Analysis of the multiplicity of steady-state profiles of two tubular reactor models ⋆

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Abstract: This paper deals with the analysis of two tubular reactor models, the non isothermal tubular reactor model and a biochemical reactor model. It is shown in particular that multiple equilibrium profiles can be exhibited if the diffusion coefficients are large enough.

Keywords: Reaction systems, multiple equilibrium profiles, tubular reactor, exothermic reaction, biochemical reaction

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1. INTRODUCTION

The dynamics of reaction systems is usually described by nonlinear models that most of the time exhibit multiple equilibrium points. The development of such models have indeed largely been motivated by practical issues and the need to emphasize phenomena encountered in the real life. The exothermic CSTR (continuous stirred tank reactor) model (e.g. (Ray (1981))) has been developed to address the issue of the presence of unstable steady-states in industrial chemical reactors, and in particular in the polymer industry, involving exothermic reactions also known as runaway reactions that require the careful design and application of appropriate feedback control laws in order to maintain the process in stable conditions. The use of the Haldane function for the specific growth rate, a non-monotonic function of the limiting substrate concentration, has been considered by (Andrews (1968)) to emphasize overloading effects in biochemical processes like the anaerobic digestion where the accumulation of volatile fatty acids may lead to the wash-out of the process, i.e. the disappearance of the active micro-organism. In ecology, Vito Volterra was motivated to develop a model, the predator-prey model, to address the periodic behaviour of the predators and the preys, an issue that had been raised by his future son-in-law Umberto D'Ancona, a marine biologist, who was puzzled by the behaviour of Selachians in the upper Adriatic sea (Kot (2001)). All these models are indeed very simple (only two differential equations), simply based on mass (and energy for the CSTR) balance considerations, yet very rich in terms of the dynamical properties. The multiplicity of the equilibrium points and their stability have been largely analyzed and explained in details in most basic textbooks on (bio)process control and mathematical ecology (e.g. (Bequette (2003))(Kot (2001))(Ogunnaike&Ray (1994))(Seborg et al. (2004)).

The CSTR model assumes that the medium in which the reactions takes place is homogeneous due to the perfect mixing of the fluid. If the perfect mixing conditions meets appropriately several configurations, it happens that the hydrodynamics in the tank may substantially differ from this ideal situation. It is even known in reactor design that the plug flow conditions typically provide higher conversion that the CSTR (Levenspiel (1999)). In such instance, the dynamics of the system have to be described by PDE's (partial differential equations) that account for the inherent non homogeneous behaviour of the system due to the different hydrodynamics. The standard configuration of such behavior is the tubular reactor (see Figure 1), which covers two configurations the convection-reaction one (also known as the plug flow reactor) and the convection-diffusion-reaction one, in which the diffusion term covers mainly the effect of back mixing in the reactor. The tubular chemical reactor is well known in the literature. The basis of the tubular biochemical model considered here comes from earlier work on the control of fixed bed bioreactors (Dochain et al. (1992)) and has been further studied in its application on anaerobic digestion in the pilot fixed bed reactor of the LBE-INRA in Narbonne (France) and the related validated model (Schoefs et al. (2004)).

The dynamical properties of the tubular reactor have been the object of many studies over the years (e.g. (Cohen&Poore (1974); Varma&Aris (1977); Georgakis et al. (1977); Dochain&Bouaziz (1994); Laabissi et al. (2004)) to cite a few). Yet the conditions for the occurrence of multiple equilibrium profiles remained unclear and poorly linked to the hydrodynamics.

In this paper we shall first present the dynamical model of both tubular reactors, their already known properties and their rewriting in dimensionless variables (Section 2). Sections 3 and 4 are dedicated to the conditions for having multiple equilibrium profiles and the related stability properties, respectively.

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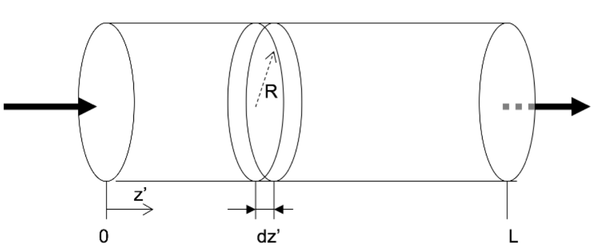

Fig. 1. Schematic view of a tubular reactor

2. TWO DYNAMICAL MODELS OF TUBULAR REACTORS

2.1 Model #1 : chemical tubular reactor

Figure 1 gives a schematic view of a tubular reactor. The dynamics of the system are derived from mass and energy considerations. This results in the following set of PDE's (e.g. (Varma&Aris (1977))):

$$\frac{\partial T}{\partial t'} = -v\frac{\partial T}{\partial z'} + \frac{\lambda_{ea}}{\rho C_p}\frac{\partial^2 T}{\partial z'^2} - \frac{\Delta H}{\rho C_p}k_0 C e^{-\dfrac{E}{RT}} + \frac{4h}{\rho C_p d}(T_w - T) \qquad (1)$$

$$\frac{\partial C}{\partial t'} = -v\frac{\partial C}{\partial z'} + D_{ma}\frac{\partial^2 C}{\partial z'^2} - k_0 C e^{-\dfrac{E}{RT}} \qquad (2)$$

with the following boundary conditions:

$$z' = 0 : \frac{\lambda_{ea}}{\rho C_p}\frac{\partial T}{\partial z'} = v(T - T_{in}), \quad D_{ma}\frac{\partial C}{\partial z'} = v(C - C_{in}) \qquad (3)$$

$$z' = L : \frac{\partial T}{\partial z'} = 0, \quad \frac{\partial C}{\partial z'} = 0 \qquad (4)$$

In the above equations, t' is the time (s), z' is the spatial variable (m)($0 \leq z' \leq L$), $T > 0$ is the temperature (K), $C > 0$ is the process component concentration (kg.m^{-3}), L (m) is the length of the reactor, v is the fluid superficial velocity (m/s), λ_{ea} is the axial energy dispersion coefficient (kJ.m^{-1}.s^{-1}.K^{-1}), D_{ma} is the axial mass dispersion coefficient (m^2/s), ΔH is the heat of reaction (kJ.kg^{-1}) (ΔH $<$ 0 for exothermic reactions, and $>$ 0 for endothermic reactions), ρ is the fluid density (kg/m^3), C_p is the specific heat (kJ.kg^{-1}.K^{-1}), k_0 is the kinetic constant (s^{-1}), E is the activation energy (kJ.kg^{-1}), R is the gas constant (kJ.kg^{-1}.K^{-1}), h is the wall heat transfer coefficient (kJ.m^{-2}.K^{-1}.s^{-1}), d is the reactor diameter (m), T_w is the coolant temperature (K), is the inlet temperature (K), C_{in} and is the inlet reactant concentration (kg.m^{-3}).

In the above equations, the kinetic term $k_0 C e^{-\frac{E}{RT}}$ corresponds to the kinetics of a non-isothermal reaction with first order kinetics with respect to the reactant concentration C and Arrhenius-type dependence with respect to the temperature T. This term indeed closely interconnects the mass and energy balance equations.

The boundary conditions are known as the Danckwerts' conditions (Danckwerts (1953)).

Note also that the diffusion terms in (1) and (2) are inspired by the Fick's law, yet covers all the contributions to intermixing of fluid flowing in the longitudinal direction, including molecular diffusion and macroscopic back mixing (dispersion)(see Levenspiel (1999)).

Note also that the above model reduces to the plug flow reactor model when the diffusion coefficients λ_{ea} and D_{ma} are both equal to zero, i.e.:

$$\frac{\partial T}{\partial t'} = -v\frac{\partial T}{\partial z'} - \frac{\Delta H}{\rho C_p}k_0 C e^{-\dfrac{E}{RT}} + \frac{4h}{\rho C_p d}(T_w - T) \qquad (5)$$

$$\frac{\partial C}{\partial t'} = -v\frac{\partial C}{\partial z'} - k_0 C e^{-\dfrac{E}{RT}} \qquad (6)$$

In that case, the boundary equations reduce to:

$$z' = 0 : T = T_{in}, \quad C = C_{in} \qquad (7)$$

The present process example is particularly interesting since it is well known that the existence of Arrhenius type nonlinearities can generate multiple equilibrium points for exothermic reactions, either stable or unstable, and that in practical applications, the unstable steady states may correspond to the operating points of interest. The study of the steady state multiplicity and stability has been the object of intensive research activity in the sixties and seventies, most of the results are gathered in (Varma&Aris (1977)). Multiple steady states have been observed experimentally, e.g., in continuous stirred tank reactors (Furusawa et al. (1969); Vejtasa&Schmitz (1970)). If the steady state multiplicity and stability of stirred tank reactors are now well understood, the tubular reactor case is still the object of research works. In this context, the seminal paper of Varma and Aris (Varma&Aris (1977)) emphasizes sufficient conditions for the uniqueness of steady states for adiabatic reactors (i.e., when there is no energy exchange with the environment, which means here the absence of a heat exchanger, i.e. when $h = 0$ in (1)) in the particular case when the energy and mass Peclet numbers are equal. They also show that in presence of multiple steady states for the aforementioned tubular reactor model, these are alternatively stable and unstable. The case of nonequal diffusion coefficients has been considered by Deimling (Deimling (1970)), who emphasized steady-state multiplicity, yet in unrealistic conditions, i.e., when the reactor temperature is lower than the inlet and cooling temperature in an exothermic reactor. More recently, the steady-state multiplicity in non-isothermal reactors has been shown in (Laabissi et al. (2004)) by using similar arguments as those considered by Deimling as well as compactness and nonlinear operator arguments. However, although there is a strong convergence of results in the literature in the direction of an alternance of stable and unstable steady states in presence of multiple equilibrium points, the existence and stability of the multiple equilibrium points for the tubular reactor model largely remains an open question.

Note also that the tubular reactor has been the object of many control studies (see e.g. (Boskovic&Krstic (2002)) (Godassi et al. (2002)) (Hudon et al. (2008)) (Orlov&Dochain (2002))).

For sake of simplicity and without loss of generality, a dimensionless model of the tubular reactor will be used. Let us consider the following time and space formulations, and change of variables:

$$t = t'\frac{v}{L},\ z = \frac{z'}{L} \tag{8}$$

$$x_1 = \frac{T - T_{in}}{T_{in}},\ x_2 = \frac{C_{in} - C}{C_{in}},\ x_w = \frac{T_w - T_{in}}{T_{in}} \tag{9}$$

Then equations (1)(2) can be rewritten as follows:

$$\frac{\partial x_1}{\partial t} = -\frac{\partial x_1}{\partial z} + \frac{1}{Pe_h}\frac{\partial^2 x_1}{\partial z^2} + Da\,\delta(1 - x_2)e^{\frac{\eta x_1}{1 + x_1}} + \sigma(x_w - x_1) \tag{10}$$

$$\frac{\partial x_2}{\partial t} = -\frac{\partial x_2}{\partial z} + \frac{1}{Pe_m}\frac{\partial^2 x_2}{\partial z^2} + Da(1 - x_2)e^{\frac{\eta x_1}{1 + x_1}} \tag{11}$$

with:

$$Pe_h = \frac{vL\rho C_p}{\lambda_{ea}},\ Pe_m = \frac{vL}{D_{ma}},\ Da = \frac{k_0 L}{v}e^{-\eta} \tag{12}$$

$$\eta = \frac{E}{RT_{in}},\ \delta = \frac{-\Delta H}{\rho C_p}\frac{C_{in}}{T_{in}},\ \sigma = \frac{4hL}{\rho C_p d v} \tag{13}$$

with the thermal Pe_h and mass Pe_m Peclet numbers, Da the (dimensionless) Damköhler number (a measure of the relative importance of kinetics and convection), and the following boundary conditions:

$$z = 0 : \frac{\partial x_1}{\partial z} = Pe_h x_1, \tag{14}$$

$$\frac{\partial x_2}{\partial z} = Pe_m x_2 \tag{15}$$

$$z = 1 : \frac{\partial x_1}{\partial z} = 0,\quad \frac{\partial x_2}{\partial z} = 0 \tag{16}$$

Note that the (dimensionless) Peclet numbers allow to evaluate the relative importance of convection versus diffusion.

2.2 *Model #2: biochemical tubular reactor*

The biochemical tubular reactor model that we study here considers an autocatlytic growth reaction with one substrate S and one biomass X in a reactor where the biomass is "fixed" (this indeed covers various configurations of fixed bed, packed bed and fluidized bed reactors). For consistency reasons (this allows to have a steady state for the biomass), a biomass death/decay reaction has to be added (this reaction can also be viewed as a detachment phenomenon of the biomass submitted to shear stress due the liquid flow in the tank). If we consider mass balances for the substrate concentration S and the biomass concentration X, the dynamics of the system in a tubular reactor is given by the following set of partial differential equations:

$$\frac{\partial S}{\partial t'} = -v\frac{\partial S}{\partial z'} + D_{ma}\frac{\partial^2 S}{\partial z'^2} - k_1\mu X \tag{17}$$

$$\frac{\partial X}{\partial t'} = \mu X - k_d X \tag{18}$$

with the following boundary conditions:

$$z' = 0 : D_{ma}\frac{\partial S}{\partial z'} = v(S - S_{in}) \tag{19}$$

$$z' = L : \frac{\partial S}{\partial z'} = 0 \tag{20}$$

In the above equations, k_1 is yield coefficient, μ is the specific growth rate (h^{-1}), k_d is the death/detachment rate (h^{-1}), and S_{in} is the inlet substrate concentration (kg.m^{-3}).

It is easy to see that if the specific growth rate μ is only a function of the substrate concentration S, the steady-state values of X and S are uniform throughout the tank. A steady-state profile can be obtained by considering a model function of both S and X, like the Contois model:

$$\mu = \frac{\mu_0 S}{K_C X + S} \tag{21}$$

Multiple steady states can be emphasized in CSTR's of biological systems in presence of an inhibition Haldane model:

$$\mu = \frac{\mu_0 S}{K_S + S + \dfrac{S^2}{K_i}} \tag{22}$$

here we consider a combined version of the above two kinetic functions, i.e.:

$$\mu(S, X) = \frac{\mu_0 S}{K_C X + S + \dfrac{S^2}{K_i}} \tag{23}$$

This model has been considered e.g. in (Dramé et al. (2008))(Schoefs et al. (2004)).

Similarly to what has been done for the chemical tubular reactor model, let us consider the following time and space formulations, and change of variables:

$$t = t'\frac{v}{L},\ z = \frac{z'}{L},\ x_1 = \frac{S_{in} - S}{S_{in}},\ x_2 = \frac{X}{S_{in}} \tag{24}$$

Then equations (17)(18) can be rewritten as follows:

$$\frac{\partial x_1}{\partial t} = -\frac{\partial x_1}{\partial z} + \frac{1}{Pe_m}\frac{\partial^2 x_1}{\partial z^2} - k_1\mu(x_1, x_2)x_2 \tag{25}$$

$$\frac{\partial x_2}{\partial t'} = \mu(x_1, x_2)x_2 - \gamma x_2 \tag{26}$$

with the following boundary conditions:

$$z = 0 : \frac{1}{Pe_m}\frac{\partial x_1}{\partial z} - x_1 = 0 \tag{27}$$

$$z = 1 : \frac{\partial x_1}{\partial z} = 0 \tag{28}$$

and with

$$\mu(x_1, x_2) = \frac{\beta(1 - x_1)}{K_C x_2 + (1 - x_1) + \alpha(1 - x_1)^2} \tag{29}$$

$$\alpha = \frac{S_{in}}{K_i},\ \beta = \frac{L}{v}\mu_0,\ \gamma = \frac{L}{v}k_d \tag{30}$$

3. MULTIPLE EQUILIBRIUM PROFILES

3.1 *The key result*

As mentioned above, there are already several results about the equilibrium profiles of the tubular reactor model.

The results developed in Laabissi et al. (2004) provide simple conditions for having multiple equilibrium points:

$$\frac{E}{RT_{in}} > 4, \ \frac{k_0 L}{v} < 1 \tag{31}$$

It happens that these conditions are quite conservative. Moreover they are difficult to meet in practice (Symptomatically the multiple equilibrium points drawn in Figure 2 correspond to a set of parameters that do not meet these conditions).

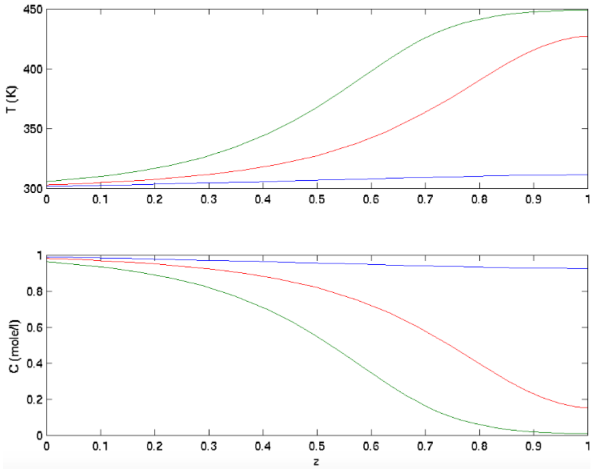

Fig. 2. Multiple equilibrium profiles of an adiabatic tubular reactor (each colour corresponds to one of three equilibrium profiles, both for the reactant concentration C in the top figure, and for the temperature T in the bottom figure)

But even more fundamentally, there is an important missing information in these conditions : the relative importance of convection and diffusion (that can be characterized by the Peclet numbers). Indeed it is well known in chemical engineering (Levenspiel (1999)) that the convection-diffusion-reaction model is an intermediate model between the plug flow reactor model (when the diffusion coefficients λ_{ea} and D_{ma} are equal to zero) and the CSTR model (when these tend to $+\infty$). As it was already pointed out in (Varma&Aris (1977)), it is obvious that the plug flow reactor can generate only one equilibrium point since it is the solution of a set of first-order differential equations with fixed initial values (7). And at the other extreme, it is well known that the CSTR can exhibit three different equilibrium points. Therefore one can conclude that there must be a value of the diffusion coefficients above which the tubular reactor model can exhibit multiple equilibrium profiles (and below which there is only one equilibrium profile).

The key result considered here has been first presented in (Dramé et al. (2008) and is based the following equation:

$$D\frac{d^2\bar{x}_1}{dz^2} - v\frac{d\bar{x}_1}{dz} + g(\bar{x}x_1) = 0 \tag{32}$$

$$D\frac{d\bar{x}_1}{dz}(0) - v\bar{x}_1(0) = \frac{d\bar{x}_1}{dz}(1) = 0 \tag{33}$$

that represents the steady-state equation of the system. Let us introduce $u(z) := \bar{x}_1(1-z)$ and $w(z) := \dfrac{d\bar{x}_1(1-z)}{dz}$ for all $0 \leq z \leq 1$. Then equation (32)(33) becomes

$$\frac{du}{dz} = -w \tag{34}$$

$$\frac{dw}{dz} = -\frac{1}{D}(vw - g(u)) \tag{35}$$

$$u(0) = a, w(0) = 0 \text{ and } w(1) = \frac{v}{D}u(1) \tag{36}$$

So by applying regular perturbation theory (with D more or less large), the following statement holds. Note that (34)-(36) can be solved by finding a parameter $v = v(a, D)$ (depending on a and D), whenever a and D are given, such that the solution (u, w) of the Cauchy problem in (34)-(36) satisfies the final condition

$$w(1) = \frac{v}{D}u(1)$$

Therefore, if there are $a_1 \neq a_2$ and $D > 0$ such that $v(a_1, D) = v(a_2, D)$, then (34)-(36) has at least two solutions. So the existence of multiple equilibrium profiles is equivalent to the existence of a_1, a_2 , . . . , and $D > 0$ such that $v(a_i, D) = v(a_j, D)$ for all i and j.

Now let us assume that D is large enough, and we introduce

$$\epsilon = \frac{1}{D}, u_\epsilon = u, \text{ and } w_\epsilon = \frac{1}{\epsilon}w$$

and we consider v as a function of ϵ $[v = v(a, \epsilon)]$ instead of a function of D. This leads to the following regular perturbation problem:

$$\frac{du_\epsilon}{dz} = -\epsilon w_\epsilon \tag{37}$$

$$\frac{dw_\epsilon}{dz} = -(v\epsilon w_\epsilon - g(u_\epsilon)) \tag{38}$$

$$u_\epsilon(0) = a, w_\epsilon(0) = 0 \text{ and } w_\epsilon(1) = \frac{v}{D}u_\epsilon(1) \tag{39}$$

Considering the non-perturbed problem, $u_0 \equiv a$, $w_0(1) = g(u_0)$, whence $va = g(a)$. Then, for $\epsilon = 0$, we have

$$v(a, 0) = \frac{g(a)}{a}$$

. If $v(a, 0)$ is a concave function, mutiple solutions are possible, and the result below directly follows

Proposition 4.1: There exists $D^* > 0$ sufficiently large and $v^* > 0$ such that for all $D \geq D^*$ the system (53)(54) has

- (i) at least three solutions if the parameter v satisfies $0 \leq v < v^*$,
- (ii) at least two solutions for $v = v^*$,

From the theorem of dependence of the solutions of ordinary differential equations on initial conditions,

$$\lim_{\epsilon \to 0} v(a, \epsilon) = v(a, 0) \quad \text{in } C^2[0, 1] \tag{40}$$

And the result follows.

□

3.2 Biochemical tubular reactor model

This idea has been first followed in the analysis of a biochemical reactor model (Dramé et al. (2008)). The equilibrium profiles $(\bar{x}_1, \bar{x}_2)$ are solutions of:

$$\frac{1}{Pe_m}\frac{d^2\bar{x}_1}{dz^2} - \frac{d\bar{x}_1}{dz} - k_1\mu(\bar{x}_1,\bar{x}_2)\bar{x}_2 = 0 \tag{41}$$

$$\mu(\bar{x}_1,\bar{x}_2)\bar{x}_2 - \gamma\bar{x}_2 = 0 \tag{42}$$

$$\frac{1}{Pe_m}\frac{d\bar{x}_1}{dz}(0) - \bar{x}_1(0) = \frac{d\bar{x}_1}{dz}(1) = 0 \tag{43}$$

The system has obviously the trivial solution $(\bar{x}_1,\, \bar{x}_2) =$ (0,0) which corresponds to the prices washout $(\bar{S},\, \bar{X}) = (\bar{S}_{in}, 0)$. In the following ware interested in the solutions that satisfy $\mu(\bar{x}_1,\bar{x}_2) = \gamma$. We readily obtain:

$$\bar{x}_2 = \frac{(1-\bar{x}_1)(M+\alpha k_d\bar{x}_1)}{k_d K_C} \tag{44}$$

with $M = \mu_0 - k_d - \alpha k_d$. The function $g(\bar{x}_1)$ is then written as follows:

$$g(\bar{x}_1) = \frac{k_1 L(1-\bar{x}_1)(M+\alpha k_d\bar{x}_1)}{K_C} \tag{45}$$

The function $v(a,0)$ is readily derived, and from direct computations, we have:

$$\frac{\partial v(a,0)}{\partial a} = \frac{-k_1 LM}{K_C a^2}(M+\alpha k_D a^2) \tag{46}$$

$$\frac{\partial^2 v(a,0)}{\partial a^2} = \frac{2k_1 LM}{K_C a^3} \tag{47}$$

It follows that $a \longrightarrow v(a,0)$ is concave (Figure 3).

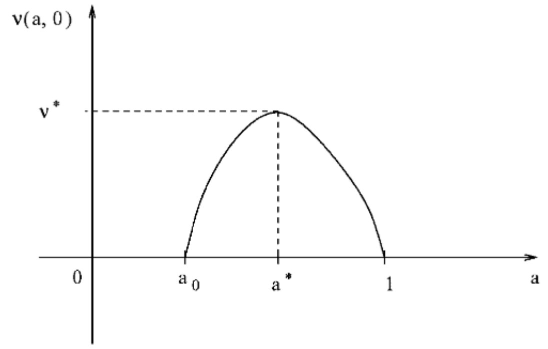

Fig. 3. The function $v(a,0)$ as a function of a for the biochemical reactor model

3.3 Chemical tubular reactor model

The development for the biochemical reactor model has been followed here also. A specific aspect is that one of the equilibrium equations is a differential equation while the other one is an algebraic equation. We further explore this idea for the adiabatic tubular reactor with equal Peclet numbers, and take advantage now of the notion of reaction invariant (an important property of the reaction system models, see e.g. in (Dochain et al. (1992, 2009)). Indeed if we consider the following change of variables :

$$y_1 = x_1,\; y_2 = x_1 - \delta x_2 \tag{48}$$

(where y_2 formally corresponds to a reaction invariant), the equilibrium equations of the adiabatic tubular reactor are rewritten as follows:

$$\frac{d^2\bar{y}_1}{dz^2} - Pe\frac{d\bar{y}_1}{dz} + Pe\,Da\,(\delta - \bar{y}_1 - \bar{y}_2)e^{\frac{\eta\bar{y}_1}{1+\bar{y}_1}} = 0 \tag{49}$$

$$\frac{d^2\bar{y}_2}{dz^2} - Pe\frac{d\bar{y}_2}{dz} = 0 \tag{50}$$

with the following boundary conditions:

$$z = 0 : \frac{d\bar{y}_1}{dz} = Pe\,\bar{y}_1,\quad \frac{d\bar{y}_2}{dz} = Pe\,\bar{y}_2 \tag{51}$$

$$z = 1 : \frac{d\bar{y}_1}{dlz} = 0,\quad \frac{d\bar{y}_2}{dz} = 0 \tag{52}$$

and $Pe = Pe_h = Pe_m$ while $\bar{y}_i(z) (i = 1,2)$ holds for the equilibrium profile values of $y_i(t,z)$.

It is straightforward to see that the solution of (50) combined with the two related boundary conditions (51)(52) is : $\bar{y}_2(z) = 0$.

The analysis of the equilibrium profiles of the tubular reactor model is therefore that of the following differential equation:

$$\frac{d^2\bar{y}_1}{dz^2} - Pe\frac{d\bar{y}_1}{dz} + Pe\,Da\,(\delta - \bar{y}_1)e^{\frac{\eta\bar{y}_1}{1+\bar{y}_1}} = 0 \tag{53}$$

$$z = 0\ :\ \frac{d\bar{y}_1}{dz} = Pe\,\bar{y}_1,\quad z = 1\ :\ \frac{d\bar{y}_1}{dlz} = 0 \tag{54}$$

Recall that $Pe = \dfrac{vL}{D}$ with $D = D_{ma} = \dfrac{\lambda_{ea}}{\rho C_p}$ and let us consider the real valued function g defined by

$$g(\bar{y}_1) = Pe\,Da\,(\delta - \bar{y}_1)e^{\frac{\eta\bar{y}_1}{1+\bar{y}_1}} \tag{55}$$

From direct computations, one can check that the first-order and second-order derivatives with respect to a are equal to:

$$\frac{\partial v(a,0)}{\partial a} = k_0 L e^{-\frac{\eta}{1+a}}\left[\frac{-(\eta+\delta)a^2 + \delta(\eta-2)a - \delta}{a^2(1+a)^2}\right] \tag{56}$$

and

$$\begin{aligned}\frac{\partial^2 v(a,0)}{\partial a^2} = k_0 L\frac{e^{-\frac{\eta}{1+a}}}{a^3(1+a)^4}[(7\delta-\eta)a^4 + (\eta - 3\delta\eta + 7\delta)a^3 \\ +(10\delta - 2\delta\eta - \eta)a^2 + (7\delta - \eta)a + 2\delta]\end{aligned} \tag{57}$$

The first-order derivative $\dfrac{\partial v(a,0)}{\partial a}$ is equal to zero if

$$-(\eta+\delta)a^2 + \delta(\eta-2)a - \delta = 0 \tag{58}$$

The discriminant ρ_e of this second-order equation in a is equal to:

$$\rho_e = \eta\delta(\eta\delta - 4\delta - 4) \tag{59}$$

If $(\mu - 4)\delta > 4$, equation (58) has two solutions:

$$a = \frac{\delta(\eta-2)}{2(\eta+\delta)} \pm \frac{1}{2(\eta+\delta)}\sqrt{\eta\delta(\eta\delta - 4\delta - 4)} \tag{60}$$

By a careful examination of $\dfrac{\partial^2 v(a,0)}{\partial a^2}$, it can be shown that the function $a \longrightarrow v(a,0)$ can be locally concave for some values of the parameters δ and η and has the following form (Figure 4).

4. CONCLUSION

This paper has been concerned with the analysis of two tubular reactor model, one with an exothermic reaction and diffusion terms for the mass and energy balance equations in adiabatic conditions with the same Peclet number for mass and energy dispersion, and one with a

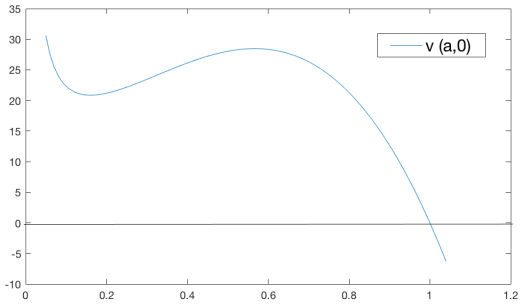

Fig. 4. The function $v(a,0)$ as a function of a for the chemical reactor model ($\delta = 1$, $\eta = 10$)

biochemical growth reaction involving substrate inhibition and diffusion terms for the mass balance of the substrate concentration. The central result shows at the multiplicity of equilibrium profiles takes place once the diffusion coefficient is large, in line with the perception that the tubular model with diffusion is an intermediate model between the plug flow (with no diffusion), for which only one equilibrium is possible, and the CSTR model (infinite diffusion coefficient), for which three equilibrium points are possible. It still remains to show that the multiplicity of equilibrium profiles also applies for the tubular reactor in non-adiabatic case with different Peclet numbers. At this point the easiest way to address this issue is to consider this case as a perturbed one of the one analyzed here. Yet a detailed analysis has still to be performed.

REFERENCES

Amundson N.R. (1965). Some further observations on tubular reactor stability. *Canadian Journal of Chemical Engineering*, 43, 49-55.

Andrews J. (1968). A mathematical model for the continuous culture of microorganisms utilizing inhibitory substrates. *Biotech. & Bioeng.*, 10, 707?-723.

Bequette W. (2003). *Process Control. Modeling, Design and Simulation*, Prentice-Hall, Upper Saddle River.

Boskovic D.M. and M. Krstic (2002). Backstopping control of chemical tubular reactors. *Computers and Chemical Engineering*, 26, 1077-1085.

Cohen D.S. and A.B. Poore, Tubular chemical reactors: The lumping approximation and bifurcation of oscillatory states. *SIAM Journal of Applied Mathematics*, 27, 416-429.

Danckwerts P. V. (1953). Continuous flow systems. Distribution of residence times. *Chem. Engin. Sci.*, 2 (1), 1Ð13.

Deimling K. (1970). *Nonlinear Functional Analysis*, Springer-Verlag.

Delattre C., D.Dochain and J. Winking (2003). Sturm-Liouville systems are Reisz-spectral systems. *Int. J. Appl. Math. Comput. Sci.*, 13 (4), 481Ð484.

Dochain D. and B. Bouaziz (1994). Approximation of the dynamical model of fixed bed reactors via a singular perturbation approach. *Mathematics and Computers in Simulation*, 37 (2-3), 165-172.

Dochain D., J.P. Babary and N. Tali-Maamar (1992). Modelling and Adaptive Control of Nonlinear Distributed Parameter Bioreactors via Orthogonal Collocation. *Automatica*, 28(5), 873-883.

Dochain D., M. Perrier and B.E. Ydstie (1992). Asymptotic observers for stirred tank reactors. *Chemical Engineering Science*, 47, 4167-4178.

Dochain D., F. Couenne and C. Jallut(2009). Enthalpy based modelling and design of asymptotic observers for chemical reactors. *International Journal of Control*, 82(8), 1389 - 1403.

Drame A.K., D. Dochain and J.J. Winkin (2008). Asymptotic behaviour and stability for solutions of a biochemical reactor distributed parameter model. *IEEE Transactions on Automatic Control*, 53(1), 412-416.

Furusawa T., H. Nishimura, and T. Miyauchi (1969), Experimental study of a bistable continuous stirred tank reactor, *Journal of Chemical Engineering Japan*, vol. 2, p.95.

Georgakis C., R. Aris and R. Amundson (1997). Studies in the control of tubular reactors i. General considerations. *Chemical Engineering Science*, 32, 1359-1369.

Godassi S., A. Caracas and A. Palazoglu (2002). Control of nonlinear distributed parameter processes using symmetry groups and invariance conditions. *Computers and Chemical Engineering*, 26, 1023-1036.

Hudon N., M. Guay, M. Perrier and D. Dochain (2008). Adaptive Extremum-Seeking Control of Convection-Reaction Distributed Reactor with Limited Actuation. *Comp. Chem.l Eng.*, 32(12), 2994-3001

Kot M. (2001). *Elements of Mathematical Ecology.* Cambridge University Press, Cambridge.

Laabissi M., D. Dochain, J.Winkin, and M. E. Achhab (2004). Multiple equilibrium profiles for a nonisothermal tubular reactor nonlinear model, *Dynamics of Continuous, Discrete and Impulsive Systems*, 11, 339-352.

Levenspiel 0. (1999). *Chemical Reaction Engineering.* 3^{rd} edition, John Wiley, New York.

Luus D. and N.R. Amundson (1967). Some general observations on tubular reactor stability. *Canadian Journal of Chemical Engineering*, 45, 341-346.

Ogunnaike B.A. and W.H. Ray (19944). *Process Dynamics, Modeling and Control*, Oxford University Press, New York.

Orlov Y. and D. Dochain (2002). Discontinuous Feedback Stabilization of Minimum Phase Semilinear Infinite-Dimensional Systems with Application to Chemical Tubular Reactors. *IEEE Transactions on Automatic Control*, 47(8), 1293-1304.

Ray W.H. (1981). New approaches to the dynamics of nonlinear system with implications for process and control system design. *Proc. CPC II, T.F. Edgar & D.E. Seborg (Eds.).*

Schoefs O., D. Dochain, H. Fibrianto and J. -P. Steyer (2004). Modelling and identification of a partial differential equation model for an anaerobic wastewater treatment process. *Proc. 10th World Congress on Anaerobic Digestion (AD10-2004), Montreal, Canada.*

Seborg D., T.F. Edgar and D.A. Mellichamp (2004). *Process Dynamics and Control*, 2^{nd} edition, Wiley, Hoboken.

Varma A. and R. Aris (1977). Stirred pots and empty tubes, *Chemical Reactor Theory*, L. Lapidus and N.R. Amundson (Eds.), Prentice-Hall, 79-154.

Vejtasa S. A. and R. A. Schmitz (1970), An experimental study of steady state multiplicity and stability in an adiabatic stirred reactor, *AIChE J.*, 16, p. 410, 1970.