v})$$

$$\nabla \cdot (\rho \vec{v} \vec{v}) = \nabla p + \nabla \cdot \bar{\tau} + f(k, \varepsilon) \quad (1)$$

$$\frac{\partial}{\partial t} (\rho E) + \nabla \cdot (\vec{v} (\rho E + p)) = \nabla \cdot \left( k_{eff} \nabla T - \sum_j h_j \bar{J}_j + (\bar{\tau}_{eff} \cdot \vec{v}) \right) + S_h$$

where  $\rho$  is the mixture density,  $\vec{v}$  the velocity vector,  $p$  the pressure,  $\vec{\tau}$  the viscous stresses,  $k_{eff}$  is the effective conductivity,  $\vec{J}_j$  the diffusion flux of species  $j$  and  $S_h$  the energy sources which includes the heat of chemical reaction. A standard  $k - \epsilon$  turbulence model has been applied with standard wall function. The turbulent flow at the inlet is assumed to be fully developed and the turbulent intensity at the inflow has been estimated through the turbulent intensity and hydraulic diameter method. The monolith is modelled adding source terms to the fluid flow equations. Three working points have been considered and the boundary conditions are set according to the experimental data from real light-vehicle conditions (see Table 2).

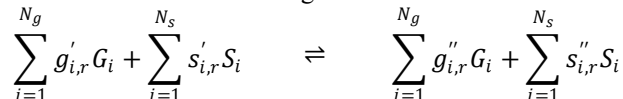
Table 2. Details of the three working points reproduced in the simulations derived by experimental data.

Working points	Units	1	2	3
Flow Rate	kg/h	77	122	200
Temperature	°C	175	210	336
CO	ppm	1.19	1.38	1.52
CO <sub>2</sub>	ppm	52946	49045	83519
NO <sub>x</sub>	ppm	53.28	76.31	125.21
NO	ppm	49.26	68.12	63.07
O <sub>2</sub>	ppm	136118.4	141172.4	93890.9
N <sub>2</sub>	ppm	810850.2	809659.3	822457.4
H <sub>2</sub> O	ppm	52133.9	49066.4	81896.0
HC	ppm	30.9	45.6	6.0

### 2.2. Chemical kinetic model

The chemical reactions are modeled by mean of a mean-field kinetic model. In the present work no volumetric reactions are considered, only surface reaction are involved in the model.

The generic  $r^{th}$  surface reaction can be written in its general form as follows:



where  $G_i$  and  $S_i$  are, respectively, the gas phase species and the surface adsorbed species,  $N_g$  and  $N_s$  the total number of these species,  $g'_{i,r}$ ,  $s'_{i,r}$ ,  $g''_{i,r}$  and  $s''_{i,r}$  the stoichiometric coefficients, respectively, for each reactant and product species  $i$ . The rate of the  $r^{th}$  reaction,  $\mathcal{R}_r$ , is

$$\mathcal{R}_r = k_{f,r} \prod_i^{N_g} [G_i]_{wall}^{g'_{i,r}} \prod_j^{N_s} [S_j]_{wall}^{s'_{j,r}} - k_{b,r} \prod_i^{N_g} [G_i]_{wall}^{g''_{i,r}} \prod_j^{N_s} [S_j]_{wall}^{s''_{j,r}}$$

where  $[ ]_{wall}$  represents molar concentrations of adsorbed species on the surface walls,  $k_{f,r}$  and  $k_{b,r}$  represent, respectively, the forward and the backward rate constants for reaction  $r$ , computed by the Arrhenius expression such as  $k_{f,r} = A_r T^{\beta_r} e^{-E_{a,r}/RT}$ , where  $A_r$  is the preexponential factor,  $E_{a,r}$  is the activation energy,  $R$  is the molar gas constant (8314,472J/(kmol K)) and  $\beta_r$  the temperature exponent. In order to modify the surface reaction rate as a function of the species site coverages, the forward rate constant is evaluated as follows:

$$k_{f,r} = A_r T^{\beta_r} e^{-E_{a,r}/RT} \prod_{i_{site}} (10^{Z_i \eta_{i,r}}) (Z_i^{\mu_{i,r}}) (e^{-\epsilon_{i,r} Z_i / RT})$$

where  $\varepsilon_{i,r}$  is the activation energy dependent from the fraction of surface sites covered by species  $i$ ,  $Z_i$  defined as  $Z_i = [S_i]/\Gamma$  in which  $\Gamma$  represents the surface site density. On the reacting surfaces, the mass flux of each gas species due to diffusion and convection to/from the surface is balanced with its rate of consumption/production. The kinetic model used contains five different reversible reactions reported in Table 3. The kinetic parameters, considering the site density  $\Gamma = 5,4734 \cdot 10^{-6} \text{ kmol/m}^2$ , are referred to those specified in Olsson et al. [7].

Table 3. Reversible reaction considered in the model of NSC storage condition, where S represents the BaO site.

R1	$\text{NO}_{2(g)} + \text{S}$	$\rightleftharpoons$	$\text{NO}_2\text{-S}$
R2	$\text{NO}_2\text{-S}$	$\rightleftharpoons$	$\text{O-S} + \text{NO}_{(g)}$
R3	$\text{NO}_{2(g)} + \text{O-S}$	$\rightleftharpoons$	$\text{NO}_3\text{-S}$
R4	$\text{NO}_{2(g)} + \text{NO}_3\text{-S}$	$\rightleftharpoons$	$\text{Ba}(\text{NO}_3)_2$
R5	$2\text{S-O}$	$\rightleftharpoons$	$2\text{S} + \text{O}_{2(g)}$

### 3. Results

#### 3.1. Flow characteristics within the catalyst.

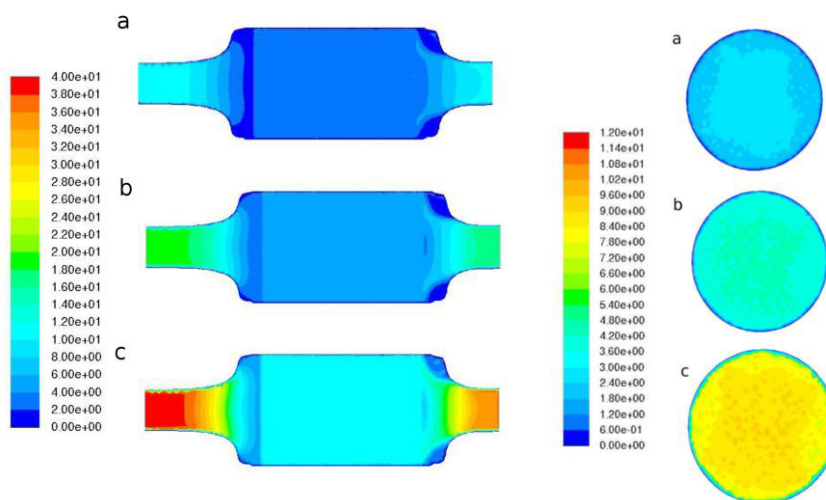


Figure 2. Contours of the velocity magnitude (m/s) within the catalyst for case 1 (a), case 2 (b) and case 3 (c). On the left: longitudinal section. On the right: transverse section of the catalyst at the inlet position of the matrix

In figure 2 the contours of the velocity magnitude in the meridian section of the catalytic converter and the axial velocity distributions at the monolith inlet section are reported. In the inflow zone a recirculation zone occurs because of the increasing area of the duct. The flow field at the monolith inlet is affected by a non-uniform distribution that indeed affects the efficiency of the catalyst. The non-uniform distribution of the inlet velocity gives a qualitative description of the efficiency loss of the catalytic converter. In order to have a quantitative estimate of the efficiency loss, due to the non-uniform distribution, the catalyst efficiency can be related to the flow quantities. The efficiency ( $\varepsilon'$ ) of a chemical reaction can be related to the resident time ( $t$ ) of a fluid particle within the monolith channel as follows  $\varepsilon' = 1 - e^{-at}$  where  $t =$

$l_{ch}/v_{ch}$ , being  $l_{ch}$  and  $v_{ch}$  the channel length and the channel mean velocity, respectively. The constant  $a$  can be assigned imposing a theoretical efficiency of  $\epsilon_{th} = 0.95$  for the case 1 and the mean velocity  $v_x$  of a single channel for a uniform mass flow distribution in the monolith, therefore  $a = -v_x/l_{ch} \ln(1 - \epsilon_{th})$ . In order to measure the effect of the non-uniform flow distribution on the efficiency of the catalyst we propose a new parameter to measure the efficiency uniformity rate ( $\epsilon_o$ ) at the inlet section of the monolith:

$$\epsilon_o = \frac{1}{A} \int \frac{\epsilon' v_x}{\epsilon_{th} \bar{v}_x} dA \quad (5)$$

where  $\bar{v}_x$  is the mean stream-wise velocity. In figure 3 the values of  $\epsilon_o$  with respect to the mass flow rate in the three working points are reported.

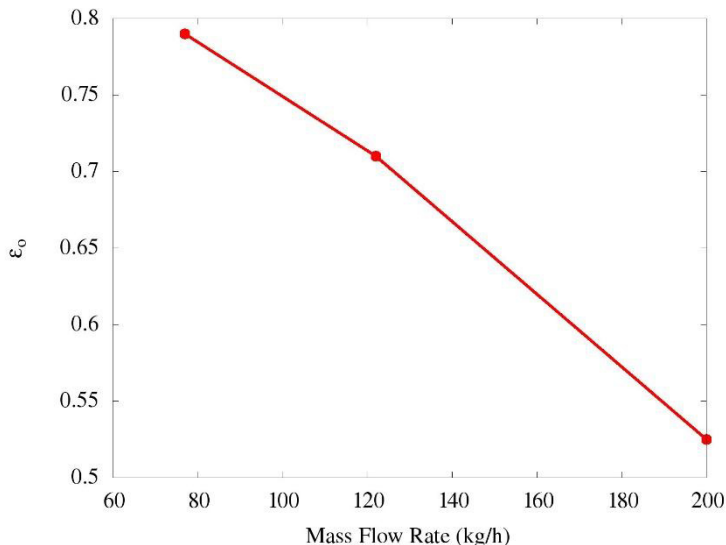


Figure 3. Efficiency uniformity rate based on equation (5) respect to the mass flow rate.

It appears that the efficiency uniformity rate decreases with decreasing of the resident time of the fluid particles. Moreover the efficiency in case 1 is the 79% of the theoretical one, according to the non-uniform distribution of the flow at the monolith inlet. The abrupt expansion of the inlet geometry mismatch the inflow path-lines producing an annular recirculation zone, which causes a non-uniform distribution of the mass flow rate in the monolith channels, hence a performance downgrading of the catalyst efficiency.

### 3.2. Flow/Chemical numerical simulation

The three dimensional flow solver has been coupled with a chemical solver to take into account the superficial chemical reaction on the catalyst surfaces as described in section 2. In an NSC catalyst the adsorption of the  $NO_x$  play a key role in terms of characterization of the performance of the catalyst itself. Therefore, the chemical mechanism that involves the  $NO_x$  influences the catalyst behaviour. The present numerical model has been validated reproducing the experiment of Olsson et al. [7]. This test consists in  $NO_x$  storage process in a simple cylindrical NSC catalyst where a  $NO_2$  flow is imposed at the inlet. In fig.4 the time plot of the  $NO_x$  volumetric concentrations and the surface coverages have been compared to the numerical and experimental findings, showing a fairly good agreement.

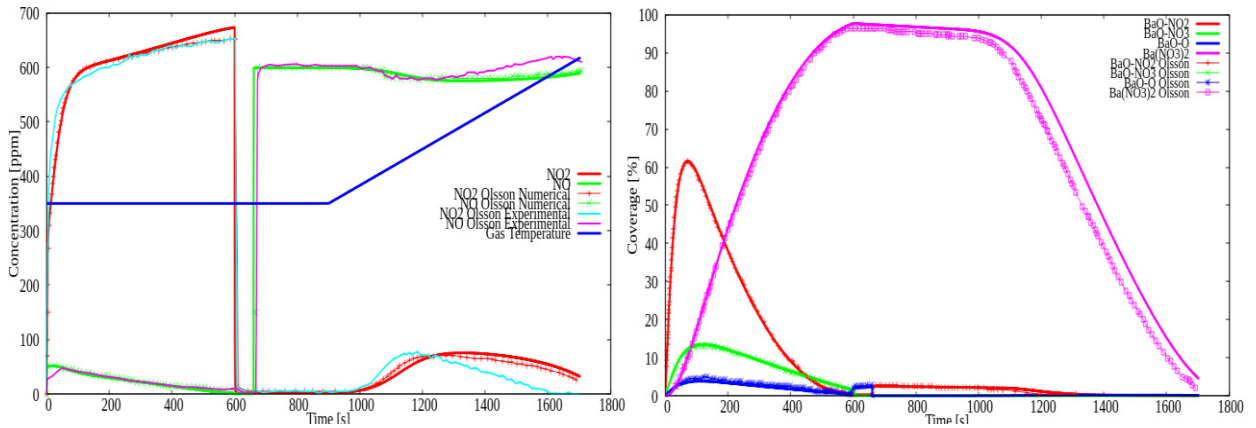


Figure 4. Validation of the model reproducing the experimental and numerical findings of Olsson [7]. On the left hand side the time series of the volumetric concentrations of the NOx are reported. On the right hand side the percentage of surface coverage of the species are reported.

After validation, the coupled model has been applied to the catalytic converter. The monolith has been treated as a porous medium by imposing the actual surface/volume ratio in order to take into account the superficial reactions. The site density has been imposed to be equal to the test case of Olsson  $\Gamma = 5,4734 \cdot 10^{-6} \text{ kmol/m}^2$ . The chemical reactions have been coupled to the above mentioned flow solver in order to reproduce the species distribution within the catalyst. According to the surface reaction model adopted in the present case an absorption of NO and NO<sub>2</sub> through the catalyst is expected. In figure 5 the mole fractions of both NO and NO<sub>2</sub> are shown confirming the above mentioned behaviour.

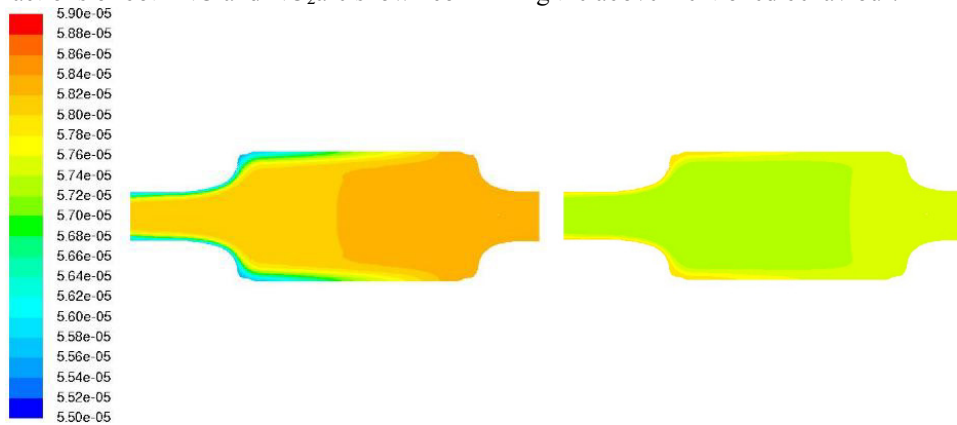


Figure 5. Mole fraction of the volumetric NOx in the main section of the catalyst where the inlet section is on the right hand side. On the left: spatial distribution of the NO. On the right: spatial distribution of the NO<sub>2</sub>.

#### 4. Summary

In this work three-dimensional flow and chemical numerical simulations of the flow field in a catalytic converter have been performed. The geometry considered has been derived from a commercial device. According to available experimental data, three working points have been considered. The monolith has been modelled as a porous medium where the pressure loss and the surface reactions associated to the

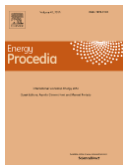
catalyst matrix channels have been modelled. In order to measure the flow effect on the efficiency, an efficiency uniformity rate has been defined. The present study highlights that the abrupt increasing of the main section in the inlet diffuser causes an annular recirculation zone inducing a non-uniform flow distribution at the monolith inlet, therefore a performance downgrade of the catalyst converter occurs. Preliminary results of the unsteady numerical flow simulations and chemical reactions for one working point have been reported. The effects on the NO<sub>x</sub> species distribution is reported confirming the reliability of the model proposed that represents a promising tool for the prediction of NSC catalyst performance.

## Acknowledgements

Concerning the working points used in this work, we acknowledge BOSCH CVIT (Bari, Italy) for the experimental data provided.

## References

- [1] Rankovic, N.; Nicolle, A. and Da Costa P. “Detailed Kinetic Modeling Study of NO<sub>x</sub> Oxidation and Storage and Their Interactions over Pt/Ba/Al<sub>2</sub>O<sub>3</sub> Monolith Catalysts” *J. Phys. Chem. C*, 114, 7102-7111 (2010)
- [2] Roy, S.; Baiker A. “NO<sub>x</sub> Storage-Reduction Catalysis: From Mechanism and Materials Properties to Storage-Reduction Performance”. *Chem. Rev.*, 109, 4054-4091 (2009)
- [3] Jeong S.J.; “A full transient three-dimensional study on the effect of pulsating exhaust flow under real running condition on the thermal and chemical behavior of closed-coupled catalyst” *Chem. Eng. Sc.* 2014, 117, 18-30
- [4] Algeri A., Bova S., De Bartolo C. and Nigro A.; “Numerical and experimental analysis of the flow field within a lean NO<sub>x</sub> trap for diesel engines” *SAE Tech. Paper. 2011, 10th International Conference on Engines and Vehicles, ICE 2011*; Naples, Italy.
- [5] Agrawal, G., Kaisare, N.S., Pushpavanam, S., Ramanathan, K.; “Modeling the effect of flow mal-distribution on the performance of a catalytic converter”; *Chem. Eng. Sc.*, 2012, 71, 310-320.
- [6] Bella, G., Rocco, V., Maggiore, M.; “Study of inlet flow distortion effects on automotive catalytic converters”; *J. of Eng. for Gas Turb. and Power* 113, 3, 419-426 (1991)
- [7] L. Olsson, H. Persson, E. Fridell, M. Skoglundh, B. Andersson, “A Kinetic Study of NO Oxidation and NO<sub>x</sub> Storage on Pt/Al<sub>2</sub>O<sub>3</sub> and Pt/BaO/Al<sub>2</sub>O<sub>3</sub>”, *J. Phys. Chem. B*. 105 68–95 (2001)
- [8] Mahzoul, H., Brillhac, J.F., Gilot, P., “Experimental and mechanistic study of NO( $\chi$ ) adsorption over NO( $\chi$ ) trap catalysts”, *Applied Catalysis B: Environmental* 20, 1, 47-55 (1999)
- [9] Fridell, E., Persson, H., Olsson, L., Westerberg, B., Amberntsson, A., Skoglundh, M., “Model studies of NO<sub>x</sub> storage and sulphur deactivation of NO<sub>x</sub> storage catalysts”, *Topics in Catalysis* 16-17, 1-4, 133-137 (2001)



## Biography

Francesco Fornarelli has a master degree in mechanical engineering at Politecnico di Bari and a Ph.D. in fluid dynamic at University of Genova. He was contract professor of Numerical Analysis, Numerical Methods for Engineers and Numerical Fluid Dynamics. Numerical simulation of flow governing equations by mean of custom and commercial numerical codes represents his main research activity.