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TECHNICAL NOTE : 54.1

Steady state of the compartments Rhodobacter, Nitrifying and Spirulina

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0	0	March 2001	Draft
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<u>Abbreviations or notations:</u>
AcOH : Acetic acid
CH : chlorophyll
CO_2 : carbon dioxide (gaseous or solvated)

EPS : exopolysaccharide
HPC : Higher Plant Chamber
NH_3 : ammonia (gaseous or solvated)
NO_2 : nitrite ion
NO_3 : nitrate ion
N_s : Nitrosomonas
N_b : Nitrobacter
PC : phycocyanin
XA : active biomass
XV : vegetative biomass

Note :
In a figure, a graph ij is located by its row i and its column j.

1. INTRODUCTION

This Technical Note gathers the study of the steady states of the Rhodobacter, Nitrifying and Spirulina compartments. This way, the main features of the compartments are kept, getting rid of the temporal behaviour which is useful for the control study only. The steady state global simulator that will be built from them will be of great interest in the study of binding the different compartments between them.

2. RHODOBACTER COMPARTMENT

2.1. Recall of mathematical relations of the simulator

2.1.1 State system of the bi-phasic compounds

The general state system of the bi-phasic compounds is described by (A1.9) in TN 54.2 and is recalled hereafter :

$$\dot{X} = A \cdot X + B \cdot U \qquad (2.1)$$

where :

- X is the column vector of the concentrations of the bi-phasic compounds in the liquid phase (for the Rhodobacter compartment, they are CO_2 , NH_3 and AcOH);
- U is the column vector of the inputs (concentrations of the bi-phasic compounds in the incoming gas and liquid phases, variation rates of the bi-phasic compounds in liquid phase);
- A and B are constant matrices if the gas and liquid flow rates are constant, or time variable matrices if these flow rates depend on time.

2.1.2. State system of the mono-phasic compounds

The general state system of the mono-phasic compounds is described by (A1.10) in TN 54.2 and is recalled hereafter :

$$\frac{db_i}{dt} = \frac{q_L}{V_L} \cdot \left(d_{Li} - b_i\right) + r_i \qquad (2.2)$$

where i is the index of the compounds defined in the table A3.1 .

Index i	Compound
1	Sulfate
2	Phosphate
3	Active biomass

Table 2.1 Index of the mono-phasic compounds

For the biomass (i = 3), the input concentration is null.
The production rate of the biomass has been established in TN 45.1 (LGCB).
Although the chemical limitation has not been studied yet for Rhodobacter, a limiting factor is introduced in the present study in order to have a general approach.
So the mean volumetric growth rate of biomass is expressed by :

$$r_X = R_X \cdot K_l \qquad (2.3)$$

where R_X is the mean volumetric growth rate under light limitation (section A2.1.4 of TN 54.2) and K_l the limiting factor depending on the concentrations of the substrates NH_3, SO_4 and PO_4.

2.2. Steady state conditions

For constant inputs, the necessary and sufficient condition of steady state is realised when the derivative of the state is null.
Then for the bi-phasic compounds, the relation (2.1) implies :

$$X = A^{-1} \cdot B \cdot U \qquad (2.4)$$

for the mono-phasic compounds i, the relation (2.2) implies :

$$b_i = d_{Li} + \frac{V_L}{q_L} \cdot r_i \qquad (2.5)$$

and for the biomass, the relation (2.5) can be rewritten in a simpler way because d_L is null (no incoming biomass) :

$$C_X = \frac{V_L}{q_L} \cdot r_X \qquad (2.6)$$

where C_X is the biomass concentration and r_X the volumetric biomass growth rate.

Considering that the initial biomass concentration C_X is fixed and that r_X depends on F_0, the relation (2.6) allows to compute the light flux F_0 , if it exists.
Then r_X is fixed and consequently the rates r_i in (2.5) and the input U in (2.4) are determined too.
So each equation of the relations (2.4) and (2.5) has one and only one solution, which determines the concentrations X and b_i in the liquid.

Existence conditions of the solution F_0 :
Relations (2.3) and (2.6)

$$R_X = \frac{q_L \cdot C_X}{V_L \cdot K_l}$$

Starting from the expression of the mean volumetric growth rate, R_X, recalled in section A2.1.4 of TN 54.2, this relation is equivalent to :

$$\Leftrightarrow J_{(Cx,F0)} = \frac{q_L}{2 \cdot \mu_M \cdot V_L \cdot K_l} \qquad (2.7)$$

As J is monotonic ascending versus F_0, the sufficient and necessary condition for the relation (2.7) to have one and only one solution is :

$$J_m \leq \frac{q_L}{2 \cdot \mu_M \cdot V_L \cdot K_l \cdot k} \leq J_M$$

$$\text{with} \quad J_m = J_{(Cx, F\min)} \qquad (2.8)$$

$$J_M = J_{(Cx, F\max)}$$

The upper limit of J, when $F_0 \rightarrow \infty$, is ½.

This latest relation is the necessary and sufficient condition for a steady state. As it implies the volume of liquid, it should be taken into account for the sizing of the reactor.

The function J is monotonic ascending versus F_0 :

To make simple the demonstration, J is assumed continuous versus F_0, which implies $\varepsilon_J = 0$.

$$\frac{\partial J}{\partial F_0} = \frac{\partial g}{\partial F_0}$$

$$\frac{\partial g}{\partial F_0} = \frac{I_\Sigma \cdot K_J \cdot x}{F_0 \cdot (I_\Sigma \cdot K_J)^2}$$

$$\frac{\partial J}{\partial F_0} > 0 \qquad \forall F_0 \in [0 \quad \infty[$$

2.3. Concentrations at steady state

The root F_0 is extracted from (2.7) by a dichotomy method. Then the concentrations of the substrates at steady state are deduced from (2.4) and (2.5).

It must be noted that F_0 depends on the biomass concentration C_X, which determines the variation rates of products (biomass, CO_2) and substrates. So, when a steady state is reached and as long as F_0 is unchanged, the relation (2.7) is true. So is the equivalent relation (2.6). Then the production rate of biomass r_X is constant. If non limiting modifications (i.e. modifications that do not change the factor K_l) occur on the inputs U or d_{Li} (of relations (2.4) and (2.5)), only the concentrations in the reactor, X and b_i, are affected but the variation rates of products and substrates are unchanged.

2.4. Examples

As it has been said just above, the chemical limitation has not been modelled yet for Rhodobacter. Nevertheless a limiting factor is introduced in the present study in order to have a general approach and to prepare a simulator ready to accept the future and correct limiting factor. So in the following simulated examples, the limiting factor K_l is supposed to be Monod type for only one substrate. This limiting substrate is supposed to be SO_4 (because SO_4 or PO_4 seems to be more adapted to a Monod type law than acetic acid or NH_3) and the value of the constant K_S is set arbitrarily :

$$K_l = \frac{C_S}{K_S + C_S} \text{ for } SO_4 \text{ in the following simulations.}$$

2.4.1. Computation of steady state

For example, the parameters of the simulated process are :

- CO_2 : null in incoming gas and liquid flows;
- NH_3 (molecular form) : 6.51 10^{-6} mol/l in gas and 7.92 10^{-4} mol/l in liquid (input flows);
- AcOH (molecular form) : 1.68 10^{-9} mol/l in gas and 8.77 10^{-5} mol/l in liquid (input flows);
- SO4 : 2.08 10^{-3} mol/l (input liquid flow);
- PO4 : 4.21 10^{-3} mol/l (input liquid flow);
- biomass : 0.6 g/l.

The condition (2.8) is fulfilled and the relation (2.7) gives the solution :

$F_0 = 29.3$ W/m^2.

Then the relations (2.4) and (2.5) give the concentrations of the substrates at steady state in the liquid phase of the reactor :

CO_2 (molecular form) : 5.92 10^{-5} mol/l
NH_3 (molecular form) : 7.46 10^{-4} mol/l
AcOH (molecular form) : 7.64 10^{-6} mol/l
SO_4 : 2.00 10^{-3} mol/l
PO_4 : 3.81 10^{-3} mol/l

2.4.2. Condition of steady state not fulfilled

It could be interesting to see what is the dynamic behaviour of the process when the condition of steady state is not fulfilled.

In the following simulation the starting point of the process is the same as the one of the previous example where the condition of steady state is fulfilled. But at time t=10h, the concentration of the limiting substrate (SO_4) in the incoming liquid is divided by 100 so that this condition is no more fulfilled. The figures 2.1 and 2.2 show the dynamic behaviour of the concentrations and production rates.

The consequence of the decreasing SO_4 step in the incoming flow is seen in the graph 41 of the figure 2.1 : SO_4 decreases because of dilution and consumption. When its concentration goes near the limiting value, the production rate of biomass decreases (at time t=100h on graph 22 in figure 2.2). So do the rates of the substrates. A new permanent equilibrium is reached at the end of the simulation. But it is not the steady state corresponding to the light flux received by the process : all the light intensity is not used in the production of biomass.

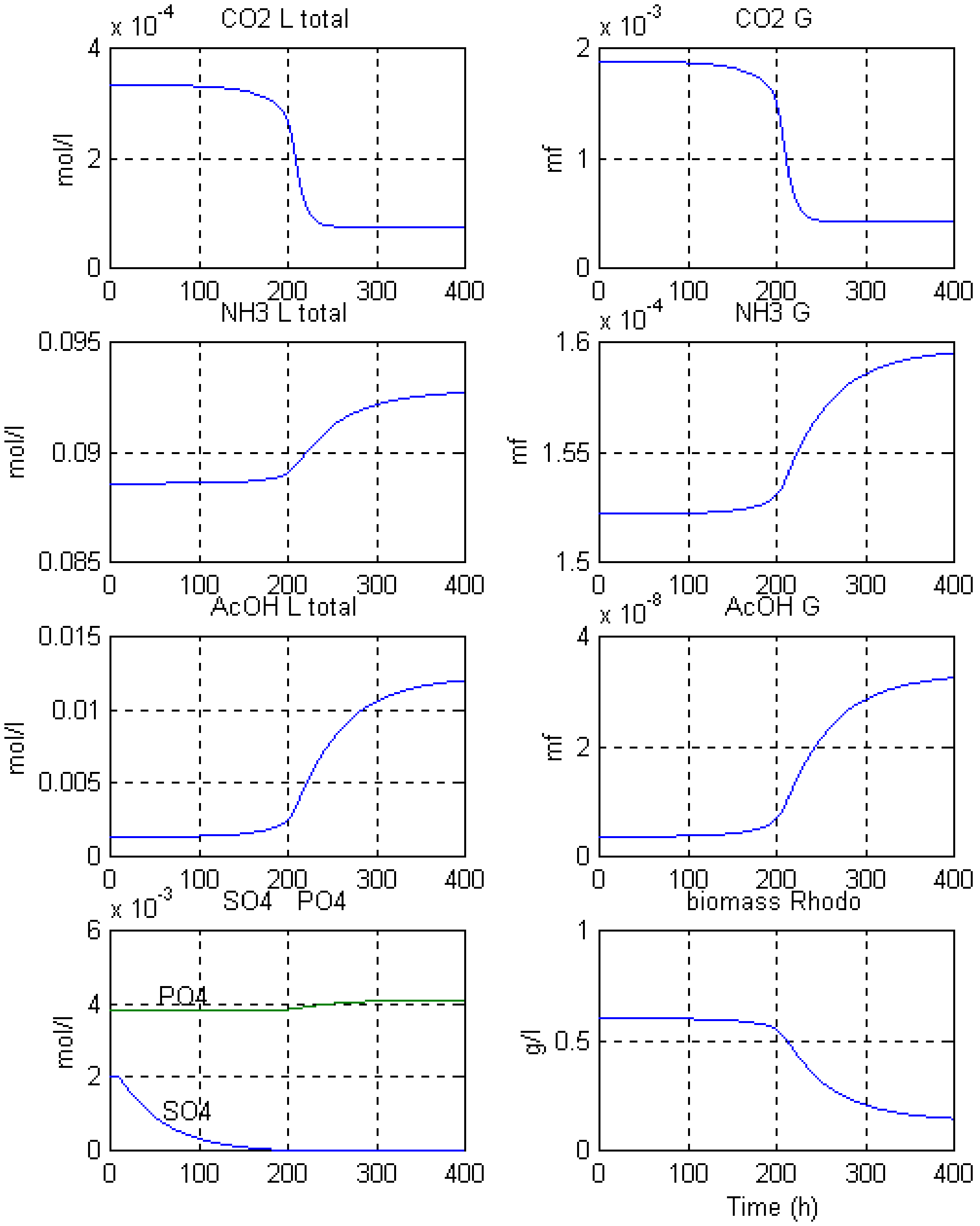

Figure 2.1 : Dynamic behaviour of the concentrations

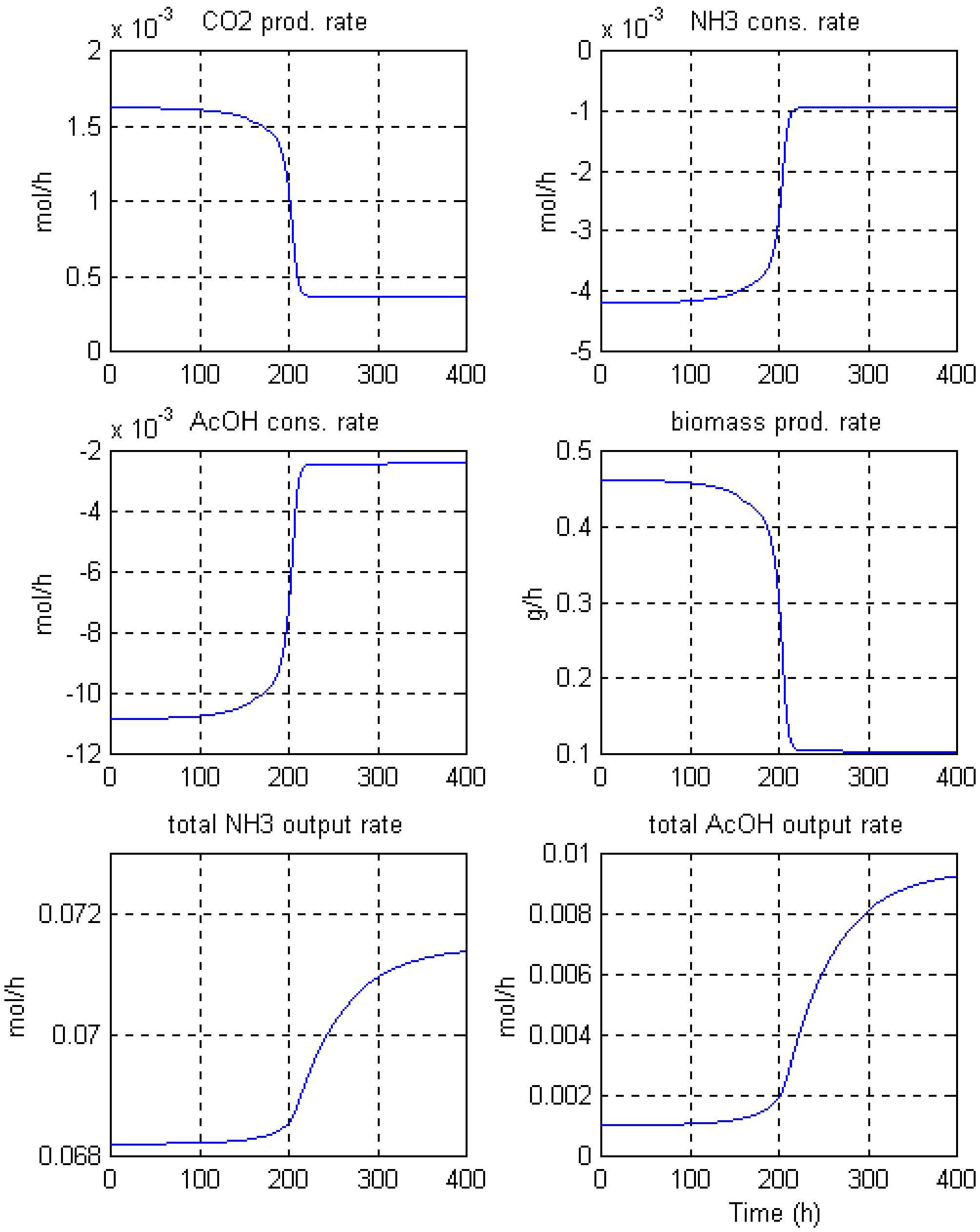

Figure 2.2 : Dynamic behaviour of the rates

3. SPIRULINA COMPARTMENT

3.1. Recall of mathematical relations of the simulator

3.1.1 State system of the bi-phasic compounds

As for Rhodobacter, the general state system of the bi-phasic compounds is described by (A1.9) of TN54.2 and is recalled hereafter :

$$\dot{X} = A \cdot X + B \cdot U \tag{3.1}$$

where :

- X is the column vector of the concentrations of the bi-phasic compounds in the liquid phase (for the Spirulina compartment, they are O_2 and CO_2);
- U is the column vector of the inputs (concentrations of the bi-phasic compounds in the incoming gas and liquid phases, variation rates of the bi-phasic compounds in liquid phase);
- A and B are constant matrices if the gas and liquid flow rates are constant, or time variable matrices if these flow rates depend on time.

Detailed description of these vectors and matrices for the Spirulina compartment:

Note : Z^t is the transpose matrix of the matrix Z.

The indices 1 and 2 are associated to O_2 and CO_2, respectively.

The variables δ_1 and δ_2 are defined in (A1.8) for O_2 and CO_2, respectively.

The variables k_1 and k_2 are the dissociation constants for O_2 and CO_2, respectively.

$$\begin{aligned} X^t &= [b_1 \;\; b_2] \\ U^t &= [d_{G1} \;\; d_{G2} \;\; d_{L1} \;\; d_{L2} \;\; r_1 \;\; r_2] \end{aligned} \tag{3.2}$$

$$\begin{aligned} A &= \begin{pmatrix} -\left(\dfrac{q_L}{V_L} + \delta_1\right) & 0 \\ 0 & -\left(\dfrac{q_L}{V_L} + \delta_2\right) \end{pmatrix} \\ B &= \begin{pmatrix} \dfrac{\delta_1}{\alpha_1} & 0 & \dfrac{q_L}{V_L} & 0 & \dfrac{1}{1+k_1} & 0 \\ 0 & \dfrac{\delta_2}{\alpha_2} & 0 & \dfrac{q_L}{V_L} & 0 & \dfrac{1}{1+k_2} \end{pmatrix} \end{aligned} \tag{3.3}$$

3.1.2. State system of the mono-phasic compounds

The general state system of the mono-phasic compounds is described by (A1.10) in TN 54.2 and is recalled hereafter :

$$\frac{db_i}{dt}=\frac{q_L}{V_L}\cdot\left(d_{Li}-b_i\right)+r_i \qquad (3.4)$$

where i is the index of the compounds defined in the table 3.1 .

Index i	Compound
1	Nitrate
2	Sulfate
3	Phosphate
4	Active biomass
5	Vegetative biomass
6	Exopolysaccaride
7	Phycocyanin
8	Chlorophyll

Table 3.1 Index of the mono-phasic compounds

For the constituents of the biomass ($4 \le i \le 8$), the input concentration is null.
The production rates of the components of the biomass are those established in TN 19.2 (LGCB), taking into account the modification (on June 5th, 1998) of the growth rate of the EPS (exopolysaccaride).
In agreement with their author and in order to avoid negative concentration of PO_4, a Monod term for PO_4 has been added to the expressions of $\left\langle r_{XA}\right\rangle,\left\langle r_{PC}\right\rangle$ and $\left\langle r_{XV}\right\rangle$. They are listed hereafter in (A3.5) :

$$\begin{aligned}
&\left\langle r_{XT}\right\rangle=\left\langle R_{XA}\right\rangle+\left\langle R_{EPS}\right\rangle\\
&\left\langle r_{XA}\right\rangle=\left\langle R_{XA}\right\rangle\cdot\frac{C_N}{K_N+C_N}\cdot\frac{C_S}{K_S+C_S}\cdot\frac{C_P}{K_P+C_P}\\
&\left\langle r_{PC}\right\rangle=z_{PC}\cdot\left\langle R_{XA}\right\rangle\cdot\left(\frac{C_N}{K_N+C_N}\cdot\frac{C_S}{K_S+C_S}\cdot\frac{C_P}{K_P+C_P}-\left(\frac{K_N}{K_N+C_N}+\frac{K_S}{K_S+C_S}+\frac{K_P}{K_P+C_P}\right)\right)\\
&\left\langle r_{XV}\right\rangle=\left\langle R_{XA}\right\rangle\cdot\left(\frac{C_N}{K_N+C_N}\cdot\frac{C_S}{K_S+C_S}\cdot\frac{C_P}{K_P+C_P}+\frac{C_{PC}}{K_{PC}+C_{PC}}\cdot\left(\frac{K_N}{K_N+C_N}+\frac{K_S}{K_S+C_S}+\frac{K_P}{K_P+C_P}\right)\right)\\
&\left\langle r_{EPS}\right\rangle=\left\langle r_{XT}\right\rangle-\left\langle r_{XV}\right\rangle\\
&\left\langle r_G\right\rangle=\left\langle r_{XV}\right\rangle-\left\langle r_{XA}\right\rangle\\
&\left\langle r_{CH}\right\rangle=z_{CH}\cdot\left\langle r_{XA}\right\rangle
\end{aligned}\qquad (3.5)$$

3.2. Steady state conditions

For constant inputs, the necessary and sufficient condition of steady state is realised when the derivative of the state is null.

Then for the bi-phasic compounds, the relation (3.1) implies :

$$X = A^{-1} \cdot B \cdot U \qquad (3.6)$$

for the mono-phasic compounds i of table 3.1, the relation (3.4) implies :

$$b_i = d_{Li} + \frac{V_L}{q_L} \cdot r_i \qquad 1 \le i \le 3 \qquad (3.7)$$

and for the biomass, the relation (3.7) can be rewritten in a simpler way because d_L is null (no incoming biomass) :

$$b_i = \frac{V_L}{q_L} \cdot r_i \qquad 4 \le i \le 8$$

$$\Leftrightarrow x_j = \gamma \cdot v_j \qquad 1 \le j = i - 3 \le 5 \qquad (3.8)$$

where x_j is the biomass concentration and v_j the volumetric biomass growth rate;
j = 1 to 5 for the components XA, XV, EPS, PC and CH, respectively;
$\gamma = \frac{V_L}{q_L}$.

The growth rates v_j of (3.8) are linked to F_0 via R_{XA} and R_{XB} as defined in (3.5) .

So, to recapitulate, the steady state is solution of the system composed of (3.6), (3.7), (3.8) and (3.5). The total number of equations is 17 for 13 unknowns. It means that on the 5 components of the biomass, only one can be chosen, the 4 other ones being linked to this first one. The system can be solved by considering first the equations from (3.8) and (3.5) that are explicitly rewritten hereafter :

$$\left| \begin{array}{l} x_1 = \gamma \cdot v_1 \\ v_1 = \alpha_1 \cdot R_{XA(x2,x4,x5,F0)} \\ \quad \text{with } \alpha_1 = \frac{C_N}{K_N + C_N} \cdot \frac{C_S}{K_S + C_S} \cdot \frac{C_P}{K_P + C_P} \end{array} \right. \qquad (3.9)$$

$$\left| \begin{array}{l} x_2 = \gamma \cdot v_2 \\ v_2 = \alpha_2 \cdot R_{XA(x2,x4,x5,F0)} \\ \quad \text{with } \alpha_2 = \alpha_1 + \beta \cdot \frac{C_{PC}}{K_{PC} + C_{PC}} \\ \qquad \beta = \frac{K_N}{K_N + C_N} + \frac{K_S}{K_S + C_S} + \frac{K_P}{K_P + C_P} \end{array} \right. \qquad (3.10)$$

$$\left| \begin{array}{l} x_4 = \gamma \cdot v_4 \\ v_4 = \alpha_4 \cdot R_{XA(x2,x4,x5,F0)} \\ \quad \text{with } \alpha_4 = z_{PC} \cdot (\alpha_1 - \beta) \end{array} \right. \qquad (3.11)$$

$$\left|\begin{array}{l} x_5 = \gamma \cdot v_5 \\ v_5 = \alpha_5 \cdot R_{XA(x2,\,x4,\,x5,\,F0)} \\ \qquad \text{with } \alpha_5 = z_{CH} \cdot \alpha_1 \end{array}\right. \tag{3.12}$$

$$\left|\begin{array}{l} x_3 = \gamma \cdot v_3 \\ v_3 = \alpha_3 \cdot R_{XA(x2,\,x4,\,x5,\,F0)} + R_{EPS(x2,\,x4,\,x5,\,F0)} \\ \qquad \text{with } \alpha_3 = 1 - \alpha_2 \end{array}\right. \tag{3.13}$$

It can be checked that the 4 first relations (3.9) to (3.12) are equivalent only and if only the following statements are true :

$$\left|\begin{array}{l} x_2 = \dfrac{\alpha_2}{\alpha_1} \cdot x_1 \\ x_4 = \dfrac{\alpha_4}{\alpha_1} \cdot x_1 \qquad\qquad \text{if } \ \alpha_1 \neq 0 \\ x_5 = \dfrac{\alpha_5}{\alpha_1} \cdot x_1 \\ \text{or} \\ x_1 = x_2 = x_4 = x_5 = 0 \quad \text{if } \ \alpha_1 = 0 \ \text{(case of a missing substrate)} \end{array}\right. \tag{3.14}$$

So, when (3.14) is true, the steady state is solution of the system composed of (3.6), (3.7), (3.9) and (3.13). Given, x_1,the concentration of XA, the solution F_0 is determined from (3.9).

Existence conditions of the solution F_0 :

Preliminarily the expressions of R_{XA} and R_{EPS} are recalled :

$$R_{XA} = 2\,.\,\mu_M\,.\,C_{PC}\,.\,J_{XA} \qquad \text{and} \qquad R_{EPS} = 2\,.\,\mu_M^{EPS}\,.\,C_{PC}\,.\,J_{EPS}$$

$$J_{XA} = \underset{Y3}{\ } g_{XA}\,.\,dx \qquad \text{and} \qquad J_{EPS} = \underset{Y3}{\ } g_{EPS}\,.\,dx \qquad\qquad Y_3 = [0 \quad x_3'] \cup [x_3 \quad 1]$$

$$g_{XA} = \frac{I_\Sigma}{K_J + I_\Sigma}\,.\,x \qquad \text{and} \qquad g_{EPS} = \frac{I_\Sigma}{K_J^{EPS} + I_\Sigma}\,.\,x$$

$$I_\Sigma = F_0\,.\,\frac{1}{x}\,.\,\frac{2\,\mathrm{ch}[\delta\,.\,x]}{\mathrm{ch}\,\delta + \alpha\,.\,\mathrm{sh}\,\delta}$$

with :

$x = \dfrac{r}{R}$: relative abscissa

R : radius of the photobioreactor

r : abscissa (locates the local cylindrical surface at distance r from the axis of the photobioreactor)

F_0 : mean incident light flux

α and δ : function of the biomass concentrations and defined in TN 19.2
x'_3 and x_3 being the roots of $I_\Sigma = E_J$

Starting from the expression of the mean volumetric growth rate under light limitation, R_{XA}, and from (3.14), the relation (3.9) becomes :

$$\Leftrightarrow J_{XA(x2,x4,x5,F0)} = \frac{1}{2 \cdot \mu_M \cdot \gamma \cdot \alpha_4} \tag{3.15}$$

As J is monotonic ascending versus F_0, the sufficient and necessary condition for the relation (3.15) to have one and only one solution is :

$$\left| \begin{aligned} & J_m \le \frac{1}{2 \cdot \mu_M \cdot \gamma \cdot \alpha_4} \le J_M \\ & \text{with} \quad J_m = J_{XA(x2,x4,x5,F\min)} \\ & \qquad\quad J_M = J_{XA(x2,x4,x5,F\max)} \\ & \qquad\quad x_2 = C_{XV} \; ; \; x_4 = C_{PC} \; ; \; x_5 = C_{CH} \; ; \\ & \qquad\quad \gamma = \frac{V_L}{q_L} \quad (\text{residence time}) \\ & \qquad\quad \alpha_4 = z_{PC} \cdot (\alpha_1 - \beta) \\ & \qquad\quad \alpha_1 = \frac{C_N}{K_N + C_N} \cdot \frac{C_S}{K_S + C_S} \cdot \frac{C_P}{K_P + C_P} \\ & \qquad\quad \beta = \frac{K_N}{K_N + C_N} + \frac{K_S}{K_S + C_S} + \frac{K_P}{K_P + C_P} \end{aligned} \right. \tag{3.16}$$

The upper limit of J, when $F_0 \to \infty$, is ½.

This latest relation is the necessary and sufficient condition for a steady state. As it implies the volume of liquid, it should be taken into account for the sizing of the reactor.

The sufficient and necessary condition (3.16) is equivalent to :

$$\left| \begin{aligned} & \frac{1}{R_M} \le \frac{\alpha_4 \cdot V_L}{C_{PC} \cdot q_L} \le \frac{1}{R_m} \\ & \text{with} \quad R_m = R_{XA(x2,x4,x5,F\min)} \\ & \qquad\quad R_M = R_{XA(x2,x4,x5,F\max)} \end{aligned} \right. \tag{3.17}$$

3.3. Concentrations at steady state

The root F_0 is extracted from (3.9) by a dichotomy method. Then the concentrations of biomass and substrates at steady state are deduced from (3.14), (3.6) and (3.7).

It must be noted that F_0 depends on the active biomass concentration x_1, which determined the variation rates of products (biomass, O_2) and substrates. So, when a steady state is reached and as long as F_0 is unchanged, the relation (3.9) is true. So are the relations (3.10) to (3.14). Then the production rates of biomass v_j are constant. If non limiting modifications (i.e. modifications that do not change the factors α_1 to α_5) occur on the inputs U or d_{Li} (of relations (3.6) and (3.7)), only the concentrations in the reactor, X and b_i, are affected but the variation rates of products and substrates are unchanged.

3.4. Example

3.4.1. Computation of steady state

As example, the parameters of the simulated process are :

- O_2 : 8.28 10^{-3} mol/l in gas and 2.34 10^{-4} mol/l in liquid of the incoming flows;
- CO_2 (molecular form) : 6.67 10^{-4} mol/l in gas and null in liquid of the incoming flows;
- SO_4 : 2.08 10^{-3} mol/l in the incoming flows
- PO_4 : 2.11 10^{-3} mol/l in the incoming flows
- active biomass XA : 1.00 g/l in the reactor.

The condition (3.16) is fulfilled and the relation (3.9) gives the solution :

$F_0 = 87.7\ W/m^2$.

Then the relations (3.14) and (3.13) give the concentrations of the biomass at steady state :

vegetative biomass : 1.00 g/l;
exopolysaccharide : 2.11 10^{-1} g/l;
phycocyanin : 1.62 10^{-1} g/l;
chlorophyll : 1.00 10^{-2} g/l.

Then the relations (3.6) and (3.7) give the concentrations of the substrates at steady state in the liquid phase of the reactor :

O_2 : 3.03 10^{-4} mol/l
CO_2 (molecular form) : 3.17 10^{-5} mol/l
NO_3 : 7.39 10^{-2} mol/l
SO_4 : 1.70 10^{-3} mol/l
PO_4 : 1.83 10^{-3} mol/l

3.4.2. Condition of steady state not fulfilled

In the following simulation the starting point of the process is the same as the one of the previous example where the condition of steady state is fulfilled. But at time t=10h, the concentration of NO_3 in the incoming liquid is divided by 100 so that this condition is no more fulfilled. The figures 3.1 and 3.2 show the dynamic behaviour of the concentrations and production rates.

The consequence of the decreasing NO_3 step in the incoming flow is seen in the graph 31 of the figure 3.1 : NO_3 decreases because of dilution and consumption. When its concentration goes near the limiting value, the production rate of biomass decreases (at time t=250h on graph 31 in figure 3.2). So do the rates of the substrates. A new permanent equilibrium is reached at the end of the simulation. But it not the steady state corresponding to the light flux received by the process : all the light intensity is not used in the production of biomass.

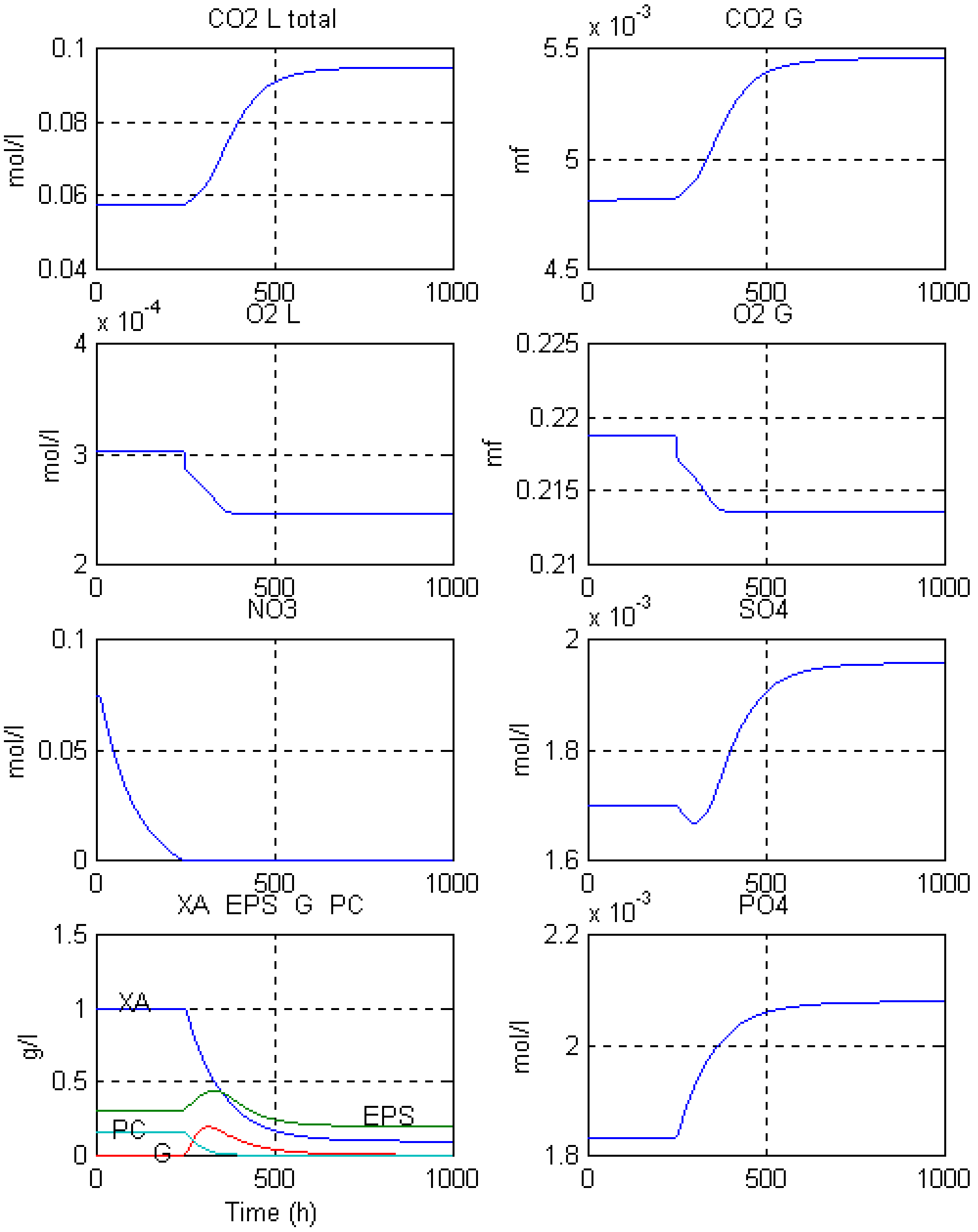

Figure 3.1 : Dynamic behaviour of the concentrations

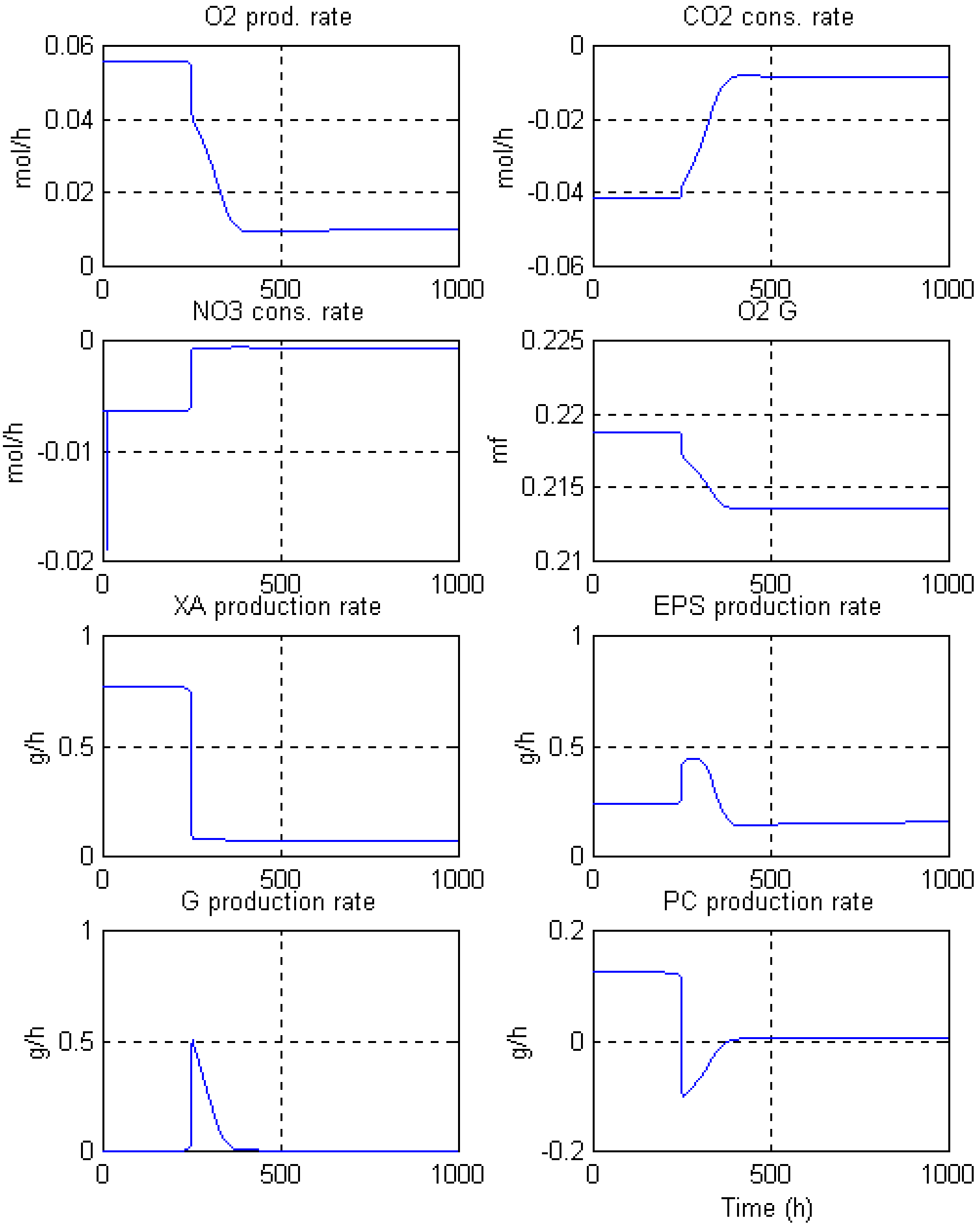

Figure 3.2 : Dynamic behaviour of the rates

4. NITRIFYING COMPARTMENT

4.1. Recall of mathematical relations of the simulator

Starting from the First Principles model by University of Clermont Ferrand (TN's 27.1 and 27.2), it has been shown in a previous study (relation (15) in TN 44.2) that the behaviour of the nitrifying compartment can be explicitly expressed under the classical form of a state system :

$$\begin{aligned} \dot{C}_x &= F \cdot C_x \\ \dot{X} &= A_e \cdot X + B_e \cdot U_0 + E \cdot J \cdot C_x \end{aligned} \qquad (4.1)$$

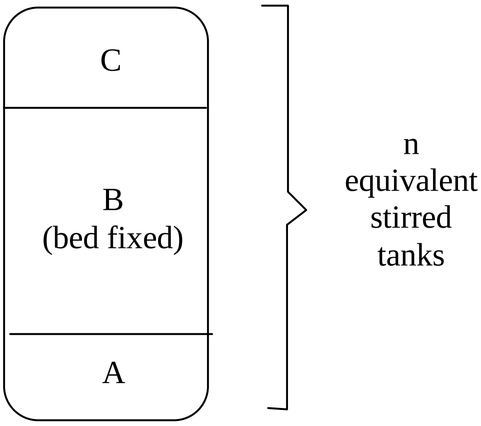

Figure 1 : State system and Scheme of the nitrifying compartment
(in the nitrifying compartment : A, B and C are the different parts of the column)

The state vector C_x represents the concentrations of the active biomass Ns and Nb in each tank of the fixed bed B.

The state vector X represents the concentrations of the substrates (O_2, CO_2 , NH_3 NO_2^- , NO_3^- , $HPO_4^=$, $SO_4^=$) in each of the n tanks of the column.

The input vector U0 represents the concentrations of the compounds in the incoming gas and liquid flows :

$$U_0 = \left| \begin{array}{l} [O_2]_G \\ [CO_2]_G \\ [NH_3]_G \\ [O_2]_L \\ [CO_2]_L \\ [NH_3]_L \\ \left[NO_2^-\right] \\ \left[NO_3^-\right] \\ \left[HPO_4^=\right] \\ \left[SO_4^=\right] \end{array} \right| \qquad (4.2)$$

The matrices A_e, B_e, E and J are given in TN 44.2 and their expressions have no interest here. The matrix F is diagonal and any term on the diagonal has the form (TN 27.1 p.40) :

$$f = \mu_M \cdot a + m \cdot Y_X \cdot (1 - a) \tag{4.3}$$

with μ_M : maximum growth rate of biomass
m : maintenance coefficient
Y_X : yield
a : limiting factor

The values of μ_M, m and Y_X depends on N_s and N_b :

	N_s	N_b
μ_M (h^{-1})	0.057	0.036
m (mol/g biomass/h)	3.38 10^{-3}	7.92 10^{-3}
Y_X(g biomass/mol substrate)	-5.0823	-1.5189

The expression of a is :

$$a = \prod_j \frac{S_j}{K_{Sj} + S_j} \tag{4.4}$$

with S_j : limiting substrate for N_s and N_b growth
K_{Sj} : half max growth rate saturation constant

4.2. Steady state conditions

The steady state is deduced from (4.1) where the derivatives are nul.

$$\left| \begin{array}{l} F = 0 \\ X = -A_e^{-1} \cdot \left(B_e \cdot U_0 + E \cdot J \cdot C_x \right) \end{array} \right. \tag{4.5}$$

The first equation and the relations (4.3) and (4.4) imply :

$$\prod_j \frac{S_j}{K_{Sj} + S_j} = \frac{m \cdot Y_X}{\mu_M - m \cdot Y_X} \tag{4.6}$$

The right hand side term of (4.6) is a constant whose value is 0.23158 and 0.25046 for N_s and N_b , respectively. That means the product of the Monod terms according to (4.4) is the same throughout the N_B tanks of the part B (fixed bed) of the column.

As the concentrations of the substrates are lower inside the column than at the its input (because they are consumed), the concentrations of the limiting substrates in the incoming flow (Gas and Liquid combined) should be such that :

$$\prod_j \frac{S_j}{K_{Sj} + S_j} \geq \frac{m \cdot Y_X}{\mu_M - m \cdot Y_X} \tag{4.7}$$

And particularly for O_2 and NH_3 that are limiting for N_s growth :

$$\boxed{\prod_j \frac{S_j}{K_{Sj} + S_j} \geq \frac{m \cdot Y_X}{\mu_M - m \cdot Y_X} = 0.23158} \tag{4.8}$$

where j = O_2 and NH_3 of the incoming flow

If this condition (4.8) is fulfilled for N_s, and if the steady state is maintained, the growth of N_b is safe too. So the condition (4.8) is also a sufficient condition for N_b.
An example where this condition is not fulfilled is given in section 4.4.2 .

4.3. Concentrations at steady state

To compute the concentrations at steady state, the following system, coming from (4.5) has to be solved :

$$\left|\begin{array}{ll} \prod_j \frac{S_j}{K_{Sj}+S_j} = \frac{m\cdot Y_X}{\mu_M - m\cdot Y_X} & (4.9)\\ X = -A_e^{-1}\cdot\left(B_e\cdot U_0 + E\cdot J\cdot C_x\right) & (4.10)\end{array}\right.$$

The unknowns are :
C_X : vector of $2*N_B$ coefficients (2 strains for each of the N_B tanks in the fixed bed);
X : vector of $(N_G+N_L)*n$ coefficients (N_G+N_L compounds in each of the $n = N_B+2$ tanks of the column).
The number of equations is :
in (4.9) : $2*N_B$ equations for each of the 2 strains in each of the N_B tanks of the fixed bed;
in (4.10): $(N_G+N_L)*n$ which is the size of X.
Then the system composed of (4.9) and (4.10) has one and only one solution vector (C_{X0}, X_0). Particularly it is shown that the determination of the biomass concentrations are not free but depend on the concentrations of substrates in the incoming gas and liquid flows. As its solution cannot be explicitly written, the system is put under the form equivalent to (4.1) where the derivatives are null (which is actually the definition of the steady state) :

$$\left|\begin{array}{l} \dot{C}_x = F\cdot C_x\\ \dot{X} = A_e\cdot X + B_e\cdot U_0 + E\cdot J\cdot C_x\\ \dot{C}_x = 0\\ \dot{X} = 0\end{array}\right. \qquad (4.11)$$

The solution of this latest system is approached by an iterative procedure where the vector :

$$Z = \begin{bmatrix} X\\ C_X\end{bmatrix} \qquad (4.12)$$

is defined.
Around a peculiar point Z_1, the system is replaced by its following local approximation :

$$\dot{Z}_1 = K_1\cdot Z_1 \qquad (4.13)$$

where K_l is the matrix of the approximate partial derivatives
The point of the next step, Z_2, is computed from the previous one, Z_1, by :

$$Z_2 = Z_1 - K_1^{-1}\cdot\dot{Z}_1 \qquad (4.14)$$

The iterative procedure is started with a point near the solution (and more particularly a point whose coefficients are the concentrations of NH_3 and NO_2 in each tank of part B that are solutions of the relation (4.9)) and is stopped when each coefficient of

$$\dot{Z}_1 = \begin{bmatrix} A_e \cdot X_1 + B_e \cdot U_0 + E \cdot J_1 \cdot C_{x1} \\ F \cdot C_{x1} \end{bmatrix}$$

is lower than 10^{-9}.

For the starting point, the concentrations of the compounds different from NH_3 and NO_2 are equal to those of the incoming flow and the concentrations of biomass are set arbitrarily to 1 g/l in each tank of the fixed bed.

4.4. Example

4.4.1. Computation of steady state

An example is given in the table 4.1 . At starting, the parameters of the simulated process are :

- N_B=5.
- O_2 : 21 % molar fraction in the incoming gas and concentration null in liquid (as if the liquid was coming from Rhodobacter);
- CO_2 : 0.55 % molar fraction in the incoming gas and 3.33 10^{-4} mol/l of the molecular form in liquid;
- NH3 : null in the incoming gas and 6.93 10^{-3} mol/l of the molecular form in liquid.
- PO_4 : 3.8 10^{-3} mol/l.
- SO_4 : 2 10^{-3} mol/l.

The solution of the problem Z_1 is obtained after 9 iterations and is such that :

- O_2 (first substrate) is minimum (1.37 10^{-4} mol/l) in tank 2 of part B;
- CO_2 (second substrate) is nearly constant (8.7 10^{-5} mol/l) along the column;
- NH_3 (third substrate) decreases along the column but its minimum is nearly reached in tank 2 of B, its consumption is negligible in the next tanks;
- so does NO_2;
- inversely NO_3 increases along the column, but its maximum is nearly already reached in tank 2 of B;
- in tank 3, the biomass is about the tenth part of its concentration in tank 1; in the next tanks, it becomes negligible.

These results tend to show that, at least at steady state, the fixed bed of the column could be approximated with N_B=2 tanks; i.e. the outputs would be nearly unchanged compared with a simulation with N_B=5 tanks and the running time would be shorter.

column	tank	compound	starting point Z_{10}	solution Z_1	derivative of solution $\dot{Z}_1$
part A	1	substrates	2.5350e-004 1.4318e-004 2.0400e-005 1.3046e-004 0	2.3420e-004 8.7824e-005 4.1264e-005 1.3183e-004 8.3837e-002	0 3.2187e-020 0 1.0588e-022 2.3636e-017

			3.8000e-003	3.6321e-003	-3.5237e-019
			2.0000e-003	1.9340e-003	5.2855e-019
part B	2	substrates	2.5362e-004	5.5424e-005	3.0407e-010
			1.4328e-004	8.6407e-005	8.2609e-013
			2.0486e-005	2.2400e-005	1.4598e-011
			1.3130e-004	1.7515e-004	-2.2248e-011
			0	8.4180e-002	-1.5634e-010
			3.8000e-003	3.6313e-003	3.4754e-013
			2.0000e-003	1.9337e-003	1.3667e-013
	3	substrates	2.5365e-004	1.3656e-004	-1.1481e-011
			1.4337e-004	8.6301e-005	-3.1709e-014
			2.0486e-005	2.0938e-005	-6.1462e-013
			1.3130e-004	1.4114e-004	4.0078e-012
			0	8.4309e-002	3.5404e-012
			3.8000e-003	3.6311e-003	-1.3337e-014
			2.0000e-003	1.9336e-003	-5.2483E-015
	4	substrates	2.5366e-004	1.8951e-004	-6.1187e-013
			1.4346e-004	8.6487e-005	-1.7122e-015
			2.0486e-005	2.0664e-005	-3.5459e-014
			1.3130e-004	1.3514e-004	3.4854e-013
			0	8.4352e-002	8.7986e-014
			3.8000e-003	3.6310e-003	-7.1982e-016
			2.0000e-003	1.9335e-003	-2.8081e-016
	5	substrates	2.5367e-004	2.1475e-004	-8.6887e-014
			1.4355e-004	8.6765e-005	-2.4442e-016
			2.0486e-005	2.0581e-005	-5.1980e-015
			1.3130e-004	1.3335e-004	5.7620e-014
			0	8.4370e-002	6.3820e-015
			3.8000e-003	3.6310e-003	-1.0512e-016
			2.0000e-003	1.9335e-003	-4.0135e-017
	6	substrates	2.5367e-004	2.2602e-004	-1.6089e-014
			1.4363e-004	8.7069e-005	-4.5375e-017
			2.0486e-005	2.0551e-005	-9.7985e-016
			1.3130e-004	1.3268e-004	1.1540e-014
			0	8.4377e-002	6.2258e-016
			3.8000e-003	3.6310e-003	-1.6416e-017
			2.0000e-003	1.9335e-003	-9.4664e-018
part C	7	substrates	2.5367e-004	2.3223e-004	1.7347e-018
			1.4370e-004	8.7383e-005	-8.1315e-020
			2.0486e-005	2.0661e-005	-9.5079e-020
			1.3130e-004	1.3268e-004	0
			0	8.4377e-002	0
			3.8000e-003	3.6310e-003	0
			2.0000e-003	1.9335e-003	0
part B	2	biomass	1.0000e+000	2.2467e+000	-9.3940e-010
			1.0000e+000	8.2253e-001	-2.3747e-010
	3	biomass	1.0000e+000	5.5199e-001	3.9704e-011
			1.0000e+000	3.0916e-001	5.3775e-012
	4	biomass	1.0000e+000	2.1630e-001	2.2964e-012
			1.0000e+000	1.0359e-001	1.3371e-013
	5	biomass	1.0000e+000	8.9991e-002	3.3697e-013
			1.0000e+000	4.1405e-002	9.7820e-015
	6	biomass	1.0000e+000	3.7867e-002	6.3555e-014
			1.0000e+000	1.7214e-002	8.2531e-016

Table 4.1 Example of starting point and solution of the system (4.11)

The substrates are successively O_2, CO_2 , NH_3 , NO_2^- , NO_3^- , $HPO_4^=$, $SO_4^=$ and expressed in mol/l. The biomass are active N_s and N_b (g/l).

4.4.2. Condition of steady state not fulfilled

In the figure 4.1, the simulation starts with incoming concentrations that fit the necessary condition (4.8) and the column behaviour is steady state (the numerical values of this steady state are given in table 4.1).

At time t=20 h a step of NH_3 concentration is realized from 6.93 10^{-3} to 2.08 10^{-5} mol/l and the condition (4.8) is no more fulfilled. Then :

- the product of the Monod terms of (4.9) fall immediately to about 0 (top graphs for N_s and N_b in the fixed bed). In the course of the simulation, the biomass is going to vanish and the concentrations of the limiting substrates are going to increase up to their concentrations in the incoming flow. So the product of the Monod terms increases. With a longer simulation, it could be seen that, for N_s, this product would reach a limit lower than 0.23158 (required by (4.8)) and, for N_b, that it would reach a maximum before falling to zero, because NO_2 is completely washed out.
- the production rates of biomass are negative : the decay is no more counterbalance.
- the concentrations of biomass (bottom graphs) are going to zero.

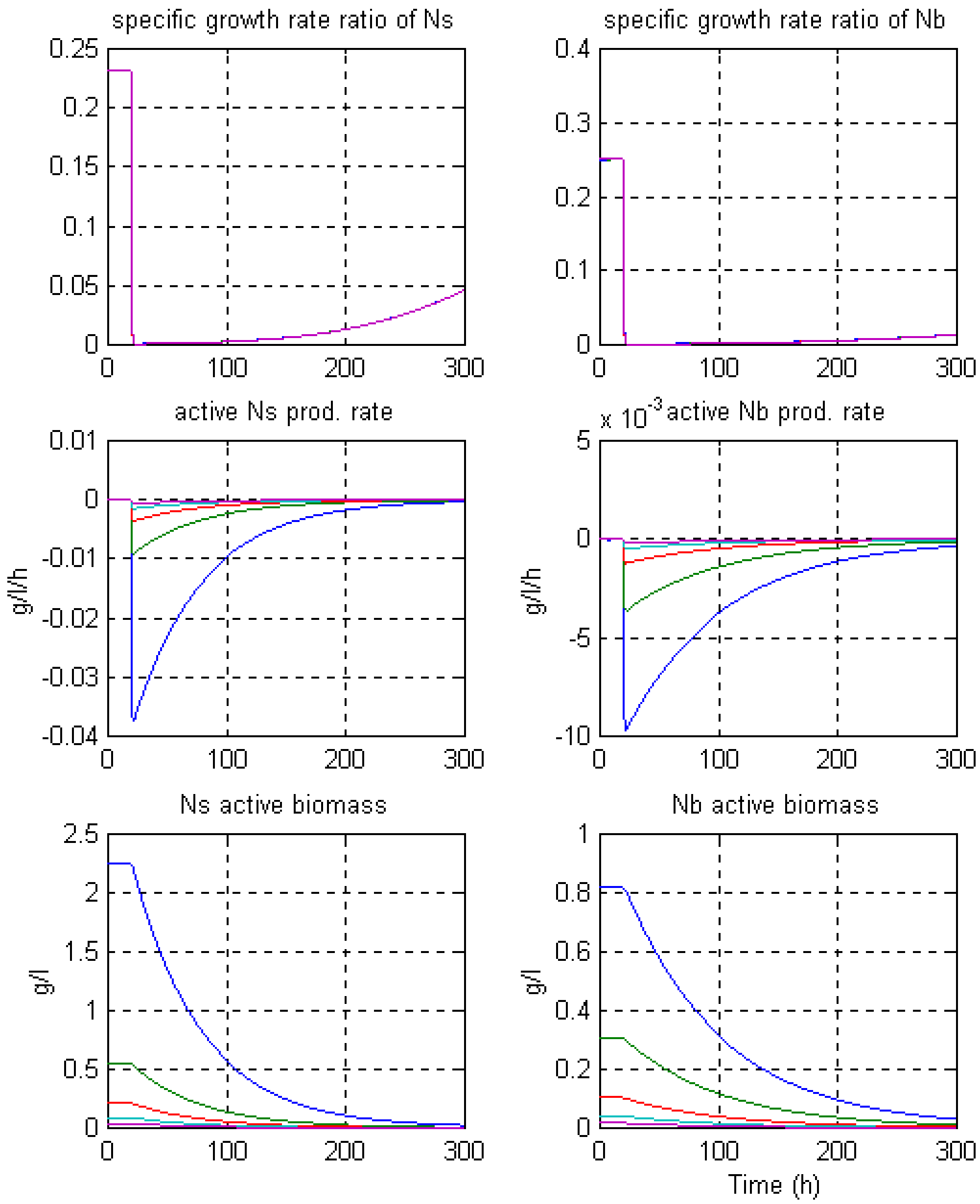

Figure 4.1 : The necessary condition (4.8) is not fulfilled
Colors blue, dark green, red, pale green, purple : for tanks 1 to 5

The column of the figure 4.1 is simulated with

- N_B=5.
- O_2 : 21 % molar fraction in the incoming gas and concentration null in liquid (as if the liquid was coming from Rhodobacter);
- CO_2 : 0.55 % molar fraction in the incoming gas and 3.33 10^{-4} mol/l in liquid.

4. CONCLUSION

The conditions of steady state are now determined for the Rhodobacter, Nitrifying and Spirulina compartments. This will allow to build the first part of the global simulator working at steady state which is more realistic than a static simulator.

The nitrifying column could be simulated with a fixed bed approximated by $N_B=2$ tanks, at least at steady state.

Moreover, for Rhodobacter and Spirulina compartments, the conditions of steady state imply the volume of liquid. They have to be studied for the sizing of these reactors.

5. REFERENCES

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