

Stability analysis of two-step biochemical reaction systems for general reaction kinetics

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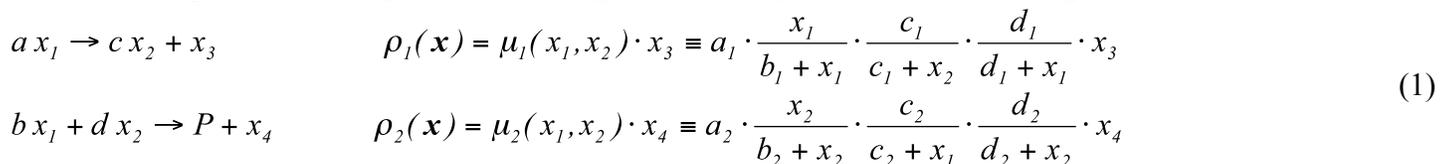
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Introduction

The steady state behaviour of (bio)chemical reaction systems is an important aspect in view of their process design and control. In particular, it is important to identify process conditions under which steady state multiplicity occurs, by which we mean that different initial reactor conditions result in different steady states reached for the same input variables. Whereas in a non-isothermal reacting system, the nonlinear dependence of the rate constant on temperature may contribute to system multiplicity, in isothermal systems like biological wastewater treatment systems, multiplicity may result from nonlinear kinetics. A widespread application in this field is the nitrification process, i.e. the oxidation of ammonium, being the main form in which nitrogen is present in wastewater. Volcke *et al.* (2007) demonstrated how microbial (inhibition) kinetics affect the number and the stability of a two-step nitrification model by considering a few different cases w.r.t. the associated reaction kinetics. While the latter contribution devoted particular attention to the physical interpretation of the results for the nitrification process, this study focuses on the mathematics behind the steady state behaviour of two-step (bio)chemical reaction systems, also related to other applications and considering more general reaction kinetics.

Two-step reaction model under study – canonical state space representation

The system under study concerns a continuous stirred tank reactor (CSTR) with constant volume, in which two reactions take place, according to the following stoichiometry (left) and kinetics (right):



These reactions are essentially consecutive (a substrate x_1 is converted to an intermediate x_2 , which is subsequently converted to a final product P), although a (small) amount of x_1 can also be consumed in the second reaction. x_3 and x_4 represent the biomass carrying out these reactions and benefiting from this through growth. This reaction scheme describes a two-step nitrification process, in which ammonium (x_1) is converted to nitrite (x_2) by ammonium oxidizing biomass (x_3) and subsequently to nitrate (P) by nitrite oxidizing biomass (x_4), using a small amount of ammonium for incorporation in biomass. Nevertheless, it can also describe other applications, such as a (simplified) two-step anaerobic digestion process (Bernard *et al.*, 2001). In this widely applied wastewater treatment process taking place in absence of oxygen, acidogenic bacteria (x_3) consume organic substrate (x_1) and produce volatile fatty acids (x_2), which methanogenic bacteria (x_4) subsequently convert to methane gas (P). The latter reaction does not involve organic substrate, so $b = 0$ in this application. Noteworthy is that accumulation of the intermediate (x_2) is highly desirable in certain nitrification reactors, but should be absolutely avoided during anaerobic digestion. The reaction rates ρ_i depend on the reactor concentrations of the components (also denoted by the respective x_i). They consist of substrate limitation terms (in b_i) and inhibition terms (in c_i and d_i).

The system's state equations in the state variables $\mathbf{x} = [x_1 \quad x_2 \quad x_3 \quad x_4]^T$ are given by the mass balances of the individual x_i . They can subsequently be transformed by defining new state space variables \mathbf{y} (left), bringing the model in a so-called canonical form (right):

$$\mathbf{y} = \begin{bmatrix} y_1 \\ y_2 \\ y_3 \\ y_4 \end{bmatrix} \equiv \begin{bmatrix} x_1 + a \cdot x_3 + b \cdot x_4 \\ x_2 - c \cdot x_3 + d \cdot x_4 \\ x_3 \\ x_4 \end{bmatrix} \Rightarrow \begin{cases} \dot{y}_1 = u_0 \cdot (u_1 - y_1) \\ \dot{y}_2 = -u_0 \cdot y_2 \\ \dot{y}_3 = (-u_0 + \lambda_1(\mathbf{y})) \cdot y_3 \\ \dot{y}_4 = (-u_0 + \lambda_2(\mathbf{y})) \cdot y_4 \end{cases} \quad (2)$$

in which $\lambda_i(\mathbf{y}) = \mu_i(\mathbf{x})$; $i = 1, 2$. u_0 represents the dilution rate (i.e. the ratio of the influent flow rate over the reactor volume), u_1 represents the substrate concentration in the influent. It has been assumed that the influent does not contain intermediate, neither biomass. The canonical model form consists of a linear part of dimension 2 coupled with a nonlinear part of dimension 2. The state variables x_i ($i=1, \dots, 4$) cannot become negative. Call \mathcal{S}_y the image of $\mathfrak{R}^{+,4} \equiv \{\mathbf{x} \in \mathfrak{R}^4 : x_i \geq 0, i = 1, \dots, 4\}$ under the transformation $\mathbf{x} \mapsto \mathbf{y}$. \mathcal{S}_y is the state space of the system defined by Eqs. 2. Every trajectory that starts at $t = 0$ in a point \mathbf{y}_0 of \mathcal{S}_y , stays in \mathcal{S}_y for $t \geq 0$.

Calculation of steady states

Using the canonical state space model representation, the calculation of steady states of the model is substantially simplified. For positive dilution rates and influent ammonium concentrations ($u_0 > 0$ and $u_1 > 0$), three types of steady states are obtained from eq. 2 in which $\dot{y}_i = 0$ ($i=1, \dots, 4$):

1. $y_{ss3} = y_{ss4} = 0$: the washout state - no biomass is present and hence no conversion takes place
2. $y_{ss4} = 0$; $y_{ss3} \neq 0$; $u_0 = \lambda_1(\mathbf{y}_{ss})$: only intermediate (x_2) is produced (further denoted by superscript α)
3. $y_{ss3} \neq 0$; $y_{ss4} \neq 0$; $u_0 = \lambda_1(\mathbf{y}_{ss}) = \lambda_2(\mathbf{y}_{ss})$: with formation of product (P) (further denoted by superscript β)

The washout state is unique and is always a physical steady state. In the latter two cases, the number of steady states depends on the conversion kinetics. They are found as (note that the steady state values in the \mathbf{x} -space can be calculated straightforwardly from the values obtained in the \mathbf{y} -space):

$$\left. \begin{matrix} y_{ss4} = 0 \\ u_0 = \lambda_1(\mathbf{y}_{ss}^\alpha) \end{matrix} \right\} \Rightarrow \mathbf{x}_{ss}^\alpha = \begin{bmatrix} x_{ss1}^\alpha \\ \frac{c}{a} \cdot (u_1 - x_{ss1}^\alpha) \\ \frac{1}{a} \cdot (u_1 - x_{ss1}^\alpha) \\ 0 \end{bmatrix} \quad (3); \quad \left. \begin{matrix} u_0 = \lambda_1(\mathbf{y}_{ss}^\beta) \\ u_0 = \lambda_2(\mathbf{y}_{ss}^\beta) \end{matrix} \right\} \Rightarrow \mathbf{x}_{ss}^\beta = \begin{bmatrix} x_{ss1}^\beta \\ x_{ss2}^\beta \\ \frac{d \cdot (u_1 - x_{ss1}^\beta) + b \cdot x_{ss2}^\beta}{a \cdot d + b \cdot c} \\ \frac{c \cdot (u_1 - x_{ss1}^\beta) - a \cdot x_{ss2}^\beta}{a \cdot d + b \cdot c} \end{bmatrix} \quad (4)$$

in which x_{ss1}^α results from

$$a_1 \cdot \frac{x_{ss1}^\alpha}{b_1 + x_{ss1}^\alpha} \cdot \frac{c_1}{c_1 + \frac{c}{a} \cdot (u_1 - x_{ss1}^\alpha)} \cdot \frac{d_1}{d_1 + x_{ss1}^\alpha} = u_0 \quad (5)$$

and x_{ss1}^β and x_{ss2}^β are calculated from

$$a_1 \cdot \frac{x_{ss1}^\beta}{b_1 + x_{ss1}^\beta} \cdot \frac{c_1}{c_1 + x_{ss2}^\beta} \cdot \frac{d_1}{d_1 + x_{ss1}^\beta} = u_0 \quad \text{and} \quad a_2 \cdot \frac{x_{ss2}^\beta}{b_2 + x_{ss2}^\beta} \cdot \frac{c_2}{c_2 + x_{ss1}^\beta} \cdot \frac{d_2}{d_2 + x_{ss2}^\beta} = u_0 \quad (6)$$

It is clear that the number of solutions of the type \mathbf{x}_{ss}^α and \mathbf{x}_{ss}^β is not always unique. Besides, one also needs to check rigorously whether the steady states calculated algebraically are also physical steady states in the sense that they lie in \mathcal{S}_y (in the \mathbf{y} -space) or $\mathfrak{R}^{+,4}$ (in the \mathbf{x} -space). The values of steady states have been calculated for a number of 'elementary' cases (model I to V in Table 1), which differ in the inhibition terms considered (c_1 , d_1 , c_2 , d_2 refer to the corresponding inhibition terms, if not mentioned this means that their value has been assumed to be infinity i.e. the corresponding inhibition term has not been considered). Table 1 further indicates the maximum number of physical steady states of type \mathbf{x}_{ss}^α and \mathbf{x}_{ss}^β , as well as the maximum total number of physical steady states (including the washout state). While some solutions of eqs. 3, 5 and 4, 6 can be excluded a priori from being physical steady states, others being physical steady states or not will depend on the values of the input variables u_0 and u_1 . This is illustrated for model III (the results for the remaining models are not shown) in Figure 1, which includes the equations for the boundaries between the different operating zones.

From the results for the elementary models I-V, the maximum number of steady states for composite models has been derived subsequently (Table 1). The conditions for each of the steady states to be a physical steady state (dependent on u_0 and u_1) has been derived as well (results not shown).

Table 1. Maximum number of steady states for elementary (I-V) and composite (VI-VIII) models

model	I	II	III	IV	V	VI	VII	VIII
inhibition terms considered	-	c_1	d_1	d_2	c_2	c_1, d_1	c_2, d_2	c_1, d_1 c_2, d_2
maximum number of steady states (type x_{ss}^α , type x_{ss}^β , total)	(1,1,3)	(1,1,3)	(2,2,5)	(1,2,4)	(1,1,3)	(2,2,5)	(1,2,4)	(2,4,7)

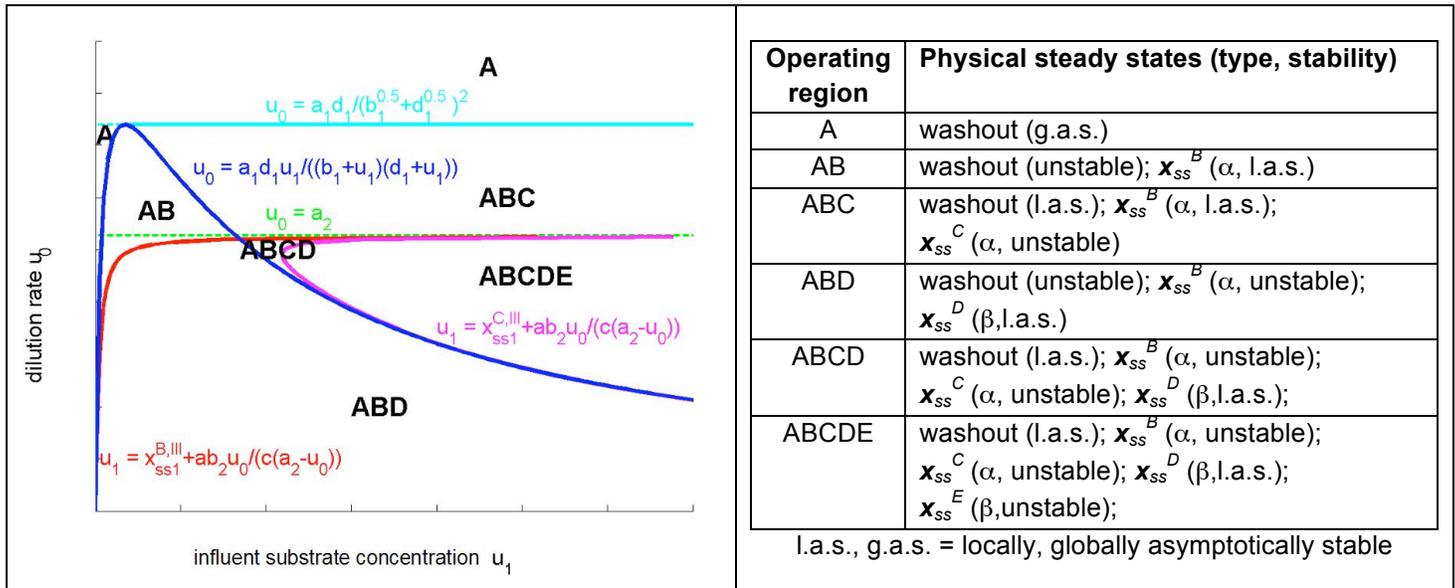


Figure 1. Occurrence and stability of steady states for model III.

Local asymptotic stability

In this contribution the term ‘steady state’ has been used synonymous to ‘equilibrium’ or ‘equilibrium state’, as a solution of the steady state process model. It should be stressed that these steady states are not a priori stable. The linearization principle has been used to investigate local asymptotic stability of the steady states. The results for model III have been indicated in Figure 1.

Conclusions

The stability of two-step biochemical reaction systems has been assessed in terms of the number of steady states, their nature and their local asymptotic stability. It has been shown possible to generalize the results obtained for models with ‘elementary’ reaction kinetics (considering one type of inhibition at a time) to models including ‘composite’ reaction kinetics, thus covering a broad range of applications.

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