Rigorous and Reduced Dynamic Models of the Fixed Bed Catalytic Reactor for Advanced Control Strategies

Eduardo C. Vasco de Toledo[a], Delba Nisi C. Melo[a], José Marcos F. da Silva[a], Viktor O. C. Concha[a], João Frederico da C. A. Meyer[b], Rubens Maciel Filho[a].

[a]*School of Chemical Engineering*
[b]*Institute of Mathematics, Statistics and Scientific Computing*
State University of Campinas - UNICAMP
PO Box: 6066 – Zip Code: 13081-970 - Campinas, SP - Brazil. FAX +55-1937883965
email: delba@lopca.feq.unicamp.br

Abstract: Rigorous and reduced heterogeneous dynamic models for fixed bed catalytic reactor were developed in this work. The models consist on mass and heat balance equations for the catalyst particles as well as for the bulk phase of gas. They also consider the variations in the physical properties and in the heat and mass transfer coefficients, the continuity equation for the fluid phase as well as the heat exchange through the jacket of the reactors. The models were used to describe the dynamic behaviour of the ethanol oxidation to acetaldehyde over Fe-Mo catalyst. The proposed models were able to predict the main characteristics of the dynamic behaviour of the reactors, and it was possible to compare the results obtained in simulations of models with different degrees of formulation complexity, thus indicating which model is more suitable for a specific application. This information is important for the real time integration implementation procedure.

Keywords: fixed bed, catalytic reactors, dynamic models, reduced models, dynamic behaviour.

1. INTRODUCTION

The design of cooled tubular reactors, involves complex tradeoffs between tube geometry, pressure drop, and heat-transfer area. Thus the behaviour of chemical reactors depends on variations in the inlet conditions, as well as in other physical and chemical parameters of the system. If the solid phase takes part in the process, e.g. heterogeneous catalysis, the task becomes very complex. The models commonly applied in simulation of heterogeneous fixed bed reactors usually gives results with quite good accuracy, but solving the model equation set is rather than difficult, when compared with pseudo-homogeneous models, because of the complex dynamic behaviour resulting from the non-linear distributed features which, among other things, give rise to inverse response resulting in catastrophic instabilities such as temperature runaway. This non-linearity is a consequence of heat generation by chemical reaction, and the inverse response arises from the presence of different heat capacities of the fluid and solid as well as the bulk flow of fluid causing interactions between heat and mass transfer phases. This causes differential rates of propagation of heat and mass transfer, which influence the heat generation through reaction on the solid catalyst. Therefore such models can be used only in a limited range, i.e. for preliminary calculation of reactor operation conditions. Solving pseudo-homogenous models is simple, but often their accuracy is low.

Without a detailed model it is not possible to make reliable predictions because the location of the regions with unstable behaviour, change in space and time are dependent on the input disturbances and control action. Obviously, it is essential to predict this behaviour for application in control. Reliable models depend on the insight of how the dominant physic-chemical mechanisms and external factors affect the overall performance. However, when on-line applications are required, reduced models have to be used, which can keep the essential characteristics of the system (McGreavy and Maciel Filho, 1989).

In this work, rigorous and reduced heterogeneous models for fixed bed catalytic reactors were developed. The proposed heterogeneous dynamic models for fixed bed catalytic reactors consist on mass and heat balance equations for the catalyst particles as well as for the gas phase, include the resistances to mass and heat transfer at the gas-solid interface and consider (or may not consider) the resistances inside the catalyst particle. The rigorous heterogeneous dynamic models are used in applications where computational accuracy may be more emphasized than computational speed, for instance, reactor design, planning of start-ups, shutdowns and emergency procedures (Martinez et al., 1985; Pellegrini et al., 1989; Elnashie and Elshishine, 1993). For real time implementation, as control and on-line optimisation, it is required to overcome the computational burden with a faster and easy numerical solution when compared to rigorous heterogeneous models. Bearing this in mind, reduced heterogeneous models were developed (McGreavy and Maciel, 1989).

The reduced models were obtained through mathematical order reduction, which eliminates the spatial co-ordinate of the catalyst particle and promote radially lumped-differential formulations (Maciel Filho, 1989; Vasco de Toledo, 1999). Therefore, one or more independent variable can be integrated leading to approximated formulations that retain detailed local information in the

remaining variables as well as medium information in the directions eliminated by the integration.
Considering the fixed bed catalytic reactor, the spatial dimension can be eliminated of the catalyst particle model (radial variable) thus generating bidimensional reduced models.
As a case study, the catalytic oxidation of the ethanol to acetaldehyde over Fe-Mo catalyst was considered, (Vasco de Toledo, 1999). It is a strongly exothermic reaction, representative of an important class of industrial processes.

2. REDUCTION TECHNIQUES

The solution of diffusion/reaction multidimensional problems present difficulties associated with a large analytic involvement and also request considerable computational effort. Consideration of such facts, becomes of interest for practical application in engineering, so that it is convenient to propose simpler formulations for the original system of partial differential equations, through the reduction of the number of its independent variables. Therefore, one or more independent variables can be integrated, leading to approximate formulations that retain detailed local information in the remaining variable as well as medium information in the directions eliminated by the integration. This information comes from the boundary conditions related to the eliminated directions. In this work, different reduction approaches(Classic, Hermite, Finlayson,Dixion,Generic) generating differentiates lumped formulations were investigated.
These techniques generate models that describe the reactor axial and radial profiles as a function of the time for the convenient explicit elimination of the dependence in the radial variable of the catalyst particle (bidimensional reduced model).Others approaches based on the use of wave propagation principle to describe the hot sport motion may be used since the could lead to have a smaller number of state what could be advantageous (Gilles and Epple, 1982; Marquardt, 1989). However, such approaches are not suitable to represent the system on all possible operating range without further identification. On the other hand models reduction based on mechanistic models are supposed to be valid in the whole domain.
Another possible way to generate a reduced model, which does not eliminate any dimension of the reactor, is to apply the method of the orthogonal collocation to the rigorous model of the reactors with only one internal collocation point in the radial direction. This technique does not simplify the mathematics/numeric solution of the reactor.
The proposed approaches for model reduction lead to different results since the model parameters are dependent upon the reduction techniques, Table 1.

2.1 Classic Reduction

This technique makes uses of the theorem of the mean value, given by equation (1) to produce the reduced models. In Table 1 is shown the parameters obtained for the Classic Reduction approach, as developed by Maciel Filho, 1989 and Vasco de Toledo, 1999.
For spherical co-ordinates:

$$[\ ]m = 3\int_0^1 r^2[\ ]dr \qquad (01)$$

where [ ]m defines a mean radial value of the amount inside of the left bracket.

2.2 Hermite Reduction

The technique makes use of the approach $H_{0,0}$ or $H_{1,1}$ and simultaneously of the theorem of the mean value for spherical co-ordinates, leading to the generation of the radial medium variables (Vasco de Toledo, 1999).

$$[\ ]m = 3\int_0^1 r^2[\ ]dr \qquad (02)$$

$$H_{0,0} = \int_0^1 y(x)dx \cong \frac{1}{2}\left[y(0)+y(1)\right] \qquad (03)$$

$$H_{1,1} = \int_0^1 y(x)dx \cong \frac{1}{2}\left[y(0)+y(1)\right]+ \frac{1}{12}\left[y'(0)-y'(1)\right] \qquad (04)$$

where [ ]m defines a mean radial value of the amount inside of the left bracket.

2.3 Finlayson Reduction

Through the discretization of the radial term of the model for orthogonal collocation, and only using one collocation point, Finlayson manipulated the obtained equations analytically and generated a reduced model similar to apply the Hermite technique (Finlayson, 1971).

2.4 Generic Reduction

This technique is the generic mathematical representation of the reduction techniques mentioned previously. It leads to the generation of other parameters besides of the generated by other techniques (Hermite and Finlayson).

2.5 Dixion Reduction

Following the same methodology of Finlayson, Dixion discretizated the radial term of the model through orthogonal collocation. He manipulated the obtained equations analytically and generated a reduced model similar to apply other reduction techniques (Dixion, 1996).

2.6 Reduction Technique Using One Point Internal Radial Collocation

Another technique used to derive a reduced model (which does not eliminate a dimension of the reactor as the other techniques above described) refers to the application of the orthogonal collocation method to the model with only one internal collocation point in radial direction, for the

solid phase. In this work, in the rigorous models, 5 internal orthogonal collocation points were employed in the catalyst particle model.

In conclusion, the use of these techniques aims to evaluate the following points: the reduced models ability to predict the dynamic behaviour of the reactor; the computational time demanded to obtain dynamic profiles; the easiness/difficulties of the implementation and numerical convergence of these techniques.

One important feature when considering the reduced models is the less quantity of heat and mass transfer parameters necessary for their formulation, which does not imply in loss of prediction capability when compared to rigorous models. It may be important in case that is not possible to obtain trustful correlations to estimate some heat and mass parameters. This may be a restriction to the development of rigorous heterogeneous models.

3. DYNAMIC MODELS

The models developed here are based on the models proposed by Jutan et al., 1977; Martinez et al.,1985; Maciel Filho, 1989; Pellegrini et al., 1989; Elnashie and Elshishine, 1993; and Vasco de Toledo, 1999.

The models of the reactor were generated under the following considerations: variation of physical properties, mass and heat transfer coefficients, along the reactor length; intraparticle gradient negligible (reduced heterogeneous models); axial dispersion was neglected. Axial dispersion is found to be no significant for reactors with relatively high length /diameters, which is typical situation of industrial fixed bed catalytic reactors.

A possible way to have further model reduction is to neglect the time derivatives in respect to concentrations, since it leads to a significant reduction in the number of states. (Maciel Filho, 1989 and Vasco de Toledo, 1999). This was not considered in this paper because for chemical reactions with several by products.

Therefore, the heterogeneous models of the fixed bed catalytic reactor developed are:

3.1 Heterogeneous Model I - Rigorous Model (Tridimensional)

Reactant Fluid Mass Balance:

$$\varepsilon \frac{\partial X_g}{\partial t} = \frac{D_{ef}}{R_t^{\,2}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial X_g}{\partial r} \right] - \frac{G}{\rho_g L} \frac{\partial X_g}{\partial z} + k_{gs}\, a_v\, (X_s^s - X_g) \tag{05}$$

Reactant Fluid Energy Balance:

$$\rho_g C_{pg} \varepsilon \frac{\partial T_g}{\partial t} = \frac{\lambda_{ef}}{R_t^{\,2}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial T_g}{\partial r} \right] - \frac{G\, C_{pg}}{L} \frac{\partial T_g}{\partial z} + h_{gs}\, a_v\, (T_s^s - T_g) \tag{06}$$

Catalyst Particle Mass Balance:

$$\varepsilon_s \frac{\partial X_s}{\partial t} = \frac{D_s}{R_p^{\,2}} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial X_s}{\partial r_p} \right) + \frac{PM\, \rho_s\, R_W(X_s, T_s)}{\rho_g} \tag{07}$$

Catalyst Particle Energy Balance:

$$\rho_s\, C_{ps} \frac{\partial T_s}{\partial t} = \frac{\lambda_s}{R_p^{\,2}} \frac{1}{r_p^{\,2}} \frac{\partial}{\partial r_p}\left(r_p^{\,2} \frac{\partial T_s}{\partial r_p} \right) + \frac{\rho_s\, (-\Delta H_R)\, R_W(X_s, T_s)}{(R+1)} \tag{08}$$

Continuity Equation:

$$\frac{\partial}{\partial z}\left(\rho_g u_g \right) = 0 \tag{09}$$

Coolant Fluid Balance:

$$\frac{\partial T_R}{\partial t} = -\frac{u_R}{L} \frac{\partial T_R}{\partial z} + \frac{4U}{D_t\, \rho_R\, C_{pR}} (T_g(1,z,t) - T_R) \tag{10}$$

Momentun Balance:

$$\frac{\partial p}{\partial z} = -\frac{G^2 L}{\rho_g\, D_p\, g_c} f \tag{11}$$

with the following boundary conditions:

$$\begin{aligned}
&r = 0 \quad \frac{\partial X_g}{\partial r} = \frac{\partial T_g}{\partial r} = 0, \\
&r_p = 0 \quad \frac{\partial X_s}{\partial r_p} = \frac{\partial T_s}{\partial r_p} = 0 \\
&r = 1 \quad \frac{\partial X_g}{\partial r} = 0, \frac{\partial T_g}{\partial r} = B_{ih}\, (T_R - T_g(1,z,t)) \\
&r_p = 1 \quad \frac{\partial X_s}{\partial r_p} = \frac{k_{gs}\, R_p}{D_s} \left(X_g - X_s^s \right), \\
&r_p = 1 \quad \frac{\partial T_s}{\partial r_p} = \frac{h_{gs}\, R_p}{\lambda_s} \left(T_g - T_s^s \right), \\
&z = 0 \quad X_g = X_s = 0, \quad T_g = T_{go}, \quad T_s = T_{so}, \\
&T_R = T_{Ro}, \quad p = p_o
\end{aligned} \tag{12}$$

The Equations 09, 10 and 11 are valid also for the remaining models.

The following notations are used, a_v is the external particle surface area per unit of catalyst volume, m^{-1}; B_{ih}, Biot number; C_p, calorific capacity, kcal/kg.K; D_{ef}, radial effective diffusivity, m/h; D_p, particle diameter, m; f, friction factor; G, mass flow velocity, $kg/m^2.h$; gc, conversion factor; h_{gs}, particle to fluid convective heat transfer coefficient, $kcal/m^2.h.K$; h_W, convective heat transfer coefficient in the vicinity of the wall, $kcal/m^2.h.K$; k_{gs}, particle to fluid mass transfer coefficient, m/s; L, length of the reactor, m; p, pressure of the reactor, atm; PM, the mean molecular weight, kg/kmol; r, dimensionless radial distance of the reactor; r_p, dimensionless radial distance of the particle; R, air/ethanol ratio; R_t, reactor radius, m; R_p, particle radius, m; R_W, rate of the oxidation, kmol of reactant mixture/h.kgcat; T, reactor temperature, K; T_{fo}, feed temperature, K; T_{go}, feed temperature, K; T_{so}, catalyst feed temperature, K; T(1,z,t), wall temperature of the reagent fluid, K;

T_R, coolant temperature, K; T_{Ro}, coolant feed temperature, K; t, time, h; u, velocity, m/h; U, global heat transfer coefficient, kcal/m^2.h.K; X, conversion; z, dimensionless axial distance. Greek letter: λ, conductivity, kcal/m.h.K; ΔH_R, enthalpy of reaction molar, kcal/kmol; ρ, density, kg/m^3; ρ_B, catalyst density, kgcat/m^3; ρs, catalyst density, kgcat/m^3; ε, porosity. Subscripts: ef, effective; f, fluid; g, gas; i, interstitial; o, feed; R, refrigerant; s, solid. Superscripts: s, condition at external surface.

3.2 - Heterogeneous Model II - Reduced Models (Bidimensional)

The use of the reduction techniques leads to the generation of the radial mean variables. The generate model describes the axial and radial profiles as a function of the time for the convenient explicit elimination of the dependence in the radial variable of the catalyst particle. The reduced models were generated applying the reduction techniques (Classic, Hermite, Finlayson, Generic and Dixion) to the Heterogeneous Model I (Rigorous Model).

Reactant Fluid Mass Balance:

$$\varepsilon \frac{\partial X_g}{\partial t} = \frac{D_{ef}}{R_t^{\,2}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial X_g}{\partial r} \right] - \frac{G}{\rho_g L} \frac{\partial X_g}{\partial z} + \alpha_m k_{gs} a_v (\lambda X_{sm} - X_g) \tag{13}$$

Reactant Fluid Energy Balance:

$$\rho_g C_{pg} \varepsilon \frac{\partial T_g}{\partial t} = \frac{\lambda_{ef}}{R_t^{\,2}} \frac{1}{r} \frac{\partial}{\partial r}\left[r \frac{\partial T_g}{\partial r} \right] - \frac{G\, C_{pg}}{L} \frac{\partial T_g}{\partial z} + \alpha_t h_{gs} a_v (\lambda T_{sm} - T_g) \tag{14}$$

Catalyst Particle Mass Balance:

$$\varepsilon_s (1-\varepsilon) \frac{\partial X_{sm}}{\partial t} = -\alpha_m k_g a_v (\lambda X_{sm} - X_g) + \frac{PM (1-\varepsilon) \rho_s R_W (X_{sm}, T_{sm})}{\rho_g} \tag{15}$$

Catalyst Particle Energy Balance:

$$(1-\varepsilon) \rho_s C_{ps} \frac{\partial T_{sm}}{\partial t} = -\alpha_t h_{gs} a_v (\lambda T_{sm} - T_g) + \frac{(1-\varepsilon) \rho_s (-\Delta H_R) R_W (X_{sm}, T_{sm})}{(R+1)} \tag{16}$$

with the following boundary conditions:

$$\begin{aligned} &r = 0 \quad \frac{\partial X_{gm}}{\partial r} = \frac{\partial T_{gm}}{\partial r} = 0, \\ &r = 1 \quad \frac{\partial X_{gm}}{\partial r} = 0, \frac{\partial T_{gm}}{\partial r} = B_{ih} (T_R - T_{gm}(1, z, t)) \\ &z = 0 \quad X_{gm} = 0, \quad T_{gm} = T_{go}, T_R = T_{Ro}, p = p_o \end{aligned} \tag{17}$$

X_{sm} and T_{sm} are mean radial conversion and temperature of the reactor solid phase.

In equations 13 to 16 the parameters α_i and λ vary according to the reduced model, as described below in Table 1.

Table 1. Bidimensional Reduced Models

MODELS	PARAMETERS	
	α_i	λ
Classic	$\alpha_m = 1$ $\alpha_t = 1$	1
Hermite $H_{0,0}$	$\alpha_m = 1$ $\alpha_t = 1$	2/3
Hermite $H_{1,1}$ factor = 4 Finlayson factor = 3; Generic factor ≠ 4.	$\alpha_m = \left(\frac{\text{factor}}{\text{factor} + B_{im}} \right)$, $\alpha_t = \left(\frac{\text{factor}}{\text{factor} + B_{ih}} \right)$, $B_{im} = \frac{K_{gs} R_p}{D_s}$, $B_{ih} = \frac{h_{gs} R_p}{\lambda_s}$	1
Dixion	$\alpha_m = \frac{3B_{im}(B_{im}+4)}{B_{im}^{\,2} + 6B_{im} + 12}$ $\alpha_t = \frac{3B_{ih}(B_{ih}+4)}{B_{ih}^{\,2} + 6B_{ih} + 12}$	1

As a case study, the catalytic oxidation of the ethanol to acetaldehyde over Fe-Mo catalyst was considered. It is a strongly exothermic reaction, representative of an important class of industrial processes (Vasco de Toledo, 1999).

$$\begin{aligned} B &= 2K_1 K_2 P_{O2} P_{ET} \\ A &= K_3 K_1 P_{ET} P_{AC} + K_1 P_{ET} + 2K_2 P_{O2} + K_3 K_4 P_{AC} P_{H2O} \\ R_W &= \frac{B}{A} \end{aligned} \tag{18}$$

P_{O2}, P_{ET}, P_{H2O}, P_{AC} are partial pressure of oxygen, ethanol, water and acetaldehyde, respectively; K_i are the kinetic constants in the Arrhenius form (Vasco de Toledo, 1999).

The numeric solution of the models was obtained using the method of the lines in conjunction with the orthogonal collocation, which showed to be an effective procedure for the space discretization (radial and axial directions), employing the LSODAR algorithm for the integration in time (Villadsen and Michelsen, 1978; Vasco de Toledo, 1999).

4. RESULTS AND DISCUSSIONS

Initially, Figures 1 and 2 show at the axial distance the dynamic profiles (surfaces) of temperature using the Heterogeneous Model I (Rigorous), which is a more realistic representation of the dynamic behaviour since it is considered a more detailed representation of the physic-chemical phenomena taking place in the system.

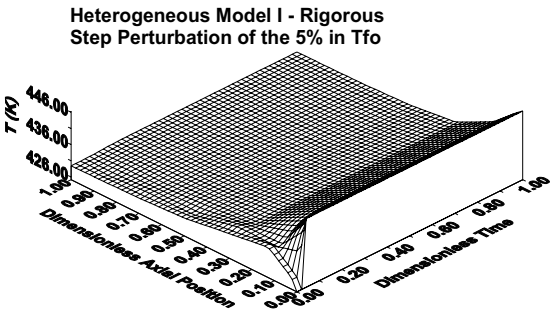

Figure 1. Temperature of the reactant fluid in the reactor: step perturbation in $T_{fo.}$

After a step perturbation in the reactant feed temperature, T_{fo}, the inverse response phenomenon is observed in the temperature profile at the beginning of the reactor (Figure 1). This is a typical characteristic of fixed bed catalytic reactors. It is also clear the great influence of the variation of T_{fo} in the dynamic behaviour. The identification of this phenomenon is very important in the elaboration of safe and efficient control strategies, since it determines the choice of manipulated and controlled variables as well the axial positions where the control of the system must be done.

Another important feature of this reactor is the presence of a hot spot located in the region where the inverse response phenomenon takes place.

In Figure 2 is represented the temperature dynamic behaviour of the reactor after a step perturbation in the coolant fluid feeding temperature, T_{ro}, where is observed an asymptotic dynamic behaviour.

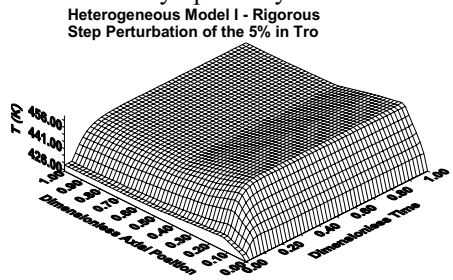

Figure 2. Temperature of the reactant fluid in the reactor: step perturbation in T_{ro}.

Comparing the results obtained in Figure 1 and 2, T_{ro} had a greater influence in the thermal profile at the axial position and this perturbation did not caused the inverse response phenomenon. Therefore, T_{ro} is more adequate to be chosen as a manipulated variable. Nevertheless, this conclusion must not be generalized for all operational and design conditions, since the determination of the manipulated variables depends on this conditions. For this reason, care should be taken in the choice of the manipulated and controlled variables in the elaboration of an efficient and safe control strategy.

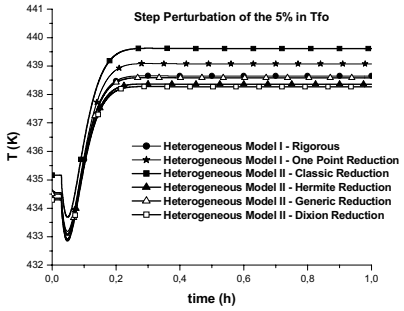

Figure 3. Temperature of the reactant fluid in the reactor ($z = 0.03$ m): step perturbation in T_{fo}

The following figures present the dynamic behaviour of the reactor predicted by the bidimensional reduced models and the rigorous tridimensional model. Figures 3, 4 and 5 show the thermal and conversion dynamic profile after a step perturbation in T_{fo}. At this condition, near the entrance of the reactor ($z = 0.03$ m) and at $z = 0.13$ m, there is an inverse response of the temperature (Figures 3 and 4, respectively). The profiles generated by the reduced models are in good agreement to those obtained with the rigorous model. This is also observed in the reactor conversion (Figure 5). It is important to mention that the computational time during simulations of the reduced models was up to 10 times less than that of the rigorous model. This time gain, without loss of prediction quality, justifies the use of the reduced models for applications in control and optimization cases represented in Figures 6 and 7 (step perturbation of T_{ro} and G, respectively).

Despite of the better reproduction of the rigorous model by the generic reduction technique, it is important to bear in mind that this result may differ according to new design and operation conditions.

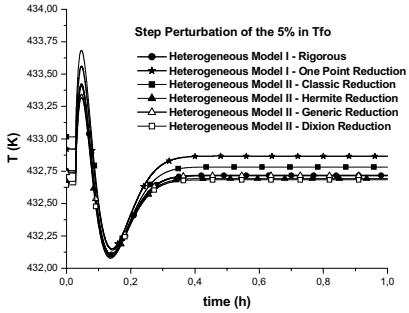

Figure 4. Temperature of the reactant fluid in the reactor ($z = 0.13$ m): step perturbation in T_{fo}

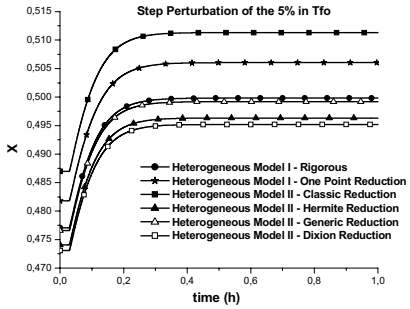

Figure 5. Conversion of the reactant fluid in the reactor (z = 0.03 m): step perturbation in T_{ro}.

In a nutshell, the results obtained with the models proposed to represent the fixed bed catalytic reactor show that the bidimensional reduced models had a good capacity to predict the dynamic behaviour described by the tridimensional model. Since all bidimensional models demanded similar computational time, the choice of a specific model will depend on the ability of the model to describe the real reactor behaviour.

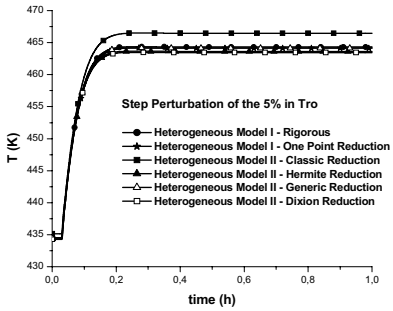

Figure 6. Temperature of the reactant fluid in the reactor (z = 0.03 m): step perturbation in T_{fo}.

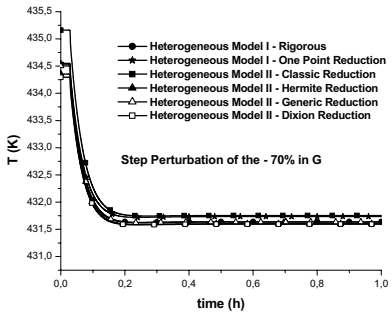

Figure 7. Temperature of the reactant fluid in the reactor (z = 0.03 m): step perturbation in G.

5. CONCLUSIONS

The proposed heterogeneous models were able to predict the main characteristics of the dynamic behaviour of the fixed bed catalytic reactor, including the inverse response phenomena and the hot spot present in the former. This knowledge is essential to design and control these reactors. The computational time demanded for the solution of the Heterogeneous Model I (rigorous) is high in comparison to the Reduced Models, which restricts the use of the rigorous models in cases where time is not a limiting factor. Otherwise, when on-line applications are required, the reduced models showed to be more adequate. The models based on reduction techniques overcame computational burden with a faster and easier numerical solution, as well as other difficulties found in rigorous heterogeneous models, especially related to the large number of parameters and sophisticated numerical procedures required to the solution. It is important to mention that for different design and operational conditions used in this work, the performance of the reduced models must be re-evaluated.

ACKNOWLEDGEMENTS

The authors are grateful to the Conselho Nacional de Desenvolvimento Científico e Tecnológico - CNPq for the financial support.

REFERENCES

Dixion, A., G. (1996). "An Improved Equation for the Overall Heat Transfer Coefficient in Packed Beds", Chemical Engineering and Processing, **35**, 323-331.

Elnashaie, S. S. E. H. and Elshishini, S. S. (1993). "Modelling, Simulation and Optimization of Industrial Fixed Bed Catalytic Reactors, Topics in chemical engineering Volume 7", Gordon and Breach Science Publishers .

Finlayson, B. A. (1971). "Packed Bed Reactor Analysis by Orthogonal Collocation", Chem. Eng. Sci., **26**, 1081-1091.

Jutan, A., Tremblay, J. P., McGregor, J. F., and Wright, J. D. (1977). "Multivariable Computer Control of a Butane Hydrogenolysis Reactor: Part I". State Space Reactor Modelling, AIChE Journal, **23**, 5, 732-742.

Maciel Filho, R. (1989). "Modelling and Control of Multitubular Reactors", Ph.D. Thesis, University of Leeds, Leeds,1989.

Marquardt, W. (1989)."Wellenausbreitung in verfahrenstechnischen Prozessen", Chemie Ingenieur Technik, **61**, 5, p. 362-377.

Gilles, E.D.; Epple, U. (1982). "Model reduction of the fixed-bed reactor", in Book: Recent advances in adsorption and ion exchange, AICHE Symposium Series.

Martinez, O. M., Pereira Duarte, S. J., and Lemcoff N., O. (1985). "Modeling of Fixed Bed Catalytic Reactors", Comp. Chem. Eng., **9**, 5, 535-545.

McGreavy, C. and Maciel Filho, R. (1989). "Dynamic Behaviour of Fixed Bed Catalytic Reactors", in "IFAC Dynamics and Control of Chemical Reactors", Maastricht, the Netherlands .

Pellegrini, L., Biardi, G. and Ranzi, E. (1989). "Dynamic Model of Packed-Bed Tubular Reactors", Comp. Chem. Eng., **13**, 4/5, 511-518.

Vasco de Toledo, E. C. (1999). "Modelling, Simulation and Control of the Fixed Bed Catalytic Reactors", Ph.D. Thesis, University of Campinas, São Paulo, Brazil .

Villadsen, J., Michelsen, M. L. (1978)."Solution of Differential Equation Models by Polynomial Approximation". Prentice-Hall, New Jersey.