Modeling a Catalytic Converter for *CO* and *NO* Emissions

J. C. Prince, C. Treviño, and M. Díaz

Abstract— **Performance of industrial and utility combustion systems is often constrained by limits on pollutant emissions such as *CO* and *NOx*. The widespread use of the catalytic converter was the response of the automotive industry to the legislation of the countries which sets limits on pollutant emissions. The catalytic combustion of *CO* + *NO* and air mixtures in a planar stagnation-point flow over a platinum foil is numerically studied in this paper. In order to optimize the operation of the platinum converter, chemical kinetic knowledge is necessary, therefore a kinetic model is proposed, based on elementary reaction steps, that allows to describe the experiments quantitatively. The heterogeneous reaction mechanism is modeled with the dissociative adsorption of the molecular oxygen and the non-dissociative adsorption of *CO*, together with a surface reaction of the Langmuir-Hinshelwood type and the desorption reaction of the adsorbed products, *CO*(*s*) and *NO*(*s*). The resulting governing equations based on the boundary layer theory have been numerically integrated by using Runge-Kutta method and the response curve has been obtained as a function of the initial mixture concentration. The reduction of *NO* and oxidation of *CO* in absence and presence of O_2 has been investigated, and the optimal oxygen feeding into the initial mixture concentration for the maximum reduction of *CO* and *NO* was found and corresponds to the reported experimental results.**

Index Terms—**Catalytic converter, Heterogeneous reactions, Numerical modeling, Pollutants reduction.**

I. INTRODUCTION

Motor vehicle emissions are one of the leading causes of air pollution. The removal of polluting agents, such as NO_X and *CO*, of combustion gases by catalytic means is one of the main subjects of interest in the environmental studies. The catalytic converter has been in use over the past three decades as an efficient and economic solution for the reduction of pollutants emitted by the internal combustion engine. This after-treatment device consists of a monolith encased in a metal designed to distribute the exhaust flow evenly [1-3]. The active catalytic material used to convert the polluting emissions is distributed over a large surface area in order for the mass-transfer characteristics between the gas phase and active catalytic surface to be enough for ensuring high catalytic conversion; the most commonly employed metals as catalytic surfaces are platinum, rhodium and palladium [4-7]. For homogeneous charged spark ignition engines, the most common after-treatment is the Three-Way Catalyst (TWC). This is because TWC is extremely effective at simultaneously oxidizing hydrocarbons (HC) and *CO*, as well as reducing NO_X provided that the engine operates at a stoichiometric fuel–air mixture, see Fig. 1.

The basic principles of heterogeneous catalysis have been described elsewhere [1-15, 18-22], where experimental and theoretical studies of catalytic combustion and ignition have been published in order to improve our knowledge about several aspects of this type of combustion processes.

Experimental studies have shown that while lower temperatures and delayed mixing are beneficial for NO_X control, they can be detrimental to *CO* emissions. *CO* oxidizes rapidly at high temperatures in the presence of oxygen, but does not oxidize as well at the cooler temperatures or less mixed conditions.

Catalytic converter models have been appearing in the literature at the same time with the development of new catalytic converter technologies. In this context, the role of modeling of the components of exhaust after-treatment systems is becoming increasingly important, especially as regards the catalytic converter, which is the most crucial device of such systems. In the numerical studies, heterogeneous reactions mechanisms are used to describe surface reactions on catalytic plates, where the chemical species are absorbed, reacting on the plate of the catalyst, later to appear the desorption. The catalytic ignition process has been studied by either using elementary chemistry or by large activation energy asymptotic analyses using a one-step overall reaction mechanism [5–15]. Reduced reaction scheme models employ a limited number of phenomenological reactions that contain only initial reactants and final products instead of elementary reactions on the catalyst active sites. The complexity and details of the reaction path is lumped into the kinetic rate expressions of these models, hence called lumped-parameter models. Rate expressions usually follow the Langmuir–Hinselwood formalism, modified by empirical terms. Necessity exists to obtain reduced kinetic schemes for the catalytic combustion, that help to construct to a bridge between the totally numerical works and the developed theories using reactions of a single passage for the kinetic one of the surface.

The objective of this work is to extend a previous work [15] to a catalytic combustion of the mixture of *CO* and NO_X of combustion gases on a platinum catalyst using the stagnation point flow configuration. An important part of this study will be the determination of a reduced chemical mechanism that allows, by one side to reduce the NO_X and on the other hand

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to oxidize the CO. Experimental data will be used for the simulation.

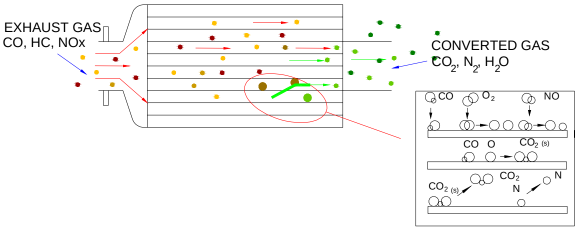

Fig. 1.- Schematic of a three way catalyst converter

II. FORMULATION

2.1 Governing equations

The physical model of the catalytic converter under study is shown in Fig. 2, where the stagnation-point flow geometry is used. A mixture of CO, NO_x gases and air described by the mass concentrations Y_{CO}^{∞}, $Y_{O_2}^{\infty}$ and Y_{NO}^{∞} flows with a velocity gradient a and temperature T^{∞}, perpendicular to a platinum plate of finite thickness h. The lower surface of the plate is kept to the same temperature T^{∞}. The boundary layer governing equations [23, 24] for the assumed frozen gas-phase are the following

$$\frac{\partial(\rho u)}{\partial x} + \frac{\partial(\rho v)}{\partial y} = 0\,, \tag{1}$$

$$\rho u \frac{\partial u}{\partial x} + \rho v \frac{\partial u}{\partial y} = \frac{\partial}{\partial y}\left(\mu \frac{\partial u}{\partial y}\right) + \rho^{\infty} a^2 x\,, \tag{2}$$

$$\rho u c_p \frac{\partial T}{\partial x} + \rho v c_p \frac{\partial T}{\partial y} = \frac{\partial}{\partial y}\left(\lambda \frac{\partial T}{\partial y}\right), \tag{3}$$

$$\rho u \frac{\partial \overline{Y}_i}{\partial x} + \rho v \frac{\partial \overline{Y}_i}{\partial y} = \frac{\partial}{\partial y}\left(\rho D_i \frac{\partial \overline{Y}_i}{\partial y}\right), \tag{4}$$

where u and v are the longitudinal and transversal components of velocity, respectively. ρ, μ, c_P and λ are the density, viscosity, specific heat at constant pressure, and thermal conductivity of the gas-phase mixture. D_i corresponds to the diffusion coefficient of species i. The associated boundary conditions are

$$u = v = \frac{\partial \overline{Y}_{CO}}{\partial y} - \frac{\omega W_{CO}}{\rho D_{CO}} = \frac{\partial \overline{Y}_{O_2}}{\partial y} - \frac{\omega W_{O_2}\sigma}{\rho D_{O_2}} = 0, \tag{5}$$

$$\frac{\partial \overline{Y}_{NO}}{\partial y} - \frac{\omega W_{NO}}{\rho D_{NO}} = \frac{\partial T}{\partial y} + \frac{\omega Q}{\lambda} - \frac{\lambda^w (T^w - T^{\infty})}{\lambda h} = 0,\ at\ y = 0$$

$$u - ax = T - T^{\infty} = \overline{Y}_i - \overline{Y}_i^{\infty} = 0, \quad y \to \infty\,. \tag{6}$$

Here W_i is the molecular weight of species i, σ is the stoichiometric ratio of the oxidizer related to the fuel of the overall surface reaction, Q is the heat released by the surface reaction per unit mol of fuel consumed, and λ_w is the thermal conductivity of the plate material. ω is the surface reaction rate given in units of mol of fuel consumed by unit time unit surface of the plate, and T_w corresponds to the temperature at the catalyst surface facing the combustible gaseous mixture.

2.2 Heterogeneous Reaction Model

The obtaining of the heterogeneous reaction model where species CO and NO_x of combustion gases can be removed is essential part of the present investigation. We assume a very simple model to describe the catalytic reactions of the CO, NO and the oxidizer O_2. The proposed chemical reaction model can be represented by the reaction mechanism shown in Table 1. The reactions finishing with *a*, *d*, and *r* represent adsorption, desorption, and surface reaction processes, respectively. $Pt(s)$ denotes then a free site on the surface of the platinum catalyst. Reaction (3*r*) is the only one surface reaction assumed to be of the Langmuir-Hinshelwood type. It must be noticed that the desorption of O by the reduction of the NO_x, is used for the oxidation of the CO; since this O is not sufficient for the complete oxidation of CO gases, then within the gases that arrive at the catalytic plate a small fraction of O_2 must arrive, as reported in experimental research. The adsorption kinetics is given by a sticking probability, *Sj* or accommodation coefficient which represents the portion of the collisions with the surface that successfully leads to adsorption. The rate of collisions, Z_w, can be computed using the classical kinetic theory with $Z_w = \frac{p}{\sqrt{2\pi m k T}}$, where p and m are the partial pressure and the mass of the involved species and k is the Boltzmann constant, $k = 1.38 \times 10^{23} J\ K^{-1}$. On the other hand, the desorption kinetics is well-represented by an Arrhenius law, with a high activation energy for both reactants. The adsorbed species concentrations are represented by the surface coverage θ_i defined by the number of sites occupied by surface species i to the total number of available sites

$$[i] = \frac{\rho^{\infty} Y_i^w}{W_i} = \frac{\rho^{\infty} Y_i^{\infty}}{W_i} y_i^w\,.$$

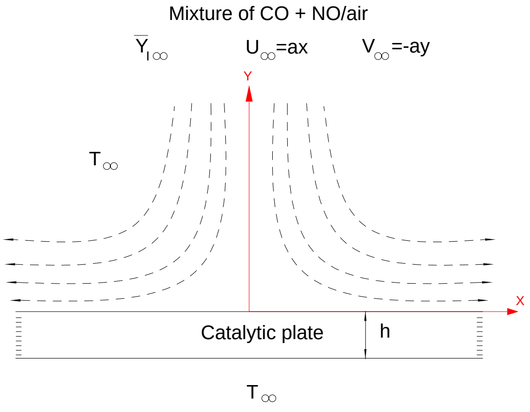

Fig. 2.- Schematic of the physical model, showing the stagnation point flow configuration.

Table 1. Heterogeneous Reaction Model

Nr	Reaction	S	A	E	k
1*a*	$CO + * \rightarrow CO*$	0.84	10^{13}		9.0×10^5
1*d*	$CO* \rightarrow CO + *$		10^{13}	125.5	
2*a*	$O_2 + 2* \rightarrow 2O*$	$\frac{21}{T}$			1.01×10^5
2*d*	$2O* \rightarrow O_2$		3.7×10^{21}	213.2	
3*r*	$CO* + O* \rightarrow CO*_2 + *$		3.7×10^{21}	105	
4*a*	$CO_2 + * \rightarrow CO^*_2$	0.05			
4*d*	$CO*_2 \rightarrow CO_2 + *$		10^{13}	20.5	
5*a*	$NO + * \rightarrow NO*$	0.08			3.38×10^5
5*d*	$NO* \rightarrow NO + *$		3.04×10^{10}	83.2	
6*d*	$2N* \rightarrow N_2 + 2*$		4.08×10^8	56.6	
7	$NO* + * \rightarrow N* + O*$		2.19×10^5	45.8	
8	$NO* + N* \rightarrow N_2O* + *$		2.16×10^5	38.3	
9*d*	$N_2O* \rightarrow N_2O + *$		2.71×10^6	45.3	
10*d*	$N_2O* \rightarrow N_2 + O*$		4.64×10^3	20.1	

k [$m^3\ mol^{-1}\ s^{-1}$]; A [s^{-1}]; E [$kJ\ mol^{-1}$]; S [-].

For the adsorbed species, the steady-state governing equations are given by

$$\frac{d\theta_{CO^*}}{dt} = k_{1a}[CO]\theta_* - k_{1d}\theta_{CO^*} - k_3\theta_{CO^*}\theta_{O^*}\ , \quad (7)$$

$$\frac{d\theta_{O^*}}{dt} = k_{2a}[O_2]\theta_*^2 - k_{2d}\theta_{O^*}^2 - k_3\theta_{CO^*}\theta_{O^*} + k_7\theta_{NO^*}\theta_* + k_{10d}\theta_{N_2O^*}\ , \quad (8)$$

$$\frac{d\theta_{CO_2^*}}{dt} = k_3\theta_{CO^*}\theta_{O^*} - k_{4d}\theta_{CO_2^*} + k_{4a}\left[CO_2\right]\theta_*\ , \quad (9)$$

$$\frac{d\theta_{NO^*}}{dt} = -k_{5d}\theta_{NO^*} - k_7\theta_{NO^*}\theta_* - k_8\theta_{NO^*}\theta_{N^*} + k_{5a}[NO]\theta_*\ , \quad (10)$$

$$\frac{d\theta_{N^*}}{dt} = -k_{6d}\theta_{N^*}^2 + k_7\theta_{NO^*}\theta_* - k_8\theta_{NO^*}\theta_{N^*}\ , \quad (11)$$

$$\frac{d\theta_{N_2O^*}}{dt} = k_8\theta_{NO^*}\theta_{N^*} - k_{9d}\theta_{N_2O^*} - k_{10d}\theta_{N_2O^*}\ , \quad (12)$$

$$\theta_* = 1 - \theta_{CO^*} - \theta_{O^*} - \theta_{CO_2^*} - \theta_{NO^*} - \theta_{N^*} - \theta_{N_2O^*}\ . \quad (13)$$

Here θ_* denotes the surface coverage of empty or vacant sites. The value of n depends on the adsorption of carbon monoxide. There is a clear evidence that $n = 2$, indicating that the adsorbed species $CO(s)$ requires two empty sites [8]. All the reaction rates in Eqs. 7 to 12 are in $1/s$ units.

2.3 Non-dimensional governing equations

The governing equations (1-4) describe the a bi-dimensional flow, when a stagnation point appears on a catalyst plate, giving rise a complex system of partial differential equations. The next step is to transform the governing equation in non-dimensional form. A stream function $\psi(x, y)$ is introduced to satisfy the mass conservation equation (1): $\rho u = \frac{\partial \psi}{\partial y}$ and $\rho v = -\frac{\partial \psi}{\partial x}$. We also define the following non-dimensional variables

$$f = \frac{\psi}{x\sqrt{\rho^\infty \mu^\infty a}}, \quad \eta = \sqrt{\frac{a}{\rho^\infty \mu^\infty}} \int_0^y \rho\left(x, y'\right) dy'\ , \quad (14)$$

$$\Phi = \frac{c_p W_{CO}(T - T^\infty)}{Q}, \ Y_{CO} = \overline{Y}_{CO}, Y_{O_2} = \frac{W_{CO}}{\sigma W_{O_2}} \overline{Y}_{O_2}\ .$$

The resulting non-dimensional governing equations now take the form

$$\frac{d^3 f}{d\eta^3} + f\frac{d^2 f}{d\eta^2} + \frac{\rho^\infty}{\rho} - \left(\frac{df}{d\eta}\right)^2 = 0\ , \quad (15)$$

$$\frac{d^2 Y_i}{d\eta^2} + f Sc_i \frac{dY_i}{d\eta} = \frac{d^2 \Phi}{d\eta^2} + f Pr \frac{d\Phi}{d\eta} = 0\ , \quad (16)$$

where Pr is the Prandtl number of the gaseous mixture, $Pr = \frac{\mu c_p}{\lambda}$, and Sc_i are the Schmidt numbers of the species, $Sc_i = \frac{\mu}{\rho D_i}$. The non-dimensional boundary conditions are then given by

$$f = \frac{df}{d\eta} = \frac{dY_i}{d\eta} - GLe_i = \frac{d\Phi}{d\eta} + G - \gamma \Phi^w = 0, \quad \eta = 0\ , \quad (17)$$

$$\frac{df}{d\eta} - 1 = \Phi = Y_i - Y_i^\infty = 0, \quad \eta \longrightarrow \infty\ , \quad (18)$$

where

$$Le_i = \frac{Sc_i}{Pr}, \quad \gamma = \frac{\lambda^w}{\lambda}\sqrt{\frac{\mu^\infty}{\rho^\infty a h^2}}, \ G = \frac{W_{CO} Pr \omega}{\sqrt{\rho^\infty \mu^\infty a}}\ ,$$

and γ is the heat loss parameter.

III. RESULTS AND DISCUSSION

For the heterogeneous reaction mechanism proposed in this work, the corresponding kinetic model is represented by the governing equations (Eqs. 7-13). These expressions have to be solved and coupled to the fluid mechanics conservation equations (Eqs. 15-16) and their corresponding boundary conditions (Eqs. 17-18). All these equations are solved based on a non-dimensional variable Y_i. For the solution of this system of equations, the Runge-Kutta method of fourth order is used. The resulting computational code was written in FORTRAN and the numerical simulation was performed in a workstation with Linux as operating system..

3.1 Composition of combustion gases

In the combustion processes, the gases are a set of chemical species such as: NO_X, CO and unburnt fuel, whose average composition can vary depending on the conditions of the used process. The composition of combustion gases used in this work, taken from [24], appears in Table 2.

Table 2. Composition of combustion gases

Components	Molar Fraction	Mass Fraction
CO	1.22 %	1.139 %
C_2H_2	280 ppm	243 ppm
C_2H_4	380 ppm	355 ppm
NO	1130 ppm	1131 ppm
O_2	7000 ppm	7471 ppm
CO_2	12.2 %	17.904 %
N_2	85.7 %	80.36 %

3.2 Reduction of NO and CO in the combustion gases

Numerical simulations were carried out for the reduction of *NO* and oxidation of *CO* in absence and presence of O_2. The mass concentrations of the chemical species represented by Y_i and the surface coverage θ_i defined by the number of sites occupied by species i in the surface of the catalyst, are influenced by the amount of O_2 presents in the combustion gases. Fig. 3 displays the *CO* and *NO* mass concentration as a function of the inlet oxygen, showing the optimal value of oxygen of 6×10^{-3}, in agreement to experimental data [25].
One of the important parameters in the elimination of the *CO* and *NO* is the temperature at which the surface reaction mechanism is carry through. On one hand, higher temperature increases the oxidation of *CO* but promotes the formation of *NO*. The results plotted in Fig. 4 indicate the optimal value of O_2 corresponds to a temperature of around 800 K. Although this figure show that greater fractions of O_2 cause that temperature diminishes considerably, these fractions do not satisfactorily contribute in the reduction of the polluting chemical species. Fig. 5 shows the surface coverage of the absorbed chemical species as a function of the temperature, for the optimal O_2 feeding of 6×10^{-3}. For the case of θ_{CO} a constant adsorption is observed for temperature lower than 800 K; once this temperature is reached the molecule reacts to oxidize and form CO_2, that separates from the catalyst, leaving vacant spaces. For the case of θ_{NO} the maximum adsorption starts close to 800 K, as well as the reduction to N_2 and O_2. In the case of θ_{O2}, the greatest surface coverage starts at 800 K prevailing a constant value since the reaction of *CO* starts.
As shown in Fig. 6, the optimal O_2 feeding considerably reduces the concentration of polluting chemical species in the combustions gases, since the reduction of *NO* does not provide oxygen enough for the oxidation of *CO*. It is observed that inlet mass fractions of *NO* and *CO* are substantially depleted once they interact to the catalytic plate at a temperature of about 800 K. For *CO* its removal is complete while for *NO* there is a considerable reduction, as should be expected in the catalytic converters.

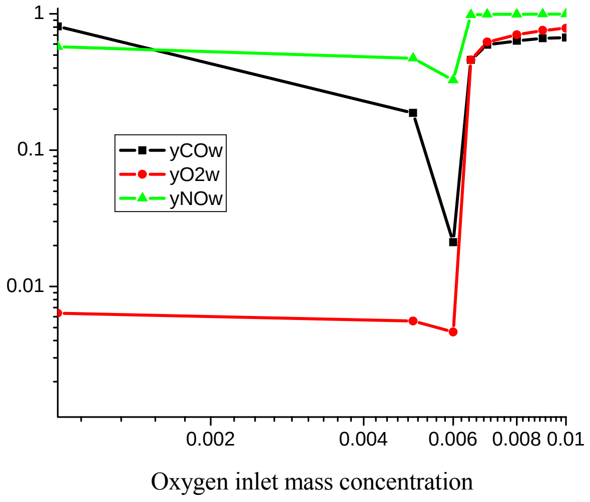

Fig. 3.- Concentration of the inlet *CO* and *NO* as a function of the inlet O_2 concentration

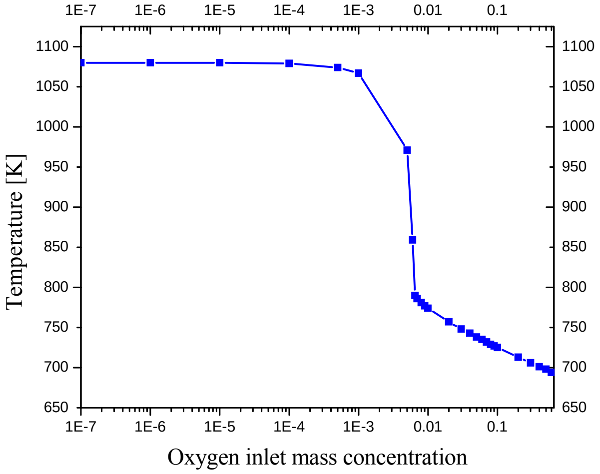

Fig. 4.- Temperature as a function of the inlet O_2 concentration

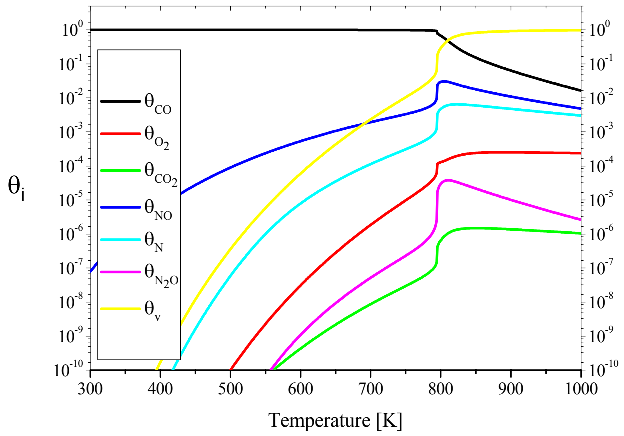

Fig. 5.- Surface coverage of the surface adsorbed species as a function of the temperature

The optimal O_2 feeding and the initial and final values of the polluting gases studied in the present research are summarized in Table 3.

Table 3. Comparison of initial and final concentration

Specie	Initial concentration	Final concentration	Temperature [K]
O_2	0.00600	0.000	
CO	0.01139	0.00060	800
NO	0.00113	0.00037	850

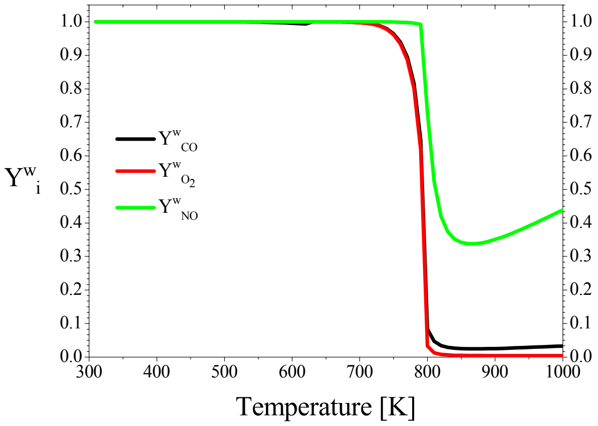

Fig. 6.- CO, NO and O_2mass concentrations as a function of the catalytic surface temperature.

IV. CONCLUSION

The numerical modeling of a catalytic converter was developed in this paper. The catalytic combustion model was for a mixture of CO, NO and air, using the stagnation-point flow geometry. The proposed chemical reaction mechanism was able for reducing NO and oxidation of CO. The numerical simulation was carried out in absence and presence of O_2. An optimal O_2 concentration feeding of 6×10^{-3} was found with a corresponding temperature of 800 K that significantly diminishes the fractions of the polluting chemical species in combustion gases.

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REFERENCES

[1] Koltsakis, G. C., and Stamatelos, A. M., 1997, ''Catalytic Automotive Exhaust Aftertreatment,'' Prog. Energy Combust. Sci., **23**, pp. 1–37.

[2] Heck, R. H., Wei, J., and Katzer, J. R., 1976, ''Mathematical Modeling of Monolithic Catalysts,'' AIChE J., **22(3)**, pp. 477–484.

[3] Baba, N; Ohsawa, K.; Sugiura, S. (1996). Analysis of transient thermal and conversion characteristics of catalytic converters during warm-up. *JSAE Review, 17*, 273–279.

[4] Oh, S. H., and Cavendish, J. C., 1982, ''Transients of Monolithic Catalytic Converters: Response to Step Changes in Feedstream Temperature as Related to Controlling Automobile Emissions,'' Ind. Eng. Chem. Prod. Res. Dev., **21**, pp. 29–37.

[5]] Montreuil, C. N., Williams, S. C., and Adamczyk, A. A., 1992, ''Modeling Current Generation Catalytic Converters: Laboratory Experiments and Kinetic Parameter Optimization—Steady State Kinetics,'' SAE paper 920096.

[6] Pontikakis, G. N., and Stamatelos, A. M., 2002, ''Catalytic Converter Modeling: Computer-Aided Parameter Estimation by use of Genetic Algorithms'' Proc. Inst. Mech. Eng., Part D: J. Automob. Eng.

[7] Konstantinidis, P.A.; Koltsakis, G.C.; Stamatelos A.M. (1998). The Role of CAE in the Design Optimization of Automotive Exhaust Aftertreatment Systems. Proc. Inst. Mech. Engrs., Part D, Journal of Automotive Engineering, 212, 1–18.

[8] Deutschmann, O., Schmidt, R., Behrendt, F., and Warnatz, J., Twenty-Sixth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, 1996, pp. 1747–1754.

[9] Seo, Y. S., Kang, S. K., Han, M. H., Baek; Y. S., Catalysis Today 47 (1999) 421-427.

[10] Treviño, C., Combust. Theory Modelling 3 (1999) 1--9.

[11] Yusuf , A. K., Arslanturk, C., Applied Thermal Engineering 24 (2004) 269--279.

[12] Liñán : C. Treviño, F. J. Higuera and A. Liñan; Proceedings of the Combustión Institute, volume 29, 2002/pp. 981-988.

[13] Marc D. Rumminger, Richard D. Hamlin, Robert W. Dibble, catalysis Today 47(1999)253-262.

[14] Treviño, C., Prince, J. Surface Science 449(2000) 61-67.

[15] Treviño; J. C. Prince; y J. M. Tejero; Combustion and Flame, 119:505-512 (1999).

[16] Brizuela, E., y Echaniz, V.; Engenharia Térmica, n. 1, 2001, p. 64-70.

[17] Li, Y. and Armor, J. N., Appl. Catal. B, 1 (1992) L31.

[18] Yogo, K. and Kikuchi, E., Zeolites and related microporous materials: state of the art 1994, 84, 1547.

[19] Kikuchi, E. et al, Catalysis Today 27 (1996) 35.

[20] Iwamoto, M., J. Weitkamp, H.G. Karge, H. Pfeifer, H. Holderich (Eds), Zeolites and related Microporous Materials: State of the art 1994, Elsevier Science and Catalysis. Vol 84, 1994, 1395.

[21] M.D. Amiridis, T. Zhang, R. Farrauto, Appl. Catal., 10, 203 (1996).

[22] S.M. Cho, Chemical Engineering Progress, 39, Enero 1994.

[23] H. Schlichting, J. Kestin. Boundary-Layer Theory. Seventh edition, ed. McGraw-Hill.

[24] F. A. Williams. Combustion Theory. 2nd Ed. The Benjamin/Cummings Publishing Co, 1985.

[25] Harmsen, J., Ph. D. Thesis, Eindhoven Technishe Universiteit: "Modeling of the dinamic behaviour of an automotive catalyst under cold start conditions".

[26] González, U. Combustion Laboratory, Instituto Mexicano del Petróleo. Private Communication, 2006.