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An invariant manifold approach for CSTR model reduction in the presence of multi-step biochemical reaction schemes. Application to anaerobic digestion

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ABSTRACT

A systematic methodology for CSTR model reduction has been developed for multi-step biochemical reaction schemes. The proposed method neglects the dynamics of the fast steps by projecting the overall system dynamics on the slow-motion invariant manifold of the system. In particular, using reaction invariants in the description of the overall system dynamics, the slow-motion invariant manifold is calculated by solving the pertinent invariance equation via series-solution or singular perturbation techniques. The proposed method is an alternative to the quasi-steady state approximation which does not rely on a priori physical information. The proposed approach is applied to two model reduction problems arising in anaerobic digestion. The results provide a rigorous answer on how to properly eliminate the fast dynamics of the acidogenesis step.

1. Introduction

Multi-step biochemical processes involve a variety of reaction schemes that relate with life. In every living organism, numerous reactions evolve simultaneously or sequentially with the aim of producing energy for production of new cells and for maintenance. From an engineering point of view, the dynamics of biochemical process schemes involved, either at a single cell level or at the level of pure or mixed microbial cultures, are particularly interesting. In particular, mixed microbial processes are quite common in numerous applications in biochemical engineering and environmental technology. In such complex microbial environments as in the activated sludge process or the anaerobic digestion process, the interactions between different microbial groups are complicated and extremely diverse (mutualistic, competitive, amensalistic, prey–predator) [1]. There are a variety of mathematical structured and unstructured models of varying complexity, aiming at describing the microbial interactions and the dependence of the process performance on the bioreactor feed characteristics and the prevailing operating conditions.

Recognizing the importance and general applicability of some of these bioprocesses, such as activated sludge and anaerobic digestion, the International Water Association (IWA) formed task groups that developed typical generic models such as the activated sludge model (ASM) [2] and the anaerobic digestion model (ADM) [3]. The IWA model for anaerobic digestion [3] defines a framework for modelling a complicated process, based on the previous kinetic and modelling studies of various researchers [4–7]. The models developed by the task groups reflect the current understanding of the key biological and physicochemical processes that take place in such complex environments. In that regard, they are quite useful as process simulators, while they also offer excellent educational tools. Since these models are sufficiently structured they must always be properly modified and calibrated in order to adequately reflect a particular situation at hand.

The use of complex models such as ASM and ADM, although valuable for general process simulation, has severe shortcomings if they are intended to be used for process control and optimisation [8]. This is because there are difficulties in determining the numerous model parameters (non-identifiability of parameters), while manipulating a large number of equations limits the applicability for the dynamic analysis, process simulation and control. In addition, although the model assumptions reflect quite well our current understanding of the physical processes involved, many of the individual steps may actually be so fast so that they do not influence the overall process dynamics. Simpler models are needed, that adequately describe the dynamics of the key measured variables. Such a reduction is meaningful from an intuitive point of view, since (a) some of the processes may have no or small impact on the measured process variables of interest, i.e. they may be unobservable, or they may be negligible (b) some processes may be lumped

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to fewer processes without again any appreciable loss of information, (c) some processes exhibit faster transients over a given time scale than others and, therefore, can be assumed to undergo instantaneous changes (d) for the specific operating conditions, stoichiometric constraints between the state variables may be valid at all times and as a result may be used to reduce the number of state variables. In complex multivariable systems such as biochemical systems, however, this intuitive basis of simplification relying on physical arguments may be risky, since the individual dynamics of the variables may be interrelated and the distinction between slow and fast often becomes obscure.

An excellent review of the existing mathematical methods for model reduction in chemical reaction systems has recently been made by Okino and Mavrovouniotis [9]. There, three general types of model reduction methods are reviewed: lumping, time-scale methods and invariant manifold methods. Such methods have been applied to reduce models for complex chemical systems [10–14], as well as complex biochemical pathways [15–18]. The Quasi Steady State (QSS) approximation has widely been used in (bio)chemical engineering [19–21] as well. Actually, the QSS approximation can be justified mathematically by applying perturbation analysis techniques, through which the dynamics of some states of the system (e.g. products with low solubility in the liquid phase or substrates involved in fast reactions) can be neglected [8,22].

These methods may be used to justify or reject a particular model reduction that has been made based on phenomenological arguments. However, to our knowledge, only limited amount of work has been done on developing mathematically solid model reduction for complex environmental processes that contain mixed cultures of microbial species.

Such systems contain a significant amount of biomass, maintained in the system through immobilisation or recycle, such as biofilm systems and the activated sludge process respectively, and are characterised by relatively slow changes in the biomass in comparison with the various soluble substrates and metabolic intermediates that are rapidly adjusted to reflect the feed characteristics and the mixed culture composition. Thus, it is common knowledge that, in such systems the overall biomass concentration and the individual microbe composition vary with time constants that are often several orders of magnitude higher than the hydraulic retention time (inverse dilution rate). However, even in cases of suspended growth systems, in which particulate biomass and substrates are removed at the same rate from the reaction system, there may be additional valid basis for model reduction. In particular, the basis for model reduction in such systems arises from the existence of fast and slow bioconversion steps (which is often the result of wide differences in specific growth rates of the involved species). In addition, the microbial network structure may often allow for approximate decoupling of the fast steps from the slow steps, allowing for further model simplification.

In this paper, a systematic methodology is proposed for the reduction of dynamic models for multi-step biochemical reaction schemes in a CSTR. The proposed methodology is based on an invariant manifold formulation of the model reduction problem, and in particular, on projecting the CSTR dynamics on the slow-motion invariant manifold. To be able to compute the slow-motion invariant manifold, the proposed method makes use of reaction invariants [10,12,23,24] in the description of CSTR dynamics, and subsequently the invariance equation is solved via series solution or singular perturbation techniques [13,14].

Once the general methodology is presented, it is applied to an important mixed culture multi-step biochemical process, the anaerobic digestion process. The importance of this process results from the fact that it finds wide application in municipal sludge treatment, in the treatment of high organic strength industrial wastewaters, in the treatment of the organic fraction of municipal solid waste and in the recent years, in the exploitation of energy crops for the production of biogas [25]. In this process, a complex microbial consortium degrades complex organic material, generating biogas (a methane and carbon dioxide mixture) which is a useful renewable energy source. The application of the proposed method results in reducing the model order to a system consisting only of what is called in chemical engineering "rate limiting steps", namely, hydrolysis of particulate matter and acetoclastic methanogenesis [26–29]. In this way, model reduction is justified through a rigorous mathematical and systematic methodology, which is complementary to the QSS approximation methodology (as applied by Perrier and Dochain [8] and Dochain and Vanlrolleghem [22].

It should be stressed, however, that although the proposed methodology has been developed for mixed microbial processes, it can also be applied to other non microbial biochemical systems, such as metabolic pathways, as well as to general chemical reaction systems, following minor modifications.

2. Background

2.1. General model for a continuous stirred tank biochemical reactor

The biochemical reactions by mixed microbial cultures, involve numerous chemical species consumed (substrates) and produced (intermediate or final metabolic products) and microbial groups mainly grown. Chemical species produced by a microbial group are often the substrate for the growth of other microbial groups, making the whole process a sequence of individual process steps in a scheme where the preceding steps may be independent of those that follow.

Assuming that biochemical reactions, generally described through

$$S_i \xrightarrow{r_k} Y_{j,k} \cdot X_j + \sum_{\substack{\iota = 1 \\ (\iota \neq i)}}^{l} C_{\iota,k} \cdot S_\iota \tag{1}$$

take place in a chemostat (continuously stirred tank reactor; CSTR), the following differential equations can be derived:

$$\begin{aligned} \dot{S}_i &= D(S_i^o - S_i) + \sum_{k=1}^{n} C_{i,k} \cdot r_k(S_1, \ldots, S_l, X_1, \ldots, X_m), \quad i = 1, \ldots, l \\ \dot{X}_j &= D(X_j^o - X_j) + \sum_{k=1}^{n} Y_{j,k} \cdot r_k(S_1, \ldots, S_l, X_1, \ldots, X_m), \quad j = 1, \ldots, m \end{aligned} \tag{2}$$

where

D is the dilution rate, S_i^o, $i = 1, \ldots, l$ are the concentrations of the chemical species (substrates) in the feed, X_j^o, $j = 1, \ldots, m$ are the concentrations of the microbial masses in the feed, S_i, $i = 1, \ldots, l$ are the concentrations of the chemical species (substrates and/or products) in the reactor, X_j, $j = 1, \ldots, m$ are the concentrations of the microbial masses in the reactor, $r_k(S_1, \ldots, S_l, X_1, \ldots, X_m)$, $k = 1, \ldots, n$ are the reaction rates, $C_{i,k}$ and $Y_{j,k}$ are the stoichiometric coefficients.

It should be noted that the consumption of a substrate (e.g. particulate matter) may not be associated with biomass growth. Moreover, a single microbial group may grow on more than one substrate and vice versa. Therefore, in the general case, the number of the substrates involved in a bioreaction scheme will not be equal to the number of microbial masses grown, that is $l \neq m$.

Introducing vector notation for the concentrations and the rates

$$\underline{S}^o = \begin{bmatrix} S_1^o \\ \vdots \\ S_l^o \end{bmatrix}, \underline{X}^o = \begin{bmatrix} X_1^o \\ \vdots \\ X_m^o \end{bmatrix}, \underline{S} = \begin{bmatrix} S_1 \\ \vdots \\ S_l \end{bmatrix}, \underline{X} = \begin{bmatrix} X_1 \\ \vdots \\ X_m \end{bmatrix},$$

$$\underline{r}(\underline{S}, \underline{X}) = \begin{bmatrix} r_1(S_1, \cdots, S_l, X_1, \cdots, X_m) \\ \vdots \\ r_n(S_1, \cdots, S_l, X_1, \cdots, X_m) \end{bmatrix}$$

and denoting by $\underline{\underline{C}}$ and $\underline{\underline{Y}}$ the $l \times n$ and $m \times n$ matrices of the stoichiometric coefficients, the model (2) takes a more compact form:

$$\begin{aligned} \dot{\underline{S}} &= D(\underline{S}^o - \underline{S}) + \underline{\underline{C}} \cdot \underline{r}(\underline{S}, \underline{X}) \\ \dot{\underline{X}} &= D(\underline{X}^o - \underline{X}) + \underline{\underline{Y}} \cdot \underline{r}(\underline{S}, \underline{X}) \end{aligned} \tag{3}$$

The general problem of model reduction for models of the form of Eq. (2) will be the subject of the present paper. Before we proceed, we will provide a brief review of the notions of reaction invariants and invariant manifold, which will play an instrumental role in the development of the proposed approach.

2.2. Reaction invariants and the notion of invariant manifold

In the general model of Eqs. (2) or (3), there are $(l+m)$ differential equations that are affected by n reaction rates. As long as $l+m>n$ and the differential equations are independent of each other, there will be $(l+m-n)$ linear combinations of the concentrations that are completely unaffected by the reaction rates and therefore completely unaffected by the progress of the chemical reactions. In the literature, these are referred to as reaction invariants; they capture the reaction stoichiometry relations, which are unaffected by the reaction rates [10,12,23].

The reaction invariants can be easily calculated from the general model of (3).

Assuming $l+m>n$ and

$$Rank \begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} = n,$$

one can find $(l+m-n)$ linearly independent row vectors α_ν, $\nu = 1,\ldots,(l+m-n)$ of length $(l+m)$ such that

$$\alpha_\nu \begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} = 0, \quad \nu = 1, \cdots, (l+m-n)$$

This means that the $(l+m-n)\times(l+m)$ matrix

$$\underline{\underline{A}} = \begin{bmatrix} \alpha_1 \\ \vdots \\ \alpha_\nu \end{bmatrix}$$

has rank $(l+m-n)$ and satisfies

$$\underline{\underline{A}} \begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} = 0 \tag{4}$$

It can then be easily verified, as a result of (2) and (3), that the quantity

$$\underline{z} = \underline{\underline{A}} \begin{bmatrix} \underline{S} - \underline{S}^o \\ \underline{X} - \underline{X}^o \end{bmatrix} \tag{5}$$

satisfies the differential equation

$$\dot{\underline{z}} = -D\underline{z} \tag{6}$$

The role of the reaction invariants can also be seen from the steady-state version of the model (3). $\underline{z} = 0$ represents exactly the $(l+m-n)$ eliminant relations from the steady-state model when the n reaction rates get eliminated. Therefore, $\underline{z} = 0$ describes the $(l+m-n)$ stoichiometry relations among the concentrations that must be satisfied at steady state.

Under dynamic conditions, the $(l+m-n)$ reaction invariants $\underline{z}$ have two very important properties, which are a direct consequence of Eq. (6):

1. If $\underline{z} = 0$ at time $t=0$, then $\underline{z}(t) = 0$ for every $t>0$. In other words, if the stoichiometry relations are initially satisfied, they will be satisfied ever after.
2. If $\underline{z}(0) \neq 0$, then $\underline{z}(t) = e^{-Dt}\underline{z}(0)$ and therefore $\lim_{t\to\infty} \underline{z}(t) = 0$. In other words, if the system is initially off stoichiometry, the initial discrepancy will decay and eventually, the concentrations will satisfy the stoichiometry relations.

In mathematical terms, property 1 states that the relation

$$\underline{\underline{A}} \begin{bmatrix} \underline{S} - \underline{S}^o \\ \underline{X} - \underline{X}^o \end{bmatrix} = 0,$$

where $\underline{\underline{A}}$ satisfies (4), defines an invariant manifold for the dynamics (3).

By definition, $\Omega = \{x \in \mathbb{R}^n | \psi(x) = 0\}$ where $\psi : \mathbb{R}^n \to \mathbb{R}^m$ is a smooth map, is called invariant manifold for the dynamics $\dot{x} = f(x)$, $x \in \mathbb{R}^n$ if it has the property that

$$\psi(x(0)) \in \Omega \Rightarrow \psi(x(t)) \in \Omega \quad \forall t > 0,$$

where $x(t)$ is the solution of $\dot{x} = f(x)$ with initial condition $x(0)$.

On the other hand, property 2 states that the invariant manifold is attractive.

By definition, given $\dot{x} = f(x)$, an invariant manifold $\Omega = \{x \in \mathbb{R}^n | \psi(x) = 0\}$ is called attractive if it has the property that for every $x(0)$ with $\psi(x(0))$ near zero, $\psi(x(t))$ is bounded and $\lim_{t\to\infty} \psi(x(t)) = 0$, where $x(t)$ is the solution of $\dot{x} = f(x)$ with initial condition $x(0)$.

2.3. The invariance equation

All invariant manifolds $\Omega = \{x \in \mathbb{R}^n | \psi(x) = 0\}$ to a given dynamics $\dot{x} = f(x)$, $x \in \mathbb{R}^n$, satisfy the invariance equation [13]:

$$\frac{\partial \psi}{\partial x}(x) f(x) = 0 \quad \forall x \in \Omega \tag{7}$$

For the system of Eq. (3), every invariant manifold $\Omega = \{(\underline{S}, \underline{X}) \in \mathbb{R}^l \times \mathbb{R}^m | \psi(\underline{S}, \underline{X}) = 0\}$ satisfies the following invariance equation:

$$\begin{aligned} &\frac{\partial \psi}{\partial \underline{S}}(\underline{S}, \underline{X})[D(\underline{S}^o - \underline{S}) + \underline{\underline{C}} \cdot \underline{r}(\underline{S}, \underline{X})] \\ &+ \frac{\partial \psi}{\partial \underline{X}}(\underline{S}, \underline{X})[D(\underline{X}^o - \underline{X}) + \underline{\underline{Y}} \cdot \underline{r}(\underline{S}, \underline{X})] = 0 \end{aligned} \tag{8}$$

for every $(\underline{S}, \underline{X}) \in \mathbb{R}^l \times \mathbb{R}^m$ such that $\psi(\underline{S}, \underline{X}) = 0$.

It is easy to verify that

$$\psi(\underline{S}, \underline{X}) = \underline{\underline{A}} \begin{bmatrix} \underline{S} - \underline{S}^o \\ \underline{X} - \underline{X}^o \end{bmatrix}$$

with $\underline{\underline{A}}$ satisfying (4), indeed satisfies the above invariance equation.

Note, however, that all possible invariant manifolds for the dynamics (3) will satisfy the invariance equation, not only the particular one generated by reaction invariants.

2.4. On the prospect of using reaction invariants for model reduction

An attractive invariant manifold can be used for the purpose of model reduction, the reduced model arising as the projection of the dynamics on the invariant manifold. Of course, there is a question of what would be an appropriate invariant manifold for the purpose of approximation of the dynamic model.

To be able to illustrate these ideas, and since we already have an invariant manifold from the calculation of reaction invariants, it would be helpful to try to evaluate its potential for model reduction. In this direction, it is convenient to perform a variable transformation on the dynamic model (3), using the $(l+m-n)$ reaction invariants $\underline{z}$ as dependent variables for the differential equations, along with n out of the original variables $[\underline{S}\ \underline{X}]^T$ that are independent of the reaction invariants.

In particular, denoting by $e_1, \ldots, e_{l+m}$ the rows of the $(l+m)\times(l+m)$ identity matrix, there will be n of them, say $e_{i_1}, \ldots, e_{i_n}$, for some indices $i_1, \ldots, i_n \in \mathbb{N}$, such that the matrix

$$\underline{\underline{E}} = \begin{bmatrix} e_{i_1} \\ \vdots \\ e_{i_n} \end{bmatrix}$$

has the property that $\begin{bmatrix} \underline{\underline{A}} \\ \underline{\underline{E}} \end{bmatrix}$ is nonsingular.

Then, the part of the state vector

$$\begin{bmatrix} \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix} = \underline{\underline{E}} \begin{bmatrix} \underline{S} \\ \underline{X} \end{bmatrix},$$

together with the reaction invariants $\underline{z}$, forms a complete set of coordinates to describe the reactor dynamics. In these coordinates, the system is described as

$$\begin{aligned} \dot{\underline{z}} &= -D\,\underline{z} \\ \begin{bmatrix} \dot{\tilde{\underline{S}}} \\ \dot{\tilde{\underline{X}}} \end{bmatrix} &= D\left(\underline{\underline{E}}\begin{bmatrix} \underline{S}^o \\ \underline{X}^o \end{bmatrix} - \begin{bmatrix} \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix}\right) + \underline{\underline{E}}\begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} \tilde{\underline{r}}(\underline{z}, \tilde{\underline{S}}, \tilde{\underline{X}}) \end{aligned} \tag{9}$$

where

$$\tilde{\underline{r}}(\underline{z}, \tilde{\underline{S}}, \tilde{\underline{X}}) = \underline{r}(\underline{S}, \underline{X})\Big|_{\begin{bmatrix} \underline{S} \\ \underline{X} \end{bmatrix} = \begin{bmatrix} \underline{\underline{A}} \\ \underline{\underline{E}} \end{bmatrix}^{-1} \begin{bmatrix} \underline{z} + \underline{\underline{A}}\begin{bmatrix} \underline{S}^o \\ \underline{X}^o \end{bmatrix} \\ \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix}} \tag{10}$$

It is interesting to observe the structure of the transformed dynamic Eq. (9) (see Fig. 1), which reveals important features of the dynamic behavior of the reactor. First of all, one can observe that in the description (9), the dynamics is decomposed in two parts: one that describes the dynamics of the reaction invariants, followed by another part that describes the speed of progress of chemical reactions. Reaction-invariant dynamics is $(l+m-n)$-dimensional and decays proportionally to e^{-Dt}, where D is the dilution rate, whereas reaction dynamics is n-dimensional and is dependent upon the reaction rate expressions.

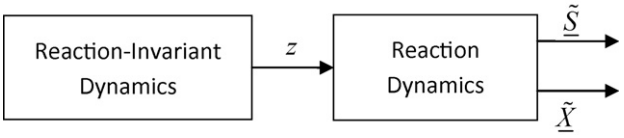

Fig. 1. Structure of the dynamic model when the reaction invariants are used as a part of the description of CSTR dynamics.

Given the previously discussed properties of invariance and attractivity of the manifold $\underline{z} = 0$, it is tempting to set $\underline{z} = 0$ in the dynamic Eq. (9) and obtain the reduced model

$$\begin{bmatrix} \dot{\tilde{\underline{S}}} \\ \dot{\tilde{\underline{X}}} \end{bmatrix} = D\left(\underline{\underline{E}}\begin{bmatrix} \underline{S}^o \\ \underline{X}^o \end{bmatrix} - \begin{bmatrix} \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix}\right) + \underline{\underline{E}}\begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} \tilde{\underline{r}}(0, \tilde{\underline{S}}, \tilde{\underline{X}}) \tag{11}$$

which is n-dimensional, instead of $(l+m)$-dimensional. The question is whether the reduced model (11) represents a meaningful approximation of the original model (3) or (9).

If the stoichiometry relations $\underline{z} = 0$ are always satisfied during the operation of a reactor and it cannot go off balance, then the reduced model (11) will perfectly match the dynamic model (3) or (9).

If, however, e.g. in the presence of pulse disturbances in the feed concentrations, instantaneous deviations from stoichiometry can occur, they will decay proportionally to e^{-Dt}. The question is then whether e^{-Dt} is significantly faster than the rest of the reactor dynamics, which is governed by the speed of the chemical reactions. In case of affirmative answer, the reduced model (11) provides a meaningful approximation, since it ignores only the fast transients of approach to the invariant manifold, while it captures the slow motion on the manifold.

In practice, however, it does not make much sense to use high dilution rates relative to the speed of progress of chemical reactions, since this would lead to unnecessarily low conversions. For this reason, in most practical applications, the invariant manifold $\underline{z} = 0$ is not expected to be the appropriate one to generate an approximate reduced-order model. One must find another invariant manifold, which is always approached through "fast" transients, whereas the motion on the manifold is governed by "slow" transients.

3. A very simple motivating example

To illustrate the ideas outlined in the previous section, a very simple example is discussed. Consider a chemostat described by the following mathematical model

$$\begin{aligned} \frac{dX}{dt} &= -D\cdot X + Y\cdot r \\ \frac{dS}{dt} &= -D\cdot S + F - r \end{aligned} \tag{12}$$

where X and S are the biomass and substrate concentrations respectively, D is the dilution rate, Y is the biomass yield, $F = D\cdot S^o$ is the feed rate of the substrate, S^o is the substrate concentration in the feed, $r = 1/Y\cdot\mu_{\max}\cdot S/(K_S+S)X$ is the reaction rate, $\mu_{\max}$ is the maximum specific growth rate constant of the biomass, K_S is the saturation constant, and assume that it operates under low dilution rate relative the growth of microorganisms: $D/\mu_{\max} \ll 1$.

The system of Eq. (12) can be easily transformed to the form (9). In particular, defining $z = X/Y + S - S^o$, the reaction invariant, and keeping the substrate as the second state, system equations become

$$\begin{aligned} \frac{dz}{dt} &= -D\cdot z \\ \frac{dS}{dt} &= D\cdot(S^o - S) - \frac{\mu_{\max}S}{K_S+S}\cdot(S^o - S + z) \end{aligned} \tag{13}$$

If it is assumed that the z-dynamics in (13) is at equilibrium and therefore $z = 0$, the system dynamics reduces to:

$$\frac{dS}{dt} = \left(D - \frac{\mu_{\max}S}{K_S+S}\right)\cdot(S^o - S) \tag{14}$$

The above differential equation, along with the stoichiometry relation

$$X = Y\cdot(S^o - S) \tag{15}$$

forms the reduced model.

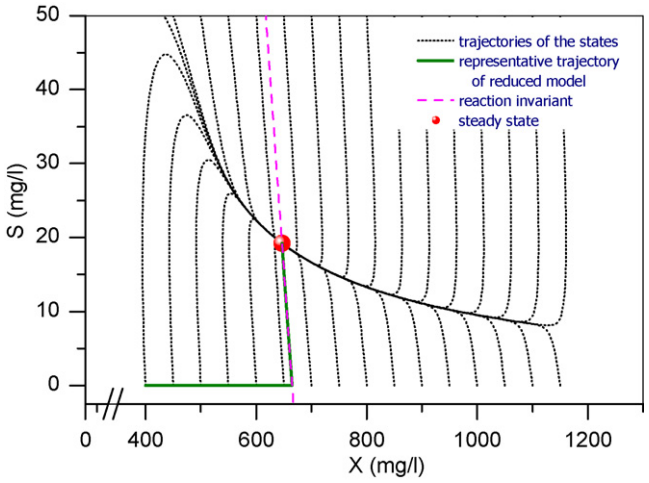

Fig. 2. Comparison of substrate (S) versus biomass (X) trajectories of full-order model (12) with reduced-order model (14)–(15).

It would be interesting to compare the reduced model of (14) and (15) to the original model of (12) or (13). For this purpose, simulations were performed for the following representative values of the parameters: $S^o = 700$ mg/l, $K_S = 21.15$ mg/l, $\mu_{max} = 0.21$ d^{-1}, $Y = 0.95$, $D = 0.1$ d^{-1} (obtained from fitting a simple Monod model on the kinetic data of [30]).

Fig. 2 depicts the phase portrait of the original model (12) for the above values of process parameters. For comparison purposes, a representative trajectory of the reduced model (14) and (15) is also traced. Whenever the system is initially satisfying stoichiometry i.e. $X(0) = Y\cdot(S^o - S(0))$, the system trajectory follows the dashed line (reaction-invariant manifold) and the reduced model exactly matches the original model. If, however, the system is initially off stoichiometry i.e. $X(0) \neq Y\cdot(S^o - S(0))$, the reduced model assumes that stoichiometry is instantaneously restored i.e. $X(0+) = Y\cdot(S^o - S(0))$, and then the system trajectory follows the reaction-invariant manifold. Comparing the representative trajectory of the reduced model to the corresponding trajectory of the full model starting from the same initial conditions, we observe that they are in gross disagreement, even though in both cases the steady state is eventually reached. The reason of the disagreement is that, in this example, the reaction dynamics is much faster than the dynamics of restoration of stoichiometry (z-dynamics in (13)). Indeed, computing the eigenvalues of the linearization of (13), we find that the eigenvalue associated with the z-dynamics is $\lambda_1 = -D = -0.1$, whereas the other eigenvalue, associated with the progress of the reaction, is $\lambda_2 = -1.85463$, almost 20 times faster. The error made in the model reduction was that the slow dynamics was rejected and the fast dynamics was retained.

It must be emphasized at this point that the theory of reaction invariants was never meant to be a general approach for model reduction. In the original paper by Asbjornsen and Fjeld [23], reaction invariants were suggested for model reduction purposes, only for those applications where the reactor cannot go off stoichiometry. However, transformation of the dynamic model to the form (9), using the reaction invariants, is always an insightful description of the reactor dynamics that can facilitate stability analysis and simulation.

Let's see now how a good engineer would derive a simple and fairly accurate reduced-order model for the chemostat via a quasi-steady-state approximation (QSSA). Under the stated low-dilution-rate conditions during chemostat operation (12), the feed rate of the substrate is expected to approximately match the rate of utilization of the substrate:

$$F - r \approx 0, \text{ or equivalently } D \cdot S^o \approx \frac{1}{Y} \cdot \frac{\mu_{max} \cdot S}{K_S + S} X \tag{16}$$

The above defines a relation between biomass and substrate that must hold approximately at all times, after a fast transient period on the substrate.

Solving the above relation for the substrate leads to

$$S = \frac{K_S \cdot Y \cdot S^o \cdot D}{X \cdot \mu_{max} - Y \cdot S^o \cdot D} \tag{17}$$

and substituting $r = F$ in the biomass balance gives $dX/dt = -D\cdot X + Y\cdot F$, i.e. that

$$\frac{dX}{dt} = -D \cdot X + Y \cdot D \cdot S^o \tag{18}$$

Thus, one obtains the following approximate 1st order model for the reactor dynamics:

$$\frac{dX}{dt} = -D \cdot (X - Y \cdot S^o) \tag{19}$$

$$S = \frac{K_S \cdot Y \cdot S^o \cdot D}{X \cdot \mu_{max} - Y \cdot S^o \cdot D} \tag{20}$$

Note that the foregoing derivation has been based on physical understanding and intuition and, at a first glance, it appears to be unjustified from a mathematical point of view. However, guided again by physical understanding and intuition, it is possible to develop a mathematical justification via singular perturbation theory. For this purpose, one must discover, or rather invent, a small parameter δ which, as it tends to zero, gives rise to the QSS approximation. In our case, the argument goes as follows.

Because $D/\mu_{max} \ll 1$, the equilibrium value of the substrate

$$S_s = \frac{D \cdot K_S}{\mu_{max} - D} = K_S \cdot \frac{D/\mu_{max}}{1 - D/\mu_{max}} \approx K_S \cdot \frac{D}{\mu_{max}}$$

will be very small. Therefore, in transient conditions as well, S is expected to be small, and it is meaningful to rescale S with respect to S_s:

$$S' = \frac{S}{S_s} \tag{21}$$

so that, after rescaling, the substrate concentration is $O(1)$. In terms of the rescaled substrate concentration, the substrate balance is written as

$$\delta \cdot \frac{dS'}{dt} = -\delta \cdot D \cdot S' + F - r \quad \text{where } \delta = S_s \tag{22}$$

In the limit as $\delta \to 0$, neglecting the $O(\delta)$ terms, leads to $0 = F - r$, i.e. to the QSS approximation.

The phase portrait of Fig. 3 has been constructed for the same values of the parameters as before. The substrate and biomass concentrations calculated from the simplified model (19) and (20) follow a trajectory which is close to the original model trajectory. In this sense, QSSA provides a suitable approximation for this class of models. Also, it should be noted that the steady state predicted by the QSSA is close but not exactly equal to the original system's steady state. This is because of the way QSSA was derived, by setting the algebraic sum of all rates involving certain species equal to zero.

QSSA is a good method as long as it is properly used. QSSA can be and has been extended to more complicated systems. However, the information needed for the application of the method, such as the species of which the algebraic sum of all rates is approximately zero, or the relevant small parameter, is based on physical understanding and intuition. Sometimes, in complicated problems, intuition can be misleading and there have been

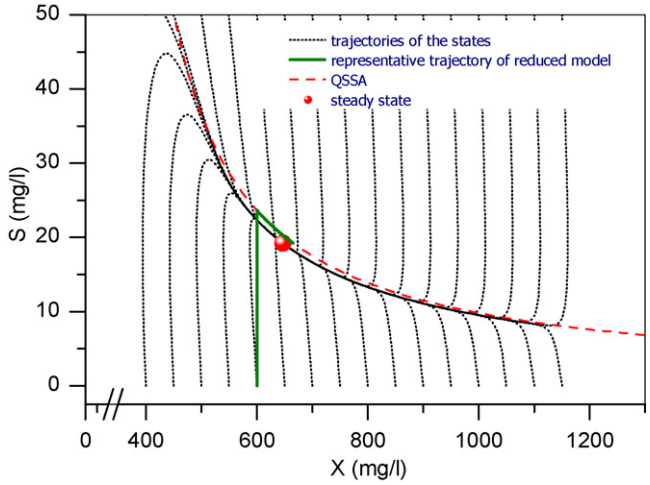

Fig. 3. Comparison of substrate (S) versus biomass (X) trajectories of full-order model (12) with reduced-order model (19)–(20).

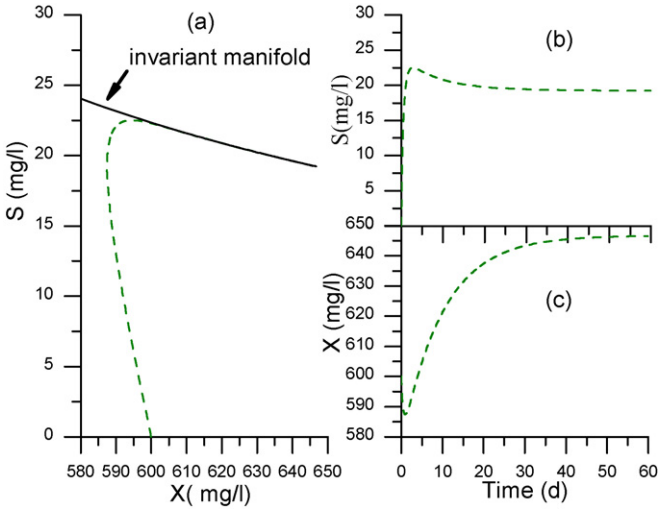

Fig. 4. (a) Trajectory of substrate concentration versus biomass concentration when initiated at $S = 0$ and $X = 600$ mg/l. The corresponding time responses of the two states are depicted in (b) and (c).

many erroneous QSS approximations suggested in the literature (see [13]).

In order to motivate the model reduction methodology to be proposed in the present work, consider again the phase portrait of the exact system (12), which was shown in Figs. 2 and 3. From the phase portrait, it is clear that all trajectories asymptotically approach a curve, which is an attractive invariant manifold. To see exactly what happens, a specific trajectory is examined in detail in Fig. 4. In Fig. 4(a), the trajectory is depicted in an S–X diagram, whereas Fig. 4(b and c) depicts the corresponding time responses.

The time responses show that the system first goes through a fast transient phase and then a slow transient phase. The substrate undergoes a large change during the fast transient phase, while the biomass changes very little; this corresponds to the high-slope part of the S–X trajectory. On the other hand, the slow transient phase corresponds to the part of the S–X trajectory that coincides with the invariant manifold. On the invariant manifold, substrate and biomass change slowly together, while being interrelated through an algebraic relationship of the form

$$\psi(S(t), X(t)) = 0$$

If this algebraic relationship can be calculated, the system trajectories can be approximated by appropriately "projecting" the system dynamics on the invariant manifold.

Fig. 5 illustrates this projection idea, on the same trajectory as in Fig. 4. The fast motion towards the invariant manifold is approximated by a straight line and the slow motion by the invariant manifold. In this way, the approximation is in error only on the curved corner of the trajectory.

The accuracy of the approximation will depend on the speed of the fast dynamics relative to the slow dynamics. If the fast dynamics is much faster than the slow dynamics (e.g. by a couple of orders of magnitude), the change in slope of the system trajectory will be very abrupt and the approximation will be very accurate. Otherwise, the error in the approximation may be more significant.

Fig. 6 gives the general picture of the model reduction approach to be developed in the next section. In general, in the presence of more than two states, the attractive invariant manifold will not necessarily be a curve; it will be a hypersurface of dimension ≥ 1. The invariant manifold will be approached after fast transients, whereas the motion on the manifold will characterize the slow transients, where the system's state variables are interrelated algebraically. The reduced model will consist of the projection the system dynamics on the slow-motion invariant manifold. The projection approximation will involve "sharp edges", ignoring the curvature of the trajectories in their approach towards the invariant manifold.

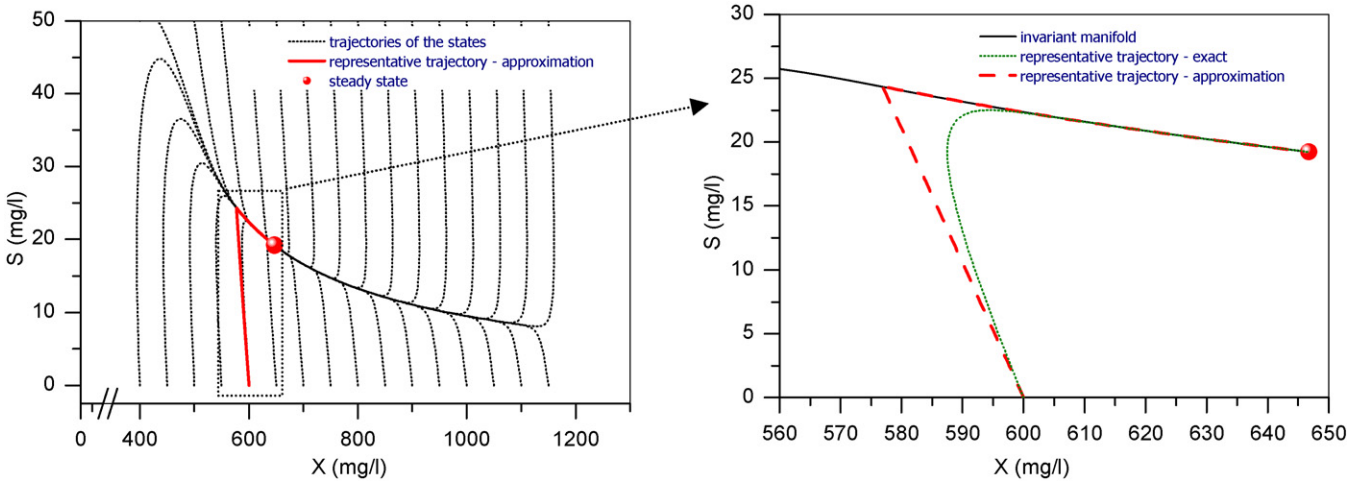

Fig. 5. Approximation of the dynamics of the states by projection on the invariant manifold. The phase portrait is depicted on the left, where the approximation of a representative trajectory is shown. The trajectories of the reduced and the original model are compared in the zoomed in area of the graph (right).

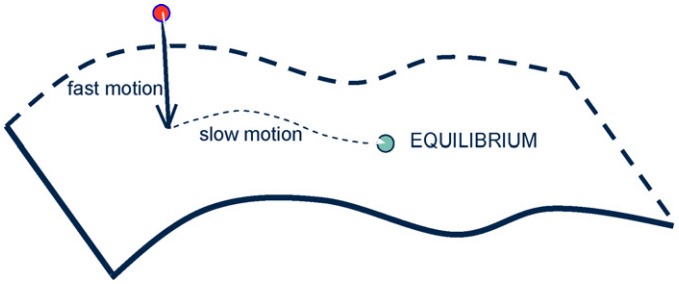

Fig. 6. Geometric interpretation of the role of invariant manifold in model reduction.

4. Proposed approach for model reduction

The goal of this section is to develop a systematic model reduction methodology for mixed culture bioprocesses described by a model of the form (2) or (3), based on projecting the system dynamics on the slow-motion invariant manifold, in the sense described qualitatively in the previous section.

Following the theoretical results of Kazantzis and Kravaris [14], the proposed methodology involves two steps:

(1) identifying and computing the appropriate slow-motion attractive invariant manifold for the reactor
(2) generating a reduced model by projecting the dynamics on that manifold.

The starting point of the proposed methodology is the dynamic model (9), which uses reaction invariants.

As a first case, consider the situation where all the chemical reactions proceed significantly faster than e^{-Dt}. Then, the system consists of a series connection of the reaction-invariant dynamics (slow) followed by the reaction dynamics (fast), as shown in Fig. 7.

The slow-motion invariant manifold can then be expressed as an algebraic relationship that gives the fast variables as a function of the slow variables:

$$\begin{bmatrix} \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix} = T(\underline{z}) \tag{23}$$

where $T : \mathbb{R}^{l+m-n} \to \mathbb{R}^{l+m}$. The invariant manifold satisfies the invariance Eq. (7), which for system (9), takes the form:

$$(-D \cdot \underline{z})\frac{\partial T}{\partial \underline{z}}(\underline{z}) = D \cdot \left(\underline{\underline{E}} \cdot \begin{bmatrix} \underline{S}^o \\ \underline{X}^o \end{bmatrix} - T(\underline{z}) \right) + \underline{\underline{E}} \cdot \begin{bmatrix} \underline{\underline{C}} \\ \underline{\underline{Y}} \end{bmatrix} \cdot \underline{\tilde{r}}(\underline{z}, T(\underline{z})) \tag{24}$$

Once the above differential equation is solved for $T(\underline{z})$, the reduced model is:

$$\begin{aligned} &\dot{\underline{z}} = -D \cdot \underline{z} \\ &\begin{bmatrix} \tilde{\underline{S}} \\ \tilde{\underline{X}} \end{bmatrix} = T(\underline{z}) \end{aligned} \tag{25}$$

Consider now the situation where, among the chemical reactions, there are some that proceed at a slow rate, which is comparable to the dilution rate, and must be accounted for in the reduced model.

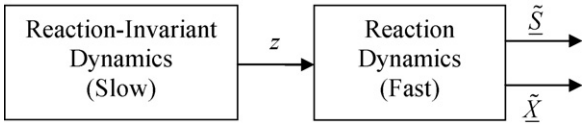

Fig. 7. Sequential structure of a reactor system where slow reaction-invariant dynamics precede the fast reaction dynamics.

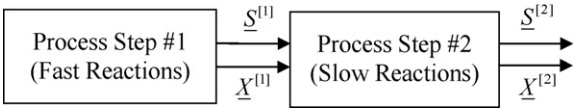

Fig. 8. Reactor dynamics in the form of a two-step process, with the reaction of the first step being faster.

For example, suppose that the bioprocess dynamics evolves in two steps, the first one involving fast reactions, while the second involves slow reactions (Fig. 8).

Here the understanding is that each process step involves a single reaction or a cluster of chemical reactions of similar speed. It is important to note that the first process step also encompasses reaction-invariant dynamics, which evolve according to the dilution rate, even though the reaction themselves may be fast. In order to describe this situation, it is useful to decompose the dynamics of the first process step (Fig. 9).

This translates into a mathematical description of the form

$$\begin{aligned} &\dot{\underline{z}}^{[1]} = -D \cdot \underline{z}^{[1]} \\ &\begin{bmatrix} \dot{\underline{S}}^{[1]} \\ \dot{\underline{X}}^{[1]} \end{bmatrix} = D \cdot \left(\underline{\underline{E}}^{[1]} \cdot \begin{bmatrix} \underline{S}^{o[1]} \\ \underline{X}^{o[1]} \end{bmatrix} - \begin{bmatrix} \tilde{\underline{S}}^{[1]} \\ \tilde{\underline{X}}^{[1]} \end{bmatrix} \right) \\ &\qquad + \underline{\underline{E}}^{[1]} \cdot \begin{bmatrix} \underline{\underline{C}}^{[1]} \\ \underline{\underline{Y}}^{[1]} \end{bmatrix} \cdot \underline{\tilde{r}}^{[1]}(\underline{z}^{[1]}, \tilde{\underline{S}}^{[1]}, \tilde{\underline{X}}^{[1]}) \\ &\dot{\underline{S}}^{[2]} = D \cdot (\underline{S}^{o[2]} - \underline{S}^{[2]}) + \underline{\underline{C}}^{[2]} \cdot \underline{r}^{[2]}(\underline{z}^{[1]}, \tilde{\underline{S}}^{[1]}, \tilde{\underline{X}}^{[1]}, \underline{S}^{[2]}, \underline{X}^{[2]}) \\ &\dot{\underline{X}}^{[2]} = D \cdot (\underline{X}^{o[2]} - \underline{X}^{[2]}) + \underline{\underline{Y}}^{[2]} \cdot \underline{r}^{[2]}(\underline{z}^{[1]}, \tilde{\underline{S}}^{[1]}, \tilde{\underline{X}}^{[1]}, \underline{S}^{[2]}, \underline{X}^{[2]}) \end{aligned} \tag{26}$$

where the superscript '[1]' refers to the variables and parameters of Step #1 and '[2]' to Step #2.

Then, the slow-motion invariant manifold can be expressed as an algebraic relationship among the state variables of the first process step, providing the fast variables as a function of the slow variables:

$$\begin{bmatrix} \tilde{\underline{S}}^{[1]} \\ \tilde{\underline{X}}^{[1]} \end{bmatrix} = T(\underline{z}^{[1]}) \tag{27}$$

where T satisfies the invariance equation

$$\begin{aligned} &(-D \cdot \underline{z}^{[1]}) \cdot \frac{\partial T}{\partial \underline{z}^{[1]}}(\underline{z}^{[1]}) \\ &\quad = D \cdot \left(\underline{\underline{E}}^{[1]} \cdot \begin{bmatrix} \underline{S}^{o[1]} \\ \underline{X}^{o[1]} \end{bmatrix} - T(\underline{z}^{[1]}) \right) + \underline{\underline{E}}^{[1]} \cdot \begin{bmatrix} \underline{\underline{C}}^{[1]} \\ \underline{\underline{Y}}^{[1]} \end{bmatrix} \cdot \underline{\tilde{r}}^{[1]}(\underline{z}^{[1]}, T(\underline{z}^{[1]})) \end{aligned} \tag{28}$$

Once the above equation is solved, the reduced model will consist of two components: a reduced model for Process Step #1 (obtained by dropping the fast modes), followed by the model for Process Step #2 (as is):

$$\begin{aligned} &\dot{\underline{z}}^{[1]} = -D \cdot \underline{z}^{[1]}, \begin{bmatrix} \tilde{\underline{S}}^{[1]} \\ \tilde{\underline{X}}^{[1]} \end{bmatrix} = T(\underline{z}^{[1]}) \\ &\dot{\underline{S}}^{[2]} = D \cdot (\underline{S}^{o[2]} - \underline{S}^{[2]}) + \underline{\underline{C}}^{[2]} \cdot \underline{r}^{[2]}(\underline{z}^{[1]}, T(\underline{z}^{[1]}), \underline{S}^{[2]}, \underline{X}^{[2]}) \\ &\dot{\underline{X}}^{[2]} = D \cdot (\underline{X}^{o[2]} - \underline{X}^{[2]}) + \underline{\underline{Y}}^{[2]} \cdot \underline{r}^{[2]}(\underline{z}^{[1]}, T(\underline{z}^{[1]}), \underline{S}^{[2]}, \underline{X}^{[2]}) \end{aligned} \tag{29}$$

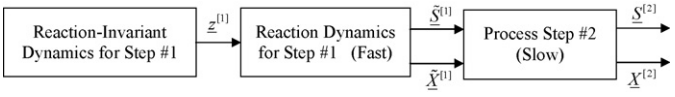

Fig. 9. Decomposition of the dynamics in a two-step reaction system.

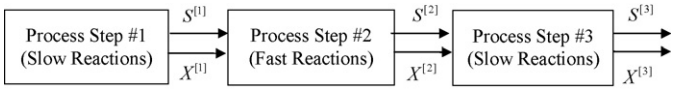

Fig. 10. Reactor dynamics involving a three-step reaction system, with the reactions of the second step being the fast reactions.

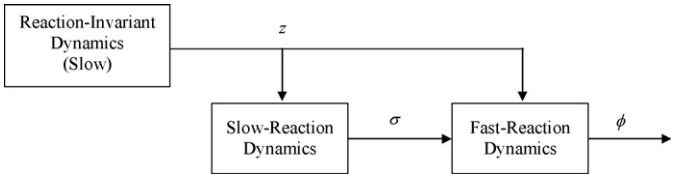

Fig. 11. General reaction dynamics decomposition.

As a second example, consider the situation of a three-step reaction system, where the fast-reactions step is the second one (Fig. 10).

Then, the slow-motion invariant manifold will be an algebraic equation relating only the variables of the first two steps $\underline{S}^{[1]}, \underline{X}^{[1]}, \underline{S}^{[2]}, \underline{X}^{[2]}$ and can be computed after appropriate decomposition of the second step into reaction-invariant dynamics (slow) and reaction dynamics (fast), and solution of the corresponding invariance equation for Steps #1 and #2.

There are many possible cases in mixed culture bioprocesses; in general, several process steps may be involved, a fast-reactions step can be anywhere between the first and the last place, and there might be more than one fast-reactions steps. Model reduction involves elimination of the dynamics of the fast reactions by projecting the system dynamics on the slow-motion invariant manifold, which can be represented as an algebraic relation among all the variables from the first process step up to the last fast-reactions step. Fast-reactions steps should be decomposed into reaction-invariant dynamics (slow) and reaction dynamics (fast) and then, the appropriate invariance equation is set up for the chain starting from the first process step and ending after the last fast-reactions step. The solution of the invariance equation will give the fast states as a function of the slow states.

Serial structure is quite common in mixed culture bioprocesses, even though it is not always the case. In the absence of a serial structure, the reaction-invariant dynamics will generally be slow whereas the reaction dynamics will incorporate both slow and fast modes. Then, it is possible to mathematically decompose the reaction dynamics into a serial connection of slow and fast modes after an appropriate coordinate transformation (see general construction in [14]) (Fig. 11).

The slow manifold

$$\underline{\phi} = T(\underline{z}, \underline{\sigma}) \tag{30}$$

can then be computed in the same spirit by considering the reaction-invariant dynamics together with the slow-reaction dynamics as one entity (slow subsystem) followed by the fast-reaction dynamics (fast subsystem), and solving an appropriate invariance equation.

5. Application to anaerobic digestion

The model reduction methodology outlined in the previous section will now be applied to two cases of anaerobic digestion. In the first case, a soluble substrate is fed to a chemostat and the processes taking place are acidogenesis and methanogenesis. In the second case, a particular substrate is fed, with a hydrolysis step preceding acidogenesis and methanogenesis. The fast dynamics is the first process step in the first case, while in the second case it lies between two slower steps. As a result, the invariant manifold equation as well as the procedure for model reduction is different in the two cases.

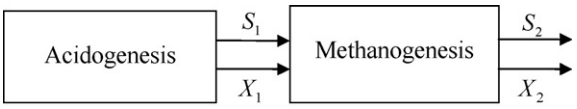

Fig. 12. Anaerobic digestion as a two-step process.

5.1. Case 1: Model reduction for anaerobic digestion with soluble substrate feed

The anaerobic digestion of a soluble substrate can be described as a two-step sequential process if it is desired to keep the model structure relatively simple (Fig. 12): the organic soluble substrate (S_1) is converted to a volatile fatty acid mixture (S_2) by the acidogenic bacteria (X_1) and finally the acids are utilized by the methanogens (X_2) to form the biogas.

Assuming that the anaerobic digestion takes place in a CSTR and that the feed only contains the organic soluble substrate (no biomass and no volatile fatty acids), the mathematical description of the dynamics takes the form:

$$\begin{aligned}
\frac{dX_1}{dt} &= -D \cdot X_1 + Y_1 \cdot \mu_1(S_1) \cdot X_1 \\
\frac{dS_1}{dt} &= D \cdot (S_1^o - S_1) - \mu_1(S_1) \cdot X_1 \\
\frac{dX_2}{dt} &= -D \cdot X_2 + Y_2 \cdot \mu_2(S_2) \cdot X_2 \\
\frac{dS_2}{dt} &= -D \cdot S_2 + c_2 \cdot \mu_1(S_1) \cdot X_1 - \mu_2(S_2) \cdot X_2
\end{aligned} \tag{31}$$

where S_1 and S_2 are the concentrations of the soluble organic substrate and volatile fatty acids respectively; X_1 and X_2 are the concentration of the acidogens and methanogens respectively, D is the dilution rate; $\mu_1(S_1) = 1/Y_1 \cdot \mu_{\max 1} \cdot S_1/(K_{S1} + S_1)$ is the specific consumption rate of S_1 under the assumption of Monod kinetics, $\mu_2(S_2) = 1/Y_2 \cdot \mu_{\max 2} \cdot S_2/(K_{S2} + S_2 + S_2^2/K_I)$ is the specific consumption rate of S_2, under the assumption of Andrews kinetics to allow for acid inhibition on methanogenesis; $\mu_{\max 1}$ and $\mu_{\max 2}$ are the maximum specific growth rate of the acidogens and methanogens respectively; K_{S1} and K_{S2} are the corresponding saturation constants; K_I is the inhibition constant; S_1^o is the substrate concentration in the feed; Y_1 and Y_2 are the biomass yield for acidogens and methanogens, and c_2 is the stoichiometric coefficient of the conversion of S_1 to S_2. It is important to observe that system (31) has a serial structure. Indeed, the first two equations (describing dynamics of the step of acidogenesis) are independent of the other two (describing the dynamics of the step of methanogenesis).

The following standing assumptions will be made throughout this section:

(A1) $\mu_{\max_1} >> \mu_{\max_2}$ and $K_{S2} > c_2 \cdot K_{S1}$ (the rate of acidogenesis is much higher than the rate of methanogenesis);
(A2) $S_1^o >> K_{S1}$ and $c_2 \cdot S_1^o >> \sqrt{K_{S2} \cdot K_I}$ (the substrate in the feed is in excess);
(A3) $D < \frac{\mu_{\max 2}}{1+2\sqrt{K_{S2}/K_I}}$ (the dilution rate is sufficiently low, to guarantee that both biomasses, X_1 and X_2 can be sustained at non zero values at steady state).

Under the above assumptions, the system (31) has four steady states: two trivial steady states (one corresponding to methanogen washout and one to washout of both acidogens and methanogens) and two non-trivial steady states. The trivial steady states are undesirable. Out of the two non-trivial steady states, only one is locally

asymptotically stable, as can be seen through a standard linear stability analysis. Anaerobic digesters are designed to operate at their non-trivial stable steady state. Therefore, the goal of this section is to derive a reduced-order model for the anaerobic digester around the non-trivial asymptotically stable steady state.

A straightforward calculation gives this steady state in terms of the process parameters:

$$\begin{aligned} S_{1s} &= \frac{D \cdot K_{s1}}{\mu_{\max 1} - D}, \quad X_{1s} = Y_1 \cdot (S_1^o - S_{1s}) \\ S_{2s} &= \frac{2 \cdot D \cdot K_{s2}}{(\mu_{\max 2} - D) + \sqrt{(\mu_{\max 2} - D)^2 - 4 \cdot D^2 \cdot K_{s2}/K_I}}, \\ X_{2s} &= Y_2 \cdot (c_2 \cdot (S_1^o - S_{1s}) - S_{2s}) \end{aligned} \tag{32}$$

Because of the stated assumptions, the above steady state is positive and therefore, feasible. The eigenvalues of the linearization of the dynamics around this steady state are given by:

$$\begin{aligned} \lambda_1 &= -D \\ \lambda_2 &= -\frac{\mu_{\max 1} \cdot K_{s1}}{(K_{s1} + S_{1s})^2} \cdot (S_1^o - S_{1s}) \\ &= -\frac{(\mu_{\max 1} - D) \cdot ((\mu_{\max 1} - D) \cdot S_1^o - D \cdot K_{s1})}{\mu_{\max 1} \cdot K_{s1}} \\ \lambda_3 &= -D \\ \lambda_4 &= -\frac{\mu_{\max 2} \cdot (K_{s2} - S_{2s}^2/K_I)}{(K_{s2} + S_{2s} + S_{2s}^2/K_I)^2} \cdot (c_2 \cdot (S_1^o - S_{1s}) - S_{2s}) \end{aligned} \tag{33}$$

and they are all negative.

Some comments regarding the above eigenvalues will be useful in subsequent developments:

(i) Because of the serial structure of the dynamic system, consisting of a series of two steps (acidogenesis and methanogenesis), the eigenvalues consist of two distinct subsets, one for each step. In particular, eigenvalues λ_1 and λ_2 characterize the local dynamics of the first step (the first two differential equations that describe acidogenesis) whereas eigenvalues λ_3 and λ_4 characterize the local dynamics of the second step (the last two differential equations that describe methanogenesis).

(ii) Eigenvalue $\lambda_1 = -D$ characterizes the reaction-invariant dynamics of the acidogenesis step, whereas $\lambda_3 = -D$ characterizes the reaction-invariant dynamics of the methanogenesis step. Eigenvalues λ_2 and λ_4 characterize the speed of the corresponding chemical reactions for the acidogenesis and the methanogenesis steps respectively.

(iii) Acidogenesis reactions proceed much faster than the corresponding reaction invariant dynamics. This is visible through the ratio of the corresponding eigenvalues:

$$\begin{aligned} \frac{\lambda_1}{\lambda_2} &= \frac{D \cdot \mu_{\max 1} \cdot K_{S1}}{(\mu_{\max 1} - D) \cdot ((\mu_{\max 1} - D) \cdot S_1^o - D \cdot K_{S1})} \\ &= \frac{1}{1 - D/\mu_{\max 1} \cdot (1 + K_{S1}/S_1^o)} - \frac{1}{1 - D/\mu_{\max 1}} \\ &\approx \left(\frac{D}{\mu_{\max 1}}\right) \cdot \left(\frac{K_{s1}}{S_1^o}\right) << 1 \end{aligned} \tag{34}$$

as a result of the previous assumptions.

(iv) Acidogenesis reactions proceed much faster than methanogenesis reactions. This is visible from the corresponding eigenvalues. Indeed, from the expression for λ_4, we have the bound: $|\lambda_4| \leq \mu_{\max 2}/K_{S2} \cdot c_2 \cdot S_1^o$, and combining with $\lambda_2 \approx -\mu_{\max 1}/K_{S1}\, S_1^o$, it follows that $|\lambda_4/\lambda_2| \lessapprox \mu_{\max 2}/\mu_{\max 1} \cdot (c_2 \cdot K_{S1}/K_{S2}) << 1$.

Assigning typical values for the model parameters [7]: $\mu_{\max 1} = 4.2\,\mathrm{d}^{-1}$, $\mu_{\max 2} = 0.36\,\mathrm{d}^{-1}$, $K_{S1} = 23$ mg/l, $K_{S2} = 138$ mg/l, $K_I = 4{,}000$ mg/l, $Y_1 = 0.11$, $Y_2 = 0.04$ and $c_2 = 1$, a substrate concentration in the feed $S_1^o = 10{,}000$ mg/l, and a typical value of the dilution rate $D = 0.2\,\mathrm{d}^{-1}$, the eigenvalues are $\lambda_1 = \lambda_3 = -0.2 = D$, $\lambda_2 = -1656.12$, $\lambda_4 = -4.22$.

The conclusion from the above comments (i)–(iv) is that the dynamics of the anaerobic digestion system conforms with the setting of Fig. 8 with $\underline{S}^{[1]} = S_1$, $\underline{X}^{[1]} = X_1$, $\underline{S}^{[2]} = S_2$, $\underline{X}^{[2]} = X_2$.

In order to proceed with model reduction, we will need to decompose the dynamics of the first step (acidogenesis) into reaction invariant dynamics and reaction dynamics, so that the overall system has the structure of Fig. 9 and Eq. (26). In particular, defining $(z = S_1 - S_1^o + X_1/Y_1)$, Eqs. (31a) and (31b) are transformed to:

$$\begin{aligned} \frac{dz}{dt} &= -D \cdot z \\ \frac{dS_1}{dt} &= D \cdot (S_1^o - S_1) - Y_1 \cdot \mu_1(S_1) \cdot (S_1^o - S_1 + z) \end{aligned} \tag{35}$$

In this way, the slow reaction-invariant dynamics precedes the fast reaction dynamics of acidogenesis. Eq. (35) together with (31c) and (31d) form the entire system for the anaerobic digestion, which has the structure of Eq. (26) and Fig. 9. The slow-motion invariant manifold is of the form

$$S_1 = T(z) \tag{36}$$

where T satisfies the invariance Eq. (28) which, in the present case, becomes

$$(-D \cdot z)\frac{dT}{dz} = D \cdot (S_1^o - T(z)) - \frac{\mu_{\max 1} \cdot T(z)}{K_{S1} + T(z)} \cdot (S_1^o - T(z) + z) \tag{37}$$

The initial condition to (37) is

$$T(0) = S_{1s} \tag{38}$$

which is a consistency condition that guarantees that the invariant manifold passes through the steady state point.

Eq. (37) is singular because at steady state, $z = z_s = 0$, and the first derivative of $T(z)$ is multiplied by zero. A sufficient condition for existence and uniqueness of solution of (37) is the following non-resonance condition:

There is no integer $N > 0$ such that $\lambda_2 = N \cdot \lambda_1$,

as a result of a general theorem on singular differential equations [31].

Therefore, the approximate reduced-order model for the dynamics of acidogenesis on the invariant manifold is calculated by (25) which, in the present case becomes:

$$\begin{aligned} \frac{dz}{dt} &= -D \cdot z \\ S_1 &= T(z) \\ X_1 &= Y_1 \cdot (S_1^o - T(z) + z) \end{aligned} \tag{39}$$

For the calculation of the invariant manifold, two alternative approaches were examined.

5.1.1. Power series solution of the invariance equation

In this method, a Taylor series expansion for the solution $T(z)$ of (37) is postulated:

$$T(z) = S_{1s} + T_1 \cdot z + T_2 \cdot \frac{z^2}{2} + T_3 \cdot \frac{z^3}{6} + \cdots \tag{40}$$

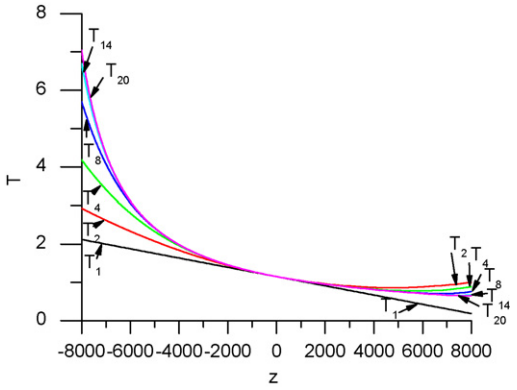

Fig. 13. Approximate calculation of the invariant manifold in the form of power series expansion.

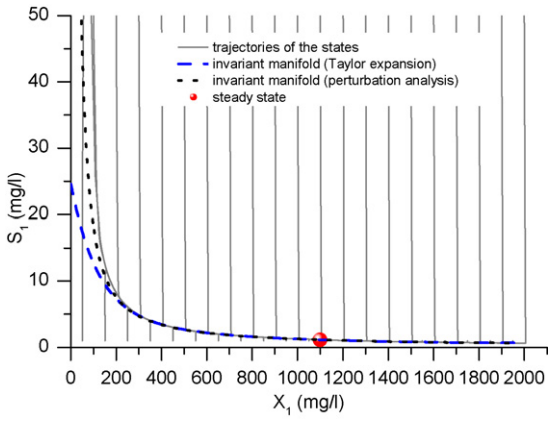

Fig. 14. Approximations of the invariant manifold in the phase portrait for the dynamics of acidogenesis (Taylor series expansion up to 14th order, 2nd order asymptotic expansion via perturbation analysis).

where $T_1, T_2, T_3, \ldots$ are the coefficients of the expansion that must be determined, and the above expression is substituted in (37) and the terms are rearranged and collected in the form of:

$$f_1 \cdot z + f_2 \cdot z^2 + f_3 \cdot z^3 + \cdots = 0 \tag{41}$$

Since (41) should hold for every z, the coefficients $f_1, f_2, f_3, \ldots$ must be zero. The resulting algebraic equations are solved for the unknown coefficients T_i and in this way, the invariant manifold, $T(z)$, is determined. For the particular numerical values of the parameters under consideration, and in the range of $z \in [-7000, 7000]$, numerical convergence was achieved at truncation order of about 14 (see Fig. 13).

5.1.2. Asymptotic expansion of the solution of the invariance equation

The invariant manifold $T(z)$ could also be approximated using perturbation analysis methods [32,33].

Setting $\varepsilon = D/\mu_{\max 1}$, differential Eq. (37) can be written as follows:

$$-\varepsilon \cdot z \cdot \frac{dT}{dz} = \varepsilon \cdot (S_1^o - T) - \frac{T}{K_{s1} + T} \cdot (S_1^o - T + z) \tag{42}$$

$T(z)$ is expanded in Taylor series with respect to the small parameter ε:

$$T(z) = T_1(z) \cdot \varepsilon + T_2(z) \cdot \varepsilon^2 + T_3(z) \cdot \varepsilon^3 + \cdots \tag{43}$$

where $T_i(z)$ are unknown coefficients that must be determined. Substituting the expression (43) for $T(z)$ in (42) and matching the coefficients of like terms in ε, the unknown coefficients are calculated. In this way the invariant manifold is approximately calculated as asymptotic series in $D/\mu_{\max 1}$:

$$\begin{aligned} T(z) = {} & K_{s1} \cdot \frac{S_1^o}{S_1^o + z} \cdot \left(\frac{D}{\mu_{\max 1}}\right) + K_{s1} \cdot \left[\left(\frac{S_1^o}{S_1^o + z}\right)^2 - \frac{2 \cdot K_{s1} \cdot S_1^o \cdot z}{(S_1^o + z)^3}\right] \\ & \cdot \left(\frac{D}{\mu_{\max 1}}\right)^2 + K_{s1}\left[\left(\frac{S_1^o}{S_1^o + z}\right)^3 - \frac{7 \cdot K_{s1} \cdot S_1^{o2} \cdot z}{(S_1^o + z)^4}\right. \\ & \left. - \frac{4 \cdot K_{s1}^2 \cdot S_1^{o2} \cdot z}{(S_1^o + z)^5} + \frac{6 \cdot K_{s1}^2 \cdot S_1^o \cdot z^2}{(S_1^o + z)^5}\right] \cdot \left(\frac{D}{\mu_{\max 1}}\right)^3 \\ & + O\left(\frac{D}{\mu_{\max 1}}\right)^4 \end{aligned} \tag{44}$$

For the particular values of the parameters under consideration and for the same range $z \in [-7000, 7000]$, the 2nd order in ε approximation provides satisfactory accuracy.

Fig. 14 compares the two alternative approximations of the invariant manifold $S_1 = T(X_1/Y_1 + S_1 - S_1^o)$ to the exact invariant manifold generated numerically in the phase portrait of the acidogenesis dynamics, over a broader range of process variables.

Appending the dynamic equations for methanogenesis (Eqs. (31c)–(31d)), after substituting S_1 and X_1 in terms of the reaction invariant variable, z, results in a 3rd-order model for the anaerobic digestion process:

$$\begin{aligned} \frac{dz}{dt} &= -D \cdot z \\ \frac{dX_2}{dt} &= -D \cdot X_2 + Y_2 \cdot \mu_2(S_2) \cdot X_2 \\ \frac{dS_2}{dt} &= c_2 \cdot Y_1 \cdot \mu_1(T(z)) \cdot (S_1^o - T(z) + z) - D \cdot S_2 - \mu_2(S_2) \cdot X_2 \end{aligned} \tag{45}$$

Using (37) to substitute the term $\mu_1 T(z))\cdot(S^o - T(z) + z)$ in (45c), the model can be rewritten as:

$$\begin{aligned} \frac{dz}{dt} &= -D \cdot z \\ \frac{dX_2}{dt} &= -D \cdot X_2 + Y_2 \cdot \mu_2(S_2) \cdot X_2 \\ \frac{dS_2}{dt} &= D \cdot (c_2 \cdot (S_1^o + \Delta(z) - S_{1s}) - S_2) - \mu_2(S_2) \cdot X_2 \end{aligned} \tag{46}$$

where $\Delta(z) = z\cdot(dT(z)/dz) - T(z) + T(0)$ and $T(0) = S_{1s} = D\cdot K_{s1}/(\mu_{\max 1} - D)$.

The term $\Delta(z)$ is a vanishing perturbation (it vanishes at equilibrium). Moreover, given the asymptotic expansion for $T(z)$, it follows that

$$\begin{aligned} \frac{\Delta(z)}{S_1^o} = {} & \left(\frac{K_{s1}}{S_1^o}\right) \cdot \left(\frac{D}{\mu_{\max 1}}\right) \left\{\frac{(z/S_1^o)^2}{(1 + z/S_1^o)^2} + \frac{(z/S_1^o)^3 + 3 \cdot (z/S_1^o)^2}{(1 + z/S_1^o)^3}\right. \\ & \left. \cdot \left(\frac{D}{\mu_{\max 1}}\right) + \frac{6 \cdot (z/S_1^o)^2}{(1 + z/S_1^o)^4} \cdot \left(\frac{K_{s1}}{S_1^o}\right) \cdot \left(\frac{D}{\mu_{\max 1}}\right) + \ldots\right\} \end{aligned} \tag{47}$$

Consequently, since $D/\mu_{\max 1} \ll 1$ and $K_{s1}/S_1^o << 1$, it follows that $\Delta(z)/S_1^o << 1$; hence the magnitude of the term $\Delta(z)$ can be neglected in (46).

Fig. 15 shows that for some representative initial values of the state variables (z, X_2, S_2), the contribution of the function $\Delta(z)$ is very small and eventually approaches zero. In particular, the dynamics of the function $\Delta(z)$ is shown after a disturbance has been imposed and has moved the system away from steady state. The disturbance was a pulse increase or decrease in the input

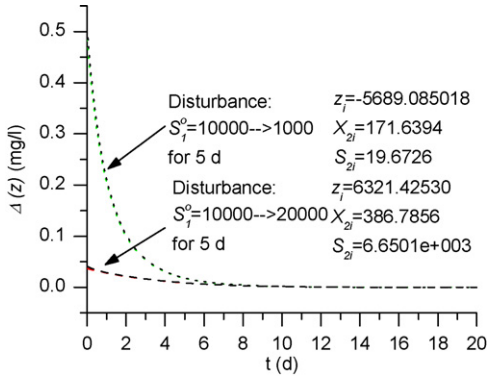

Fig. 15. Dynamic response of the function $\Delta(z)$ for representative initial conditions corresponding to pulse disturbances.

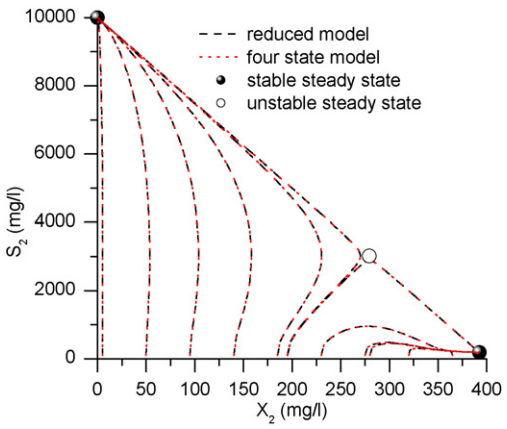

Fig. 16. Trajectories of S_2 versus X_2 from the original four-state model (31) and reduced two-state model (48) lie on top of each other.

concentration which lasted for 5d and afterwards, the input concentration returned to its normal value of 10,000 mg/l. The values of state variables at the moment the pulse was "off", z_i, X_{2i} and S_{2i}, were set as initial conditions for the dynamics. It is seen from Fig. 15 that the function $\Delta(z)$ hardly contributes to (46c) compared to the other terms of the equation and therefore it could be neglected.

By neglecting the term $\Delta(z)$, the dynamics of z no longer affects the system, therefore the differential equation for z can be dropped and the model further reduces to:

$$\begin{aligned}\frac{dX_2}{dt} &= -D\cdot X_2 + Y_2\cdot\mu_2(S_2)\cdot X_2\\ \frac{dS_2}{dt} &= D\cdot(c_2\cdot(S_1^o - S_{1s}) - S_2) - \mu_2(S_2)\cdot X_2\end{aligned} \tag{48}$$

Consequently, the original four-state model (31), with the exception of very short times, is reducible to the three-dimensional model described by (45) or (46) and finally to the two-dimensional model (48). The model reduction was made possible because the acidogenic biomass growth is a slow process compared to soluble substrate utilisation (see how abrupt the change in substrate concentration is, compared to the biomass concentration in Fig. 14); the substrate level is very quickly adjusted to a certain level (corresponding to a point on the invariant manifold) and then it is slowly converted as the biomass level adjusts slowly. Moreover, the effect of the reaction invariant dynamics of the acidogenesis process on the methanogenesis process (accounted for by the term $\Delta(z)$ in equation (46c)) is minuscule and therefore can be neglected, leading to a further reduction of the model. The dynamic responses of X_2 and S_2 from the two-state system (48) are almost identical to the ones from original four-state system (31), as can been seen by a comparison of the phase portrait of (48) and the projection of the phase portrait of (31) on the X_2–S_2 plane (Fig. 16).

5.2. Case 2: Model reduction for anaerobic digestion in the presence of particulate substrate

In order to describe the anaerobic digestion of solid wastes or wastewaters with a high solid content, a three-step process is considered, as depicted in Fig. 17. The first process step is hydrolysis and the subsequent steps are acidogenesis and methanogenesis. Hydrolysis of the particulate matter is an extra-cellular enzymatic step and usually follows first-order kinetics. The acidogenesis and methanogenesis steps involve both bacterial growth and substrate consumption, as in the four-state model (31) described in the previous section. These considerations result in a five-state model expressed by the following set of mass balances applied to a continuously stirred tank reactor (CSTR).

$$\begin{aligned}\frac{dS_P}{dt} &= D\cdot S_p^o - D\cdot S_P - k\cdot S_P\\ \frac{dX_1}{dt} &= -D\cdot X_1 + Y_1\cdot\mu_1(S_1)\cdot X_1\\ \frac{dS_1}{dt} &= D\cdot S_1^o - D\cdot S_1 + c_1\cdot k\cdot S_P - \mu_1(S_1)\cdot X_1\\ \frac{dX_2}{dt} &= -D\cdot X_2 + Y_2\cdot\mu_2(S_2)\cdot X_2\\ \frac{dS_2}{dt} &= -D\cdot S_2 + c_2\cdot\mu_1(S_1)\cdot X_1 - \mu_2(S_2)\cdot X_2\end{aligned} \tag{49}$$

where S_p and S_p^o are the concentrations of the particulate substrate inside the reactor and the feed respectively, k is the hydrolysis rate constant, and c_1 is the stoichiometric coefficient of the conversion of the particulate to the dissolved substrate. The other variables and parameters have already been defined in Section 5.1.

The main implication of including a hydrolysis step in the anaerobic digestion process is that this step precedes a faster step (i.e. acidogenesis). The serial structure of the system is clearly visible in the model (49). Indeed, the first equation (describing dynamics of the step of hydrolysis) is independent of the other equations. The next two equations (describing dynamics of the step of acidogenesis) are independent of the last two equations (describing the dynamics of the step of methanogenesis).

Throughout this section, it will be assumed that Assumptions (A1) and (A3) of Section 5.1 still hold, while (A2) holds with S_1^o replaced by $S_1^o + c_1\cdot S_p^o\cdot k/(D+k)$, which represents the total available dissolved substrate (including the dissolved substrate resulting from the hydrolysis of particulate matter):

(A2) $S_1^o + c_1\cdot\frac{S_p^o\cdot k}{D+k} >> K_{S1}$ and
$c_2\cdot\left(S_1^o + c_1\cdot\frac{S_p^o\cdot k}{D+k}\right) >> \sqrt{K_{S2}\cdot K_I}$

Moreover, an extra assumption is made in this case:

(A4) The hydrolysis constant, k, and the dilution rate, D, are of the same order of magnitude.

Fig. 17. Anaerobic digestion as a three-step process.

Under the above assumptions, system (49) has two non-trivial steady states, out of which, only one is locally asymptotically stable, as in the case of the four-state model (31). In the numerical calculation that will follow, typical values of the additional parameters used in the five-state model were used: $k = 0.1\ \mathrm{d}^{-1}$ [34], $c_1 = 1$, $S_p^o = 50{,}000$ mg/l. The values of dilution rate and the other parameters were kept the same as before. The values of the state variables at the corresponding asymptotically stable non-trivial steady state are $S_{ps} = 33{,}333.33$ mg/l, $X_{1s} = 2933.21$ mg/l, $S_{1s} = 1.15$ mg/l, $X_{2s} = 1059.3$ mg/l and $S_{2s} = 182.96$ mg/l. Linearizing the system (49) around the above steady state, the corresponding eigenvalues are given by:

$$\lambda_1 = -(D + k) = -0.3$$

$$\lambda_2 = -D = -0.2$$

$$\lambda_3 = -\frac{\mu_{\max 1} \cdot K_{s1}}{(K_{s1} + S_{1s})^2} \cdot (S_1^o - S_{1s} + c_1(S_p^o - S_{Ps})) = -4416.65$$

$$\lambda_4 = -D = -0.2$$

$$\lambda_5 = -\frac{\mu_{\max 2} \cdot (K_{s2} - S_{2s}^2/K_I)}{(K_{s2} + S_{2s} + S_{2s}^2/K_I)^2} \cdot (c_2 \cdot (S_1^o - S_{1s} + c_1 \cdot (S_p^o - S_{Ps})) - S_{2s}) = -11.39$$

and they are all negative.

Keeping in mind the serial structure of the system (49), the eigenvalue λ_1 characterizes the dynamics of hydrolysis, while the eigenvalues λ_2 and λ_3 characterize the dynamics of acidogenesis, and the eigenvalues λ_4 and λ_5 characterize the dynamics of methanogenesis. In particular, eigenvalues λ_3 and λ_5 characterize the speed of the reactions for the acidogenesis and the methanogenesis steps respectively, while eigenvalues $\lambda_2 = \lambda_4$ characterize the corresponding reaction-invariant dynamics. Here, similarly to Section 5.1, the "speed" of acidogenesis reaction is much higher than that of the reaction-invariant dynamics

$$\frac{\lambda_2}{\lambda_3} \approx \left(\frac{D}{\mu_{\max 1}}\right) \cdot \left(\frac{K_{s1}}{S_1^o + c_1 \cdot S_p^o \cdot k/(D + k)}\right) << 1$$

and also, it is much higher than the speed of methanogenesis reaction

$$\frac{\lambda_5}{\lambda_3} \lessapprox \frac{\mu_{\max 2}}{\mu_{\max 1}} \cdot \frac{c_2 \cdot K_{S1}}{K_{S2}} << 1$$

Keeping in mind that, because assumption (A4), the dynamics of hydrolysis is of similar speed to reaction-invariant dynamics (λ_1 and λ_2 are of the same order of magnitude), the conclusion is that there is only one fast mode (characterized by eigenvalue λ_3), and it belongs to the acidogenesis step. Therefore, the dynamics of the anaerobic digestion system conforms with the setting of Fig. 10 with the fast-reaction process step (acidogenesis) in between two slow steps (hydrolysis and methanogenesis). The slow-motion invariant manifold will be an algebraic equation relating only the variables of the first two steps (hydrolysis and acidogenesis) S_p, X_1, S_1.

Fig. 18 depicts the phase portrait for the hydrolysis and acidogenesis steps. For every initial state, the trajectory is initially an almost vertical line, indicating an abrupt change in S_1 while S_p and X_1 remain practically unchanged, until it "hits" a surface and subsequently lies on the surface, ending at the steady state (large dot). The picture is similar to Fig. 14, with the exception that the invariant manifold is now a 2-dimensional surface instead of a curve.

In order to proceed with model reduction, we must isolate the fast reaction dynamics of acidogenesis from the slow reaction-invariant dynamics and the slow hydrolysis dynamics. In particular, defining the reaction invariant

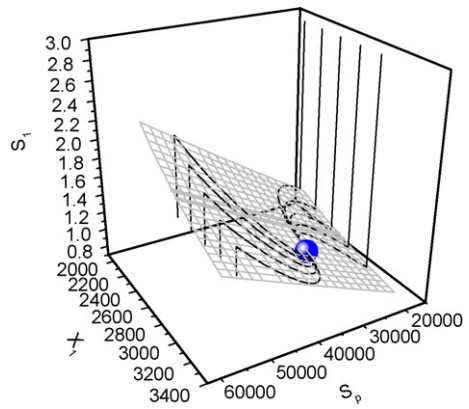

Fig. 18. Phase portrait for the hydrolysis and acidogenesis steps at $D = 0.2\ \mathrm{d}^{-1}$. The surface corresponds to the slow-motion invariant manifold.

$$z = c_1(S_P - S_p^o) + S_1 - S_1^o + \frac{X_1}{Y_1} \tag{50}$$

and using z, S_P, S_1 as dependent variables, the dynamic equations for hydrolysis and acidogenesis (49a)–(49c) are transformed to:

$$\begin{aligned} \frac{dz}{dt} &= -D \cdot z \\ \frac{dS_P}{dt} &= D \cdot S_p^o - D \cdot S_P - k \cdot S_P \\ \frac{dS_1}{dt} &= D \cdot (S_1^o - S_1) - Y_1 \cdot \mu_1(S_1) \cdot (S_1^o - S_1 + c_1 \cdot (S_p^o - S_P) + z) \\ &\quad + c_1 \cdot k \cdot S_P \end{aligned} \tag{51}$$

In the transformed system, the slow reaction-invariant dynamics (z) together with the slow hydrolysis dynamics (S_P) precede the fast reaction dynamics (S_1). The slow-motion invariant manifold is of the form

$$S_1 = T(z, S_P) \tag{52}$$

and satisfies the invariance equation:

$$\begin{aligned} &(-D \cdot z)\frac{\partial T}{\partial z} + (D \cdot S_p^o - (D + k) \cdot S_P)\frac{\partial T}{\partial S_P} \\ &\quad = D \cdot (S_1^o - T(z, S_P)) - \frac{\mu_{\max 1} \cdot T(z, S_P)}{K_{S1} + T(z, S_P)} \\ &\qquad \cdot (S_1^o - T(z, S_P) + c_1 \cdot (S_p^o - S_P) + z) + c_1 \cdot k \cdot S_P \end{aligned} \tag{53}$$

This must be solved with initial condition

$$T\left(0, \frac{D \cdot S_p^o}{D + k}\right) = S_{1s}, \quad \text{where } S_{1s} = \frac{D \cdot K_{s1}}{\mu_{\max 1} - D} \tag{54}$$

which states that the invariant manifold must pass through the steady state point.

The partial differential Eq. (53) is singular at the point around which it should be solved ($z_s = 0, S_{ps} = D \cdot S_p^o/(D + k)$), since the coefficients of the partial derivatives of the unknown function vanish at that point. A sufficient condition for existence and uniqueness of solution of (53) is the following non-resonance condition:

There are no non negative integers M, N with $M + N > 0$ such that $\lambda_3 = M \cdot \lambda_1 + N \cdot \lambda_2$, as direct result of Lyapunov's auxiliary theorem for singular partial differential equations [31].

Eq. (53) can be solved via power series around the point ($z_s = 0, S_{ps} = D \cdot S_p^o/(D + k)$) up to a certain truncation order, or via a singular perturbation approach for small $D/\mu_{\max 1}$, similarly to (37).

For the particular numerical values of the parameters under consideration and over the ranges of $z \in [-20{,}000,\ 20{,}000]$ and $S_P \in [-20{,}000,\ 50{,}000]$, numerical convergence of the power series expansion is achieved at truncation order of 7. Singular perturbation analysis leads to the following expression for the invariant manifold:

$$\begin{aligned} T(z,S_P) = {} & K_{s1}\cdot\frac{S_1^o + c_1\cdot k/D\cdot S_P}{S_1^o + c_1\cdot(S_p^o - S_P) + z}\cdot\left(\frac{D}{\mu_{\max 1}}\right) \\ & + K_{s1}\left[\left(\frac{S_1^o + c_1\cdot k/D\cdot S_P}{S_1^o + c_1\cdot(S_p^o - S_P) + z}\right)^2\right. \\ & - \frac{K_{s1}\cdot c_1\cdot k/D(S_p^o - (1+k/D)\cdot S_P)}{\left(S_1^o + c_1\cdot\left(S_p^o - S_P\right) + z\right)^2} \\ & \left. - \frac{2\cdot K_{s1}(S_1^o + c_1\cdot k/D\cdot S_P)(z + c_1\cdot(S_p^o - (1+k/D)\cdot S_P))}{(S_1^o + c_1\cdot(S_p^o - S_P) + z)^3}\right] \\ & \times\left(\frac{D}{\mu_{\max 1}}\right)^2 + O\left(\frac{D}{\mu_{\max 1}}\right)^3 \end{aligned} \tag{55}$$

Both methods result in the same accuracy of approximation of the invariant manifold surface (Fig. 18). The three-dimensional system (51) that describes the hydrolysis and acidogenesis steps reduces to two differential equations plus the algebraic equation of the invariant manifold:

$$\begin{aligned} \frac{dz}{dt} &= -D\cdot z \\ \frac{dS_P}{dt} &= D\cdot S_P^o - D\cdot S_P - k\cdot S_P \\ S_1 &= T(z,S_P) \\ X_1 &= Y_1(S_1^o - T(z,S_P) + c_1\cdot(S_p^o - S_P) + z) \end{aligned} \tag{56}$$

Appending the dynamic equations for methanogenesis (Eqs. (49d) and (49e)), the resulting 4th-order model can be rearranged in the form:

$$\begin{aligned} \frac{dz}{dt} &= -D\cdot z \\ \frac{dS_P}{dt} &= D\cdot S_P^o - D\cdot S_P - k\cdot S_P \\ \frac{dX_2}{dt} &= -D\cdot X_2 + Y_2\cdot\mu_2(S_2)\cdot X_2 \\ \frac{dS_2}{dt} &= D\cdot\left(c_2\cdot\left(S_1^o + c_1\cdot\frac{S_P^o\cdot k}{D+k} + \Delta(z,S_P) - S_{1s}\right) - S_2\right) \\ & \quad - \mu_2(S_2)\cdot X_2 + c_1\cdot c_2\cdot k\cdot\left(S_P - \frac{D\cdot S_P^o}{D+k}\right) \end{aligned} \tag{57}$$

where $S_{1s} = D\cdot K_{s1}/(\mu_{\max 1} - D)$

and

$$\begin{aligned} \Delta(z,S_P) = {} & z\frac{\partial T}{\partial z}(z,S_P) - \left(S_p^o - \frac{D+k}{D}\cdot S_P\right)\frac{\partial T}{\partial S_P}(z,S_P) \\ & - T(z,S_P) + T\left(0,\frac{D\cdot S_P^o}{D+k}\right) \end{aligned} \tag{58}$$

The term $\Delta(z,S_P)$ is a vanishing perturbation (it vanishes at equilibrium). Moreover, given the asymptotic expansion for $T(z,S_P)$, it follows that:

$$\begin{aligned} & \frac{\Delta(z,S_P)}{S_1^o + c_1\cdot S_P^o\cdot k/(D+k)} \\ & = \left(\frac{K_{s1}}{S_1^o + c_1\cdot S_P^o\cdot k/(D+k)}\right)\cdot\left(\frac{D}{\mu_{\max 1}}\right) \\ & \quad\times\left[\frac{c_1\cdot((k/D)^2 - 1)\cdot(S_P - D\cdot S_P^o/(D+k)) + z}{S_1^o + c_1\cdot(S_P^o - S_P) + z}\right. \\ & \quad\left. + \frac{(S_1^o + c_1\cdot k/D\cdot S_P)\cdot[-z + c_1\cdot(1+k/D)\cdot(S_P - D\cdot S_P^o/(D+k))]}{(S_1^o + c_1\cdot(S_P^o - S_P) + z)^2}\right] \\ & \quad + \text{higher-order terms} \end{aligned} \tag{59}$$

Consequently, since $D/\mu_{\max 1} \ll 1$ and $K_{s1}/(S_1^o + c_1\cdot S_P^o\cdot k/(D+k)) << 1$, the magnitude of the term $\Delta(z,S_P)$ can be neglected. Then, the differential equation for z can be dropped and the model finally reduces to:

$$\begin{aligned} \frac{dS_P}{dt} &= D\cdot S_P^o - D\cdot S_P - k\cdot S_P \\ \frac{dX_2}{dt} &= -D\cdot X_2 + Y_2\cdot\mu_2(S_2)\cdot X_2 \\ \frac{dS_2}{dt} &= D\cdot(c_2\cdot(S_1^o - S_{1s}) - S_2) - \mu_2(S_2)\cdot X_2 + c_1\cdot c_2\cdot k\cdot S_P \end{aligned} \tag{60}$$

In summary, the original five-state model (49), with the exception of very short times, is reducible to the four-dimensional model (57) and further to the three-dimensional model (60). Model reduction to (57) was made possible by projecting the dynamics of hydrolysis and acidogenesis on their slow-motion invariant manifold. Subsequently, because the effect of the corresponding reaction invariant dynamics on the dynamics of methanogenesis was negligible, further reduction of the model to (60) was possible.

6. Conclusions

Biochemical reaction systems are multistep processes. The rates of some individual steps may differ significantly, while the rates of other steps may vary at similar levels. In this work, we have developed a systematic methodology for the reduction of the order of the general system considered, based on the calculation of the slow-motion invariant manifold, on which the process dynamics is projected. Further reduction in the system order may be achieved if certain slow modes have negligible contribution to the overall dynamics of the system. All these aspects were considered to eliminate the fast dynamics of the acidogenesis step involved in the anaerobic digestion process, in the cases of a five- and a four-dimensional model. Neglecting acidogenesis, altogether leads to a three- and two-dimensional model respectively which describes only the dynamics of hydrolysis (if a particulate substrate is present) and methanogenesis.

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