

MELISSA SIMULATION AND MODELLING

Gas streams

- Thermodynamic model of gas-liquid equilibria
- Influence of pH upon CO₂ solubility
- Gas-liquid flowsheet of MELISSA

TECHNICAL NOTE 17.1

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T.N 17.1: MELiSSA SIMULATION AND MODELLING: GAS STREAMS

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INTRODUCTION

Simulation of the entire MELiSSA loop needs a thermodynamic study of gas-liquid equilibria, in order to determine equilibria compositions of the liquid and gas phases in the different compartments of MELiSSA.

The process simulator ProSim (ProSim S.A., France) used to simulate the MELiSSA loop, can solve mass balance equations and gas-liquid equilibria. Each unit process or operation is modelled by a unit module chosen from the ProSim library unit modules or by a unit module built to model a particular operation (automatic calculation of coefficients of a stoichiometric equation for example). To determine the thermodynamic equilibria of chemical compounds, ProSim have a library of several thermodynamic models and a data file of physical and thermodynamic constants for each chemical compound (Appendix 1).

As ProSim is a chemical process simulator, modification were carried on to take into account the biological aspects of MELiSSA (characterisation of each compartment by sets of stoichiometric equations) and the calculation of gas-liquid equilibria including uncondensable gas solubilities.

The purpose of this note is to describe the thermodynamic approach chosen to simulate gas-liquid equilibria in the MELiSSA loop, with the ProSim simulator, including the effect of pH upon the carbon dioxide equilibria in the liquid phase. Moreover, a complete flow sheet of MELiSSA with gas and liquid streams has been reestablished considering the oxygenic and anoxygenic constraints of the different compartments.

1-MODEL FOR GAS-LIQUID EQUILIBRIA

For the simulations, a thermodynamic outline (Annexe 2) has to be defined. Several thermodynamic outlines are available in the ProSim library, using different combinations of thermodynamic models. In order to use a thermodynamic model, each compound has to be well defined by a data file including its physical properties (*i.e.* molar mass, volumic mass, density, standard enthalpies of formation...) and constants which are necessary to the estimation of the thermodynamic properties (vapor pressure, enthalpies...) versus temperature and pressure.

In the present simulation design of the MELiSSA loop, the sole thermodynamic process taken into account is the gas-liquid equilibria. To model it, an ideal behaviour is considered and a flash module, taken in the module library of ProSim, is used.

1.1-Thermodynamic outline

The ProSim simulator is conceived as a chemical steady state process simulator. MELiSSA is a biological system, thus several compounds like biomass, urea, palmitic acid or nitrate do not exist in the compound library of ProSim, and their data files have to be created. Some values needed in these

data files can be calculated (the molar mass as an example) or found in the literature, but many constants, are unknown.

The gas-liquid equilibria in a compartment of MELiSSA are simulated by using a flash module after a reactor module(s) (which simulate(s) the metabolism of the microorganism colonizing the compartment) (figure 1), under defined temperature and pressure conditions. In that case, transfer rate limitation between the two phases are not considered and a thermodynamic equilibria for each compound is supposed.

The distribution of a compound i between the gas and liquid phases is then given by the partition coefficient k_i :

$$k_i = \frac{y_i}{x_i}$$

x_i : molar fraction of the compound i in the liquid phase

y_i : molar fraction of the compound i in the gas phase

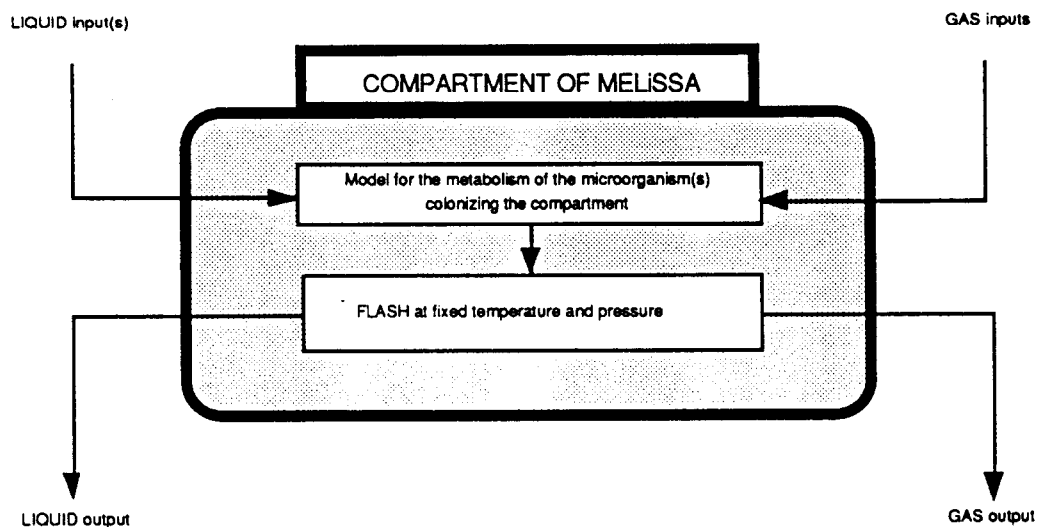


Figure 1: schematic representation of a compartment for simulations

Several models are available in the ProSim library of thermodynamic models, for the calculation of the equilibrium constant k_i , but whatever the model chosen, it needs data which are not known for all the compounds. So a model was built to calculate the partition coefficient k_i for the compounds involved in the MELiSSA loop. This model is used by the flash module for calculating the thermodynamic equilibria of the gas and liquid phases.

Two assumptions were made to establish this model for gas-liquid equilibria:

1- the sole compounds considered in the gas-liquid equilibria are dinitrogen, oxygen, carbon dioxide, hydrogen and water; all other compounds are supposed to stay in the liquid phase ($k_i=0$);

2- the gas phase is considered as ideal; the influence of dissolved compounds in the liquid phase upon the gas solubilities and upon the water activity is neglected.

1.1.1-Determination of k_i for carbon dioxide, oxygen, nitrogen, hydrogen and water.

The solubility x_i of gases in water, under a partial pressure of the gas of 1 atmosphere, can be expressed as a function of the temperature T in Kelvin (1, 2), by a fitted correlation obtained from experimental data. For nitrogen, oxygen and hydrogen, the relation takes the form:

$$\ln x_i = A_i + \frac{B_i}{T^*} + C_i \ln T^*$$

where:

$$T^* = \frac{T}{100}$$

For dissolved carbon dioxide, a similar correlation is proposed:

$$\ln x_i = A_i + \frac{B_i}{T} + C_i \ln T + D_i \cdot T$$

The equation constants, the standard deviation for $\ln x_i$ and the temperature range over which the equation applies are given in table 1 for dinitrogen, oxygen, hydrogen and carbon dioxide.

Table 1: constants for the determination of the gases solubility

Compound	A	B (K)	C	D (K ⁻¹)	Std. deviation	Temp. range (K)
Hydrogen	-48.1611	55,2845	16,8893		+/- 0.54%	273.15-353.15
Oxygen	-66.7354	87.4726	24.4726		+/- 0.36%	273.15-348.15
Dinitrogen	-67.3877	86.3213	24.7981		+/- 0.72%	273.15-348.15
Carbon dioxide	-159.854	8741.68	21.6694	-1.103 10 ⁻³	+/-0.54%	273.15-353.15

Considering the previous assumptions, the solubility of a gas i under a partial pressure of 1 atm. is characterized by the partition coefficient k_i calculated as follows:

$$k_i = \frac{1}{x_i}$$

The partial pressure of water (P_w) is satisfactorily expressed through the ANTOINE law as a function of the temperature:

$$\ln P_w = A - \frac{B}{C + T}$$

where T is in Kelvin,
 P_w is in mm Hg,
 $A=18.3036$
 $B=3816.44$ (K⁻¹)
 $C=-46.13$ (K)

Considering that the activity of water remains equal to 1, k_w , the partition coefficient of water is defined as:

$$k_w = \frac{P_w}{P_t}$$

where P_t stands for the total pressure in the gas phase (760 mmHg).

It must be kept in mind that the previous correlations enable to calculate the k_i 's as functions of temperature at the reference atmospheric pressure. At present time, it is supposed that all gas streams in MELiSSA remain at 1 atm., which prevents to recalculate the k_i 's as a function of pressure by:

$$k_i(P) = \frac{k_i(1 \text{ atm.})}{P}$$

1.1.2- k_i for the other compounds

The other compounds involved in the MELiSSA loop are supposed to remain in the liquid phase, thus their molar fraction in the gas phase y_i and their equilibrium constant k_i are equal to 0.

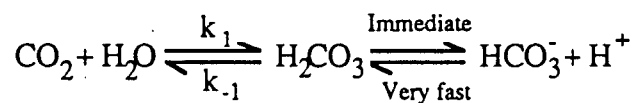
The solubility models of ammonia and volatile fatty acids are under investigation in order to be included in the gas-liquid equilibria.

Using the different relations and assumptions, a global model for the gas-liquid equilibria of the components involved in the MELiSSA loop has been built. This model of the k_i calculations (as a function of the temperature) is computed in order to be used by the flash modules in the simulations of the loop by the process simulator

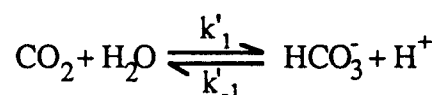
1.2-Influence of pH

When the carbon dioxide is dissolved in water, the equilibrium between the gas and the liquid phases must be considered with the chemical equilibria between the different reacting forms of CO_2 . Upon dissolution in water, CO_2 forms carbonic acid which gives two ionic compounds: bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). The various concentrations of this compounds depend on the pH value.

1.2.1-The bicarbonate form



According to the literature, the equilibria between the carbonic acid and the bicarbonate is immediate, because the speed of the reaction cannot be measured (3, 4, 5). The reaction can be rewritten as below:

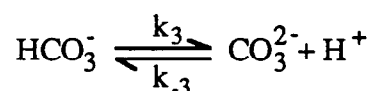


and the equilibrium constant of the reaction is

$$K_1 = \frac{k'_1}{k'_{-1}} = \frac{a_{\text{HCO}_3^-} a_{\text{H}^+}}{a_{\text{CO}_2} a_{\text{H}_2\text{O}}}$$

where a_i is the activity of the compound i .

1.2.2-The carbonate form



and the equilibrium constant of the reaction is:

$$K_3 = \frac{k_3}{k_{-3}} = \frac{a_{\text{CO}_3^{2-}} a_{\text{H}^+}}{a_{\text{HCO}_3^-}}$$

1.2.3-Determination of the equilibrium constants

Edwards et al. (6) have proposed correlations to calculate the equilibrium constants K_1 , K_3 as a function of temperature:

$$\ln K_1(T) = \frac{-12092.1}{T} - 36.7816 \ln T + 235.482$$

$$\ln K_3(T) = \frac{-12431.7}{T} - 35.4819 \ln T + 220.067$$

where T is the temperature in Kelvin. The activity a_i is in mol/kg.

The activity of a compound i can be expressed as follows:

$$a_i = \gamma_i \cdot [i]$$

γ_i is the activity coefficient of i and $[i]$ is the concentration in mol/kg of the compound i in the solution. Considering the ideality of the solution, the activity coefficient is equal to 1 :

$$a_i = [i]$$

thus, the equilibrium constants are expressed by:

$$K_1(T) = \frac{[\text{HCO}_3^-] \cdot [\text{H}^+]}{[\text{CO}_2]}$$

$$K_3(T) = \frac{[\text{CO}_3^{2-}] \cdot [\text{H}^+]}{[\text{HCO}_3^-]}$$

Calculating the gas-liquid equilibria, the concentration of carbon dioxide ($[\text{CO}_2]$) dissolved in the solution is known. Considering the definition of pH, $\text{pH} = -\log [\text{H}^+]$, or $[\text{H}^+] = 10^{-\text{pH}}$, the concentration of bicarbonate and carbonate in solution can be calculated, as shown below, as a function of $[\text{CO}_2]$, pH and temperature.

$$[\text{HCO}_3^-] = \frac{K_1(T) [\text{CO}_2]}{10^{-\text{pH}}}$$

$$[\text{CO}_3^{2-}] = \frac{K_3(T) K_1(T) [\text{CO}_2]}{10^{-2 \cdot \text{pH}}}$$

The values of $[\text{HCO}_3^-]$ and $[\text{CO}_3^{2-}]$ resulting of the equilibria of CO_2 in solution can be expressed as an equivalent of carbon dioxide dissolved, $[\text{CO}_2]^{\text{eq}}$. Summing the two preceding equations, $[\text{CO}_2]^{\text{eq}}$ can be expressed as a function of carbon dioxide dissolved in the solution, pH and temperature:

$$[\text{CO}_2]^{\text{eq}} = [\text{HCO}_3^-] + [\text{CO}_3^{2-}]$$

thus

$$[\text{CO}_2]^{\text{eq}} = [\text{CO}_2] \xi(\text{T}, \text{pH})$$

where

$$\xi(\text{T}, \text{pH}) = \frac{K_1(\text{T})}{10^{-\text{pH}}} \left(1 + \frac{K_3(\text{T})}{10^{-\text{pH}}} \right)$$

Total dissolved carbon dioxide is then given by:

$$[\text{CO}_2]^{\text{tot}} = [\text{CO}_2] + [\text{CO}_2]^{\text{eq}}$$

In the MELiSSA loop simulation it is easier to use this expression, which represents the total carbon dioxide dissolved under its three forms (CO_2 , HCO_3^- and CO_3^{2-}) in solution, because that avoids to add ionic compounds (HCO_3^- and CO_3^{2-}) in the simulation (with all modifications that implies on the compartments).

1.3-A model for gas-liquid equilibria as a function of temperature and pH

In the paragraph 1.1, a model for the k_i calculation was established. Although the value of the equilibrium constant k_i is not affected by pH, pH modifies the quantity of total carbon dioxide dissolved in the solution (under its different forms), thus pH acts indirectly upon the molar fraction x_i of the different compounds in the solution and through the equilibrium constant, upon the molar fraction y_i in the gas phase.

Consequently, the effect of the pH upon the solubility of carbon dioxide has to be considered and treated at the same step of the gas-liquid equilibria, and solved by using an iterative method to determine the compounds dissolved fraction in the liquid phase.

For simplicity, a new model for the carbon dioxide equilibrium between the two phases is built, considering a pseudo-solubility for the carbon dioxide compound. As mentioned in paragraph 1.2.3, if bicarbonate and carbonate are considered as an equivalent of carbon dioxide dissolved in solution, a new gas-liquid partition coefficient can be written:

$$k_{\text{CO}_2}^{\text{ap}} = \frac{y_{\text{CO}_2}}{x_{\text{CO}_2}^{\text{ap}}}$$

It is considered here that $x_{\text{CO}_2}^{\text{ap}}$ is the apparent molar fraction in the liquid phase which takes into account both the values of CO_2 and CO_2^{eq} and that the real equilibrium constant (as defined in paragraph 1.1.1) is:

$$k_{\text{CO}_2}(\text{T}) = \frac{y_{\text{CO}_2}}{x_{\text{CO}_2}}$$

A relation can be established between this two partition coefficients:

$$k_{\text{CO}_2}^{\text{ap}}(\text{T}, \text{pH}) = \frac{(k_{\text{CO}_2}(\text{T}) + y_{\text{CO}_2} \xi(\text{T}, \text{pH}))}{1 + \xi(\text{T}, \text{pH})}$$

Instead of $k_{\text{CO}_2}(\text{T})$, $k_{\text{CO}_2}^{\text{ap}}(\text{T}, \text{pH})$ is considered as the carbon dioxide equilibrium constant in the model for the gas-liquid equilibria. The concentration of CO_2 obtained in the liquid phase by using this model is in fact the value of the total carbon dioxide dissolved (CO_2 , HCO_3^- and CO_3^{2-}).

2-FLOWSHEET OF THE MELISSA LOOP

Considering the oxygenic and anoxygenic constraints in the different compartments of the MELiSSA loop, a flowsheet including liquid and gas streams has been conceived. Each unit operation or unit process is modelled by a unit module chosen from the ProSim library of unit modules, or by a unit module built to model a particular operation.

Each module is treated separately with its own inputs and outputs (the outlet vector being determined from the inlet one). The entire system is described using unit operation modules *i.e.* reactor modules, flash modules, separator modules, stream divider or mixer modules. A compartment for example is described using two types of unit operation modules (figure 1), one for the operations in charge of the compartment and one for the gas-liquid equilibria (flash module). The behaviour of the five compartments of MELiSSA, considered as perfectly mixed reactors, is described by one or more stoichiometric equations which are reported in appendix 3.

For simulation purposes, MELiSSA is regarded as a semi-closed system, as shown in figure 2. There are two main reasons for this:

- 1- water management is not considered (waste water is not recycled);
- 2- the biomass cannot supply all the diet.

Hence, because of the steady state conditions, inputs and outputs have to be considered in the MELiSSA loop.

2.1-Solid (BIOMASS) management

The five compartments colonized by microorganisms are followed by solid-liquid separators that separate fresh biomass (30% dry matter, 70% water) from the liquid effluent. *Rhodobacter* are led to a divider that recycles a percentage Y of the incident mass flow rate towards the diet control module. Likewise, a percentage Z of the *Spirulina* produced by the photosynthetic compartment is led to the diet control module. Small amounts of nitrifying bacteria are assumed to be wasted.

The diet composition constraints (table 2) have been included in the simulation design. To balance the loss of nitrogen by the waste biomass, an ammonia input is necessary for overall nitrogen balance over the loop.

Table 2: Well-balanced diet values. Nucleic acids in biomass are not considered here.

	% of energy demand	% mass of diet	Mass (g/d.p) for 3000 kcal/d.p
Protein	13.5	17.3	101
Lipids	40.1	23	133.7
Carbohydrate	46.4	59.7	348.1

2.2-Liquid phase management

The liquid streams between the compartments contain mostly water and dissolved products and substrates.

Importantly, the microorganisms and their key substrates were chosen to obtain no dissolved species in the liquid effluent of the photosynthetic compartment except the dissolved gases CO₂, O₂ and N₂. Water leaving the *Spirulina* compartment is considered as waste and is not recycled, since at

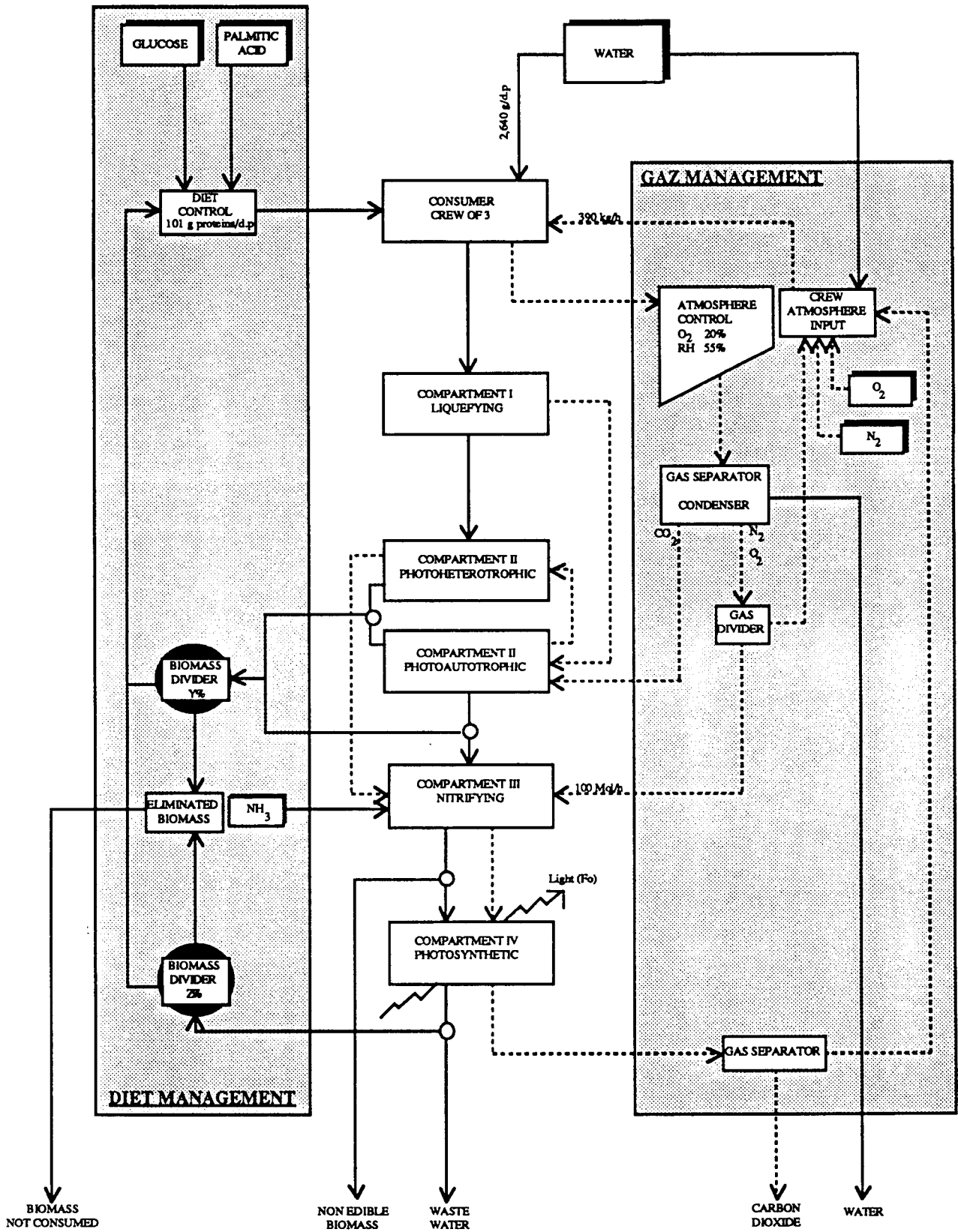


Figure 2: Simplified representation of the simulation design of the MELISSA loop

○ : biomass extraction ; □ external input
 ----- Gas ——— Liquid / solid

the present stage of simulation of MELiSSA, the description of the liquid phase does not allow for the presence of minor and ionic components such as minerals, and phosphorus or sulphur compounds.

The dissolved gas concentrations in the liquid streams were calculated by a flash module assuming the model for gas-liquid equilibria established in the first part of this note, as function of temperature and pH, and assuming a total pressure of 1 atmosphere.

2.3-Gas management

The management of the gas fluxes is more complex than it appeared in the previous preliminary studies. The main difficulties come from the needs of the consumer compartment. For the consumers, several atmosphere parameters have to be considered: ventilation (0.08 - 0.2 m/s), relative humidity (R.H. 25% -70%), gas composition (O_2 20%, CO_2 < 0.5%) and temperature (18°C - 27°C). No values have yet been defined for the air flow in MELiSSA, though the literature gives some values:

- Spacelab (single rack) 349 kg/h (7)
- Spacelab (double rack) 682 kg/h (7)
- Space Station Logistic Module 390 kg/h (8)

The last value was chosen for the total air flow rate inside the consumer compartment. Also, the oxygen composition was set at 20% (oxygen pressure 0.2 atm) and the relative humidity (R.H.) to 55% (water pressure 0.013 atm at 20°C). For these conditions, the results of the simulations indicate that the CO_2 composition remains below the tolerance limits and is typically lower than 0.02% (200 ppm).

The consumer compartment cannot be treated by the schematic representation given in figure 1 and valid for the four other compartment of the MELiSSA loop. Because of the high value of the gas flux, a flash module, which assumes equilibria between the gas and liquid phases, cannot be considered to simulate the gas-liquid equilibria in the consumer compartment. As there is not an actual liquid phase inside this compartment, the dissolved gas composition of the liquid phase cannot be calculated. But the quantity of water vaporized can be estimated, considering that the daily water produced by perspiration and respiration represents an average of 1500 g of water/day (9), what corresponds to 65% of the water vaporized by human activity (7).

Thus, the gas flux coming from the consumer compartment needs to be treated separately as an independant stream. Three main steps are considered in the present simulation design.

a- Gas separation. The carbon dioxide is separated from the other gas compounds in order to establish a CO_2 gas flux for the anoxygenic compartment II. In the present simulation design, the totality of the carbon dioxide is supposed to be separated from the consumer gas flux; considering the carbon dioxide production by the liquefying compartment and the low needs of carbon dioxide in the compartment II, a partial separation of the carbon dioxide from the consumer compartment gas output will be sufficient.

b- Condensation. The vaporized water is condensed, but in the present simulations, it is not recycled.

c- Gas flux division. In order to provide oxygen to the oxygenic compartments III and IV, a dry gas stream of oxygen and dinitrogen (20% O_2 and 80% N_2) is obtained by separating CO_2 from the exit gas stream of the consumer compartment (step a). The value of this gas flow rate has been fixed on a value which exceeds the requirements of the compartments III and IV, *i.e.* on 100 mol/h.

After the last compartment (*Spirulina*), the gas output is sent to the gas input of consumers, but in order to provide a gas flux free of carbon dioxide, a gas separator module is added in the loop design to put the CO₂ not recovered out of the MELiSSA loop.

Special attention must be drawn to gas streams of the compartments II. The liquid and the gas fluxes are in counter-current, in order to provide a maximal assimilation of the organic compounds (supposed to be in the liquid input stream) by the photoheterotrophs and of the hydrogen (supposed to be in the gas input stream) by the photoautotrophs.

2.4-Degrees of freedom and behaviour of the ecosystem.

As presented in technical notes 14.1 and 14.2, two degrees of freedom for ten components in inlet or outlet streams were found. With these two variables, the ecosystem displayed two extreme types of behaviour:

- near complete recycling of nitrogen and low atmosphere regeneration;
- near complete regeneration of the atmosphere and low recycling of nitrogen.

In this new version of the MELiSSA design, seven components are involved in the different inlet streams (glucose, palmitic acid, drinking water, vaporized water, oxygen, dinitrogen and ammonia), and nine components in the outlet streams (three types of biomass, oxygen, dinitrogen, hydrogen, carbon dioxide, waste water, vaporized water). Seven constraints resulted from set values for the composition of the atmosphere in the consumer compartment (air flow, R.H., partial oxygen pressure) and for the composition of the diet (drinking water, proteins, lipids and carbohydrates). Considering dinitrogen as an inert gas, the gas-liquid equilibrium between vaporized and liquid water and the four balance equations for the elements C.H.O.N., the number of degrees of freedom to be considered is three.

Two have already been used (TN 14.1 and 14.2) with a slightly different definition:

- percentage Y of *Rhodobacter* biomass produced that is consumed by the crew;
- percentage Z of *Spirulina* biomass used in the diet (figure 2).

Y and Z have a direct influence on the diet composition and an indirect one on the behaviour of the compartments that produce biomass.

The third degree of freedom is the light incident flux F_0 , which acts directly on the working of the photosynthetic compartment.

In addition of these degrees of freedom, several other parameters have been fixed (diet constraints, value of the fractional conversions of the key substrates, stoichiometric equations, temperature and pH conditions in a compartment). This can affect the simulation results without any change of the design of the MELiSSA loop. Thus, all conditions of a simulation have to be described before presenting results.

3-RESULTS OF A SIMULATION

3.1-Parameters of the simulation

The purpose is to present the conditions in which the simulation is performed (working conditions of the compartments, values of the constraints and of the degrees of freedom for the simulation). The detailed assumptions (metabolic pathways) leading to the stoichiometric description of the compartments will be considered in further technical notes.

Description of the compartments

The stoichiometric equations which describe the working of the different compartments are reported in the appendix 3.

- Consumer -

Pressure = 1 atm.

Temperature = 293 K

Faeces composition: $\text{CH}_{1.649}\text{O}_{0.15}\text{N}_{0.1055}$

Oxygen need considered:

$$\text{O}_2 = 0.2975 \text{ ED} - 0.2$$

where ED is the Energy Demand in kcal/p.d.,

thus, for ED = 3000 kcal/p.d.

$$\text{O}_2 = 892.3 \text{ mol/p.d.}$$

It is supposed that 1500 g of water/p.d. is vaporized by perspiration and respiration.

The key substrate is the food (glucose, palmitic acid and biomass), with a fractional conversion equal to 1.

- Compartment I (Liquefying) -

Pressure = 1 atm.

Temperature = 330 K

pH = 5

The key substrate for the first equation is the faeces, and for the second the urea, both with a fractional conversion equal to 1.

- Compartment II (Phototrophs) -

Pressure = 1 atm.

Temperature = 303 K

pH = 7

The key substrate for the photoautotrophs is hydrogen with a fractional conversion equal to 1. The key substrates for the photoheterotrophs are volatile fatty acids (respectively acetate and butyrate) with fractional conversions equal to 1.

- Compartment III (Nitrifying) -

Pressure = 1 atm.

Temperature = 303 K

pH = 8

The key substrate is ammonia with a fractional conversion equal to 1.

-Compartment IV (*Spirulina*)

Pressure = 1 atm.

Temperature = 309 K

pH = 9.5

Light radiant incident flux (F_0) = 150 W/m²

The key substrate is nitrate with a fractional conversion equal to 1.

- Gas separator and condenser -

The operations on the gas fluxes are supposed to be perfect (*i.e.* complete separation of the different compounds)

Constraints and degrees of freedom

The values for the three degrees of freedom are fixed on the following values:

100% for Y (the totality of the biomass produced by the *Rhodobacter* is consumed);

50% for Z (only the half of the biomass produced by the *Spirulina* is consumed);

150 W/m² for F_0 , what is a medium value for the light incident flux.

The constraints applied on the flowsheet of the MELiSSA loop are the following:

-the diet constraints are those determined in the last column of table 2 for an energy demand by the consumers of 3000 kcal/p.d. The protein needs are supposed to be provided only by the consumption of biomass;

-the gas composition in the consumer compartment is maintained to 20% of oxygen, less than 0.5% of carbon dioxide and a relative humidity of 55%. The gas input in the compartment is fixed on 390 kg/h;

-the dinitrogen/oxygen flux to the oxygenic compartments (III and IV) is fixed on 100 mol/h.

3.2-Results

3.2.1-Inputs and recycling performances

The behaviour of the ecosystem is determined by its recycling performances. The recycling percentages of nitrogen (RN), carbon (RC), oxygen (RO₂) and carbon dioxide (RCO₂) are considered. In the present conditions of simulation, the recycling percentages are the following:

$$\begin{aligned} RN &= 60.28\% \\ RC &= 34.15\% \\ RO_2 &= 50.40\% \\ RCO_2 &= 60.65\% \end{aligned}$$

The ecosystem has an intermediate behaviour (between a maximal N recycling and a maximal atmosphere regeneration): it recovers only 50% of the oxygen and recycles 60% of the element N. The carbon recycling percentage is the lowest and simulations performed in other conditions have shown that it can not increase over 40%.

The different inputs of the system are presented in table 3. It is important to note that water is not recycled, which explains the high values of the water inputs.

Table 3: Inputs in the MELiSSA loop. Palm. acid: palmitic acid. Water (d): water for drinking (consumers). Water (a): water for atmosphere humidity. Total (a) with water, (b) without water.

	oxygen	dinitrogen	ammonia	glucose	palm. acid	water (d)	water (a)	total
mass	60.499	2.7 10 ⁻³	1.835	34.019	14.934	330	3244.55	3685.84 ^a
g/3p.h.								111.29 ^b
moles	1.891	9.7 10 ⁻⁴	0.108	0.189	5.82 10 ⁻²	18.318	180.102	200.667 ^a
mol/3p.h.								2.247 ^b

3.2.2-Gas and liquid streams at the output of the compartments

The results are presented as molar fraction in the gas or liquid output streams for the different compounds. For each compartment the total mass flux and molar flux are indicated.

Table 4: Liquefying compartment

	oxygen	carbon dioxide	dinitrogen	hydrogen	water	acetate	butyrate	ammonia
Liquid	0	$9.9 \cdot 10^{-4}$	0	$6.99 \cdot 10^{-5}$	0.981	$5.2 \cdot 10^{-3}$	$1.3 \cdot 10^{-3}$	$1.27 \cdot 10^{-2}$
Gas	0	0.299	0	0.535	0.166	0	0	0

Liquid stream - total mass flux: 234.88 g/3p.h.
 - total molar flux: 12.825 mol/3p.h.
 Gas stream - total mass flux: 55.039 g/3p.h.
 - total molar flux: 3.412 mol/3p.h.

Table 5: Photoautotrophs compartment

	oxygen	carbon dioxide	dinitrogen	hydrogen	water	ammonia	biomass (dry)
Liquid	0	$2.91 \cdot 10^{-3}$	0	0	0.980	$7.88 \cdot 10^{-3}$	$8.98 \cdot 10^{-3}$
Gas	0	0.96	0	0	0.04	0	0

Liquid stream - total mass flux: 227.944 g/3p.h.
 - total molar flux: 12.5733 mol/3p.h.
 Gas stream - total mass flux: 126.364 g/3p.h.
 - total molar flux: 2.9416 mol/3p.h.

Table 6: photoheterotrophs compartment

	oxygen	carbon dioxide	dinitrogen	hydrogen	water	ammonia	biomass (dry)
Liquid	0	$2.91 \cdot 10^{-3}$	0	$4 \cdot 10^{-10}$	0.972	$9.35 \cdot 10^{-3}$	$1.58 \cdot 10^{-2}$
Gas	0	0.960	0	$3.1 \cdot 10^{-5}$	0.04	0	0

Liquid stream - total mass flux: 236.789 g/3p.h.
 - total molar flux: 13.037 mol/3p.h.
 Gas stream - total mass flux: 124.454 g/3p.h.
 - total molar flux: 2.897 mol/3p.h.

Table 7: nitrifying compartment

	oxygen	carbon dioxide	dinitrogen	hydrogen	water	nitrate	biomass (dry)
Liquid	$4 \cdot 10^{-5}$	$6.64 \cdot 10^{-4}$	$8.3 \cdot 10^{-6}$	$1 \cdot 10^{-11}$	0.970	$2.38 \cdot 10^{-2}$	$5.18 \cdot 10^{-3}$
Gas	0.184	0.026	0.750	$8.4 \cdot 10^{-7}$	0.04	0	0

Liquid stream - total mass flux: 159.266 g/3p.h.
 - total molar flux: 8.325 mol/3p.h.
 Gas stream - total mass flux: 3068.64 g/3p.h.
 - total molar flux: 106.692 mol/3p.h.

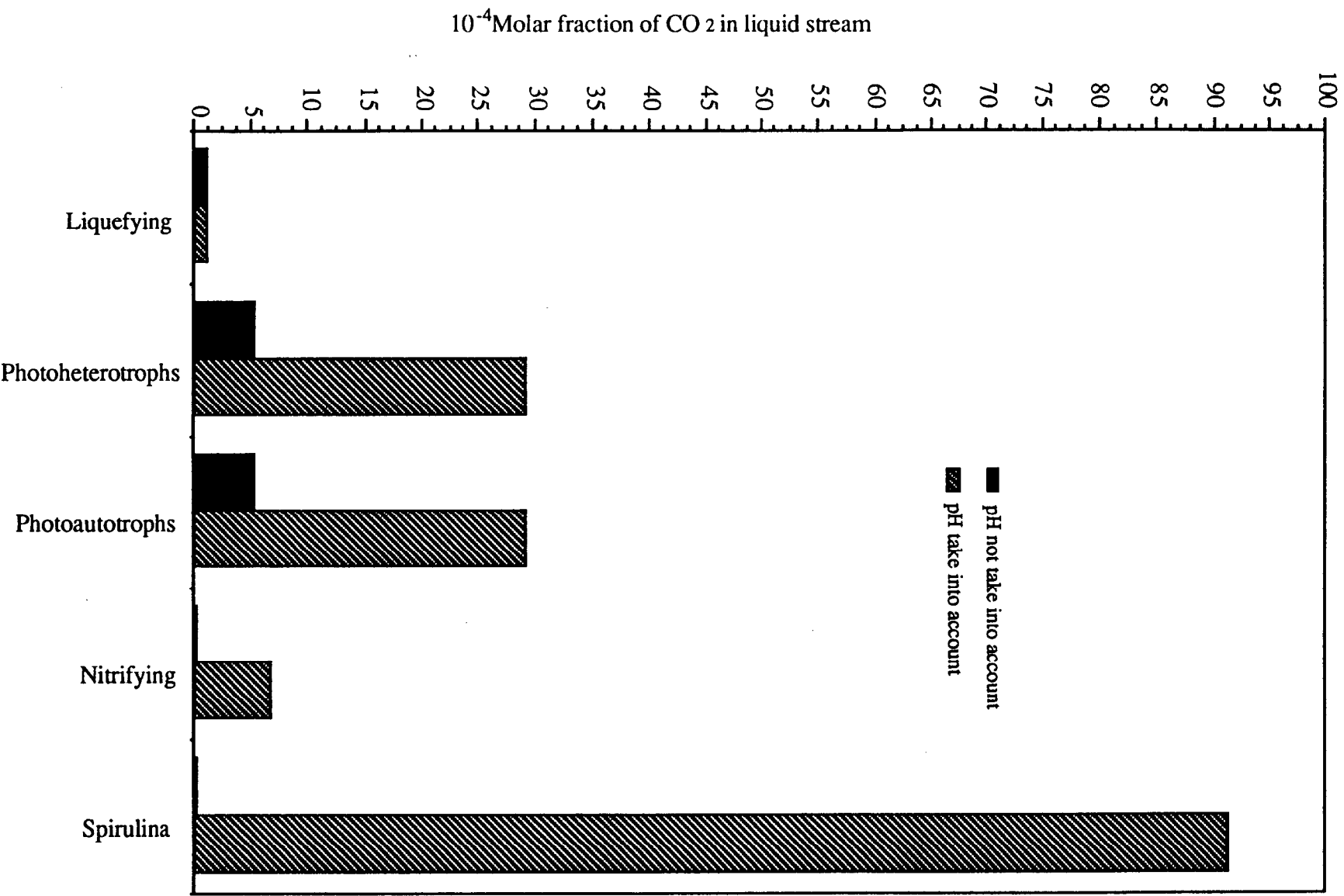


Figure 3: CO₂ dissolved in the liquid phase at the output of each compartment with and without the effect of pH

Table 8: *Spirulina* compartment

	oxygen	carbon dioxide	dinitrogen	hydrogen	water	nitrate	biomass (dry)
Liquid	5.59 10 ⁻⁶	1.26 10 ⁻²	1.07 10 ⁻⁵	1 10 ⁻¹¹	0.822	0	0.165
Gas	0.203	0.011	0.752	8.4 10 ⁻⁷	0.035	0	0

Liquid stream - total mass flux: 175.779 g/3p.h.
 - total molar flux: 9.086 mol/3p.h.
 Gas stream - total mass flux: 3049.32 g/3p.h.
 - total molar flux: 106.438 mol/3p.h.

In the output streams of the photoheterotrophs compartment (table 6), H₂ is present. The dissolved hydrogen in the output liquid stream of the liquefying compartment is revaporized in the photoheterotrophs compartment but if the liquid output of this compartment is led to the photoautotrophs, the gas stream is led to the nitrifying compartment, thus the most part of this hydrogen is not recovered. To correct this problem the loop design has to be modified.

At present time, the simulations indicate that the molar fractions of water in the different compartments lies in the range 0.970-0.981, except for the *Spirulina* compartment where the molar fraction is 0.822. It must be considered that these values are somewhat unrealistic and that it would be necessary to supply each compartment with additional water inputs. This point might be cleared in further studies considering more precisely the water management in the MELiSSA loop.

It is important to note here that the different values of gas streams will depend on the dimensions and on the characteristics of the different reactors. In the case of the nitrifying compartment for example, the maximal conversion rate of ammonia in nitrate in a fixed bed will be obtained for an air flow of 10 VVM (10). These points have not been taken into account at the moment because it implies kinetic description of the sets of stoichiometric equations and gas-liquid transfer characterization of the compartment.

3.2.3-Effects of pH on the liquid dissolved gas composition

The main effect of pH acts upon the carbon dioxide solubility. Considering the ionic forms bicarbonate and carbonate as carbon dioxide equivalent, the molar fraction of carbon dioxide in liquid phase will change with pH. The molar fractions of the other dissolved gases (O₂, N₂, H₂) are interrelated through the gas-liquid partition coefficients, but they are practically unaffected by the pH (in the *Spirulina* compartment where there is the highest value of the pH, the molar fraction of O₂ is 4.070 10⁻⁶ considering the pH and 4.064 10⁻⁶ without the influence of the pH).

The values of the molar fraction of CO₂ (flash without influence of pH) and CO₂^{eq} (flash with the influence of pH) are reported in figure 3. The difference between the two values in one compartment is due to the ionic forms of CO₂ in solution. For the *Spirulina* compartment (pH=9.5) the ratio CO₂/CO₂^{eq} is equal to 1820, which lies in the range of the expected values.

CONCLUSION

A gas-liquid equilibria model has been established in order to build a flowsheet of the MELiSSA loop including separate gas and liquid streams. This model, based upon the calculation of partition coefficients of five compounds (water, O₂, N₂, H₂, CO₂) with the hypothesis of ideal phases and of

a total pressure of 1 atm. in the gas stream, takes into account the temperature and pH conditions in the compartments.

A new flowsheet including this model and new constraints for the gas streams composition and fluxes has been established.

The two types of the ecosystem behaviour, observed in the previous studies (maximal N recycling and low atmosphere regeneration; maximal atmosphere regeneration and low N recycling) are not affected by this new flowsheet.

The results obtained for an intermediate behaviour of the ecosystem (60% N recycled, 60% CO₂ assimilated and 50% O₂ recovered), show that:

- instead H₂ is a key substrate and that its fractional conversion is equal to 1 (in order to eliminate it in the compartment II), the flowsheet, designed to take into account the heterotrophic and the autotrophic aspects of the compartment, lead to allow an output of H₂. Thus, the key substrate H₂ is present in the output of the ecosystem. Such a problem would probably increase, for H₂ and the other compounds, if a non ideal working of the compartments is considered;

-the main default of the actual flowsheet is the lack of a water management system, which leads to unrealistic values for the concentrations in solution, especially in the last compartment.

A complete water management had thus to be considered before the studies of the non ideal working of the compartment and the introduction of the kinetic aspects in the simulation of the MELiSSA loop.

Volatile fatty acids and ammonia are not considered in the actual gas-liquid equilibria model as compounds of a gas phase. Further studies had to be conducted in order to determine the gas-liquid equilibrium of these compounds, especially for ammonia, the dissolved fraction of which in solution is affected by pH.

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APPENDICES

APPENDIX I

Description of ProSim compound data file

1-Num	Identification number
2-M	Molar mass
3- T_f	Fusion point
4- T_{eb}	Boiling point
5- T_c	Critical temperature
6- P_c	Critical pressure
7- V_c	Critical volume
8- Z_c	Critical compressibility factor
9- ω	Acentric factor of PITZER
10- ρ_L	Volumic liquid mass at T_p
11- T_p	Reference temperature for ρ_L
12- μ_d	Dipole moment
13-A	Constants for the ideal gas heat capacity (T in Kelvin) $C_p^* = A + BT + CT^2 + DT^3 + E/T + F \ln T$
14-B	
15-C	
16-D	
17-E	
18-F	
19-VISB	Constants for liquid viscosity
20-VISTO	$\log(\mu) = VISB[(1/T) - (1/VISTO)]$
21- ΔH_f^0	Standard enthalpy of formation (298 K, 1 atm)
22- ΔG_f^0	Gibbs energy of formation (298 K, 1 atm)
23- ΔH_v	Heat of vaporisation at T_b
24-A	Coefficients of the ANTOINE law $\ln P^0 = A - B/(T + C)$ T in Kelvin Temperature range $T_{min} - T_{max}$
25-B	
26-C	
27- T_{max}	
28- T_{min}	
29-A	Coefficients of the HARLACHER-BRAUN equation $\ln P^0 = A + B/T + C \ln T + DP^0/T^2$ T in Kelvin
30-B	
31-C	
32-D	
33- r_i	UNIQUAC and MQUAC parameters
34- q_i	Area and Volume of Van der Waals
35- q'_i	Modified area of Van der Waals
36- δ_i	Solubility
37- ω'_i	modified acentric factor of PITZER
38- V_iL	Molar pure liquid volume
39-	not used
40-	not used

APPENDIX II

Thermodynamic outline to define for a simulation

Thermodynamic calculations	Model available in the ProSim library	Model chosen for our simulations
Heat of vaporisation	1-Clausius Clapeyron 2-Watson	Clausius Clapeyron (not used)
Equation of state	1-ideal gas 2-Soave-Redlich-Kwong 3-Peng-Robinson 4-Lee-Kesler-Plocker 5-Redlich-Kwong	ideal gas
Vapor pressure	1-Antoine 2-Harlacher-Braun 4-Lee-Kesler 3-Riedel-Plank-Miller	Antoine (not used)
Activity coefficient	1-ideal 2-Margules 3-Scatchard-Hildebrand 4-Wilson 5-NRTL 6-UNIQUAC 7-MQUAC 9-NRT6	Ideal
Thermodynamic model	1-Treatment by state equation 2-Classical treatment	defined by the user
Volumic liquid mass	1-Rackell 2-Gunn-Yamada 3-Soave-Redlich-Kwong 4-Peng-Robinson 5-Lee-Kesler-Plocker 6-Redlich-Kwong	
Fugacity of pure liquide at standard state	1- $f_i^{0L} = \phi_L^0 P_L^0$ 2- Chao-Seader 3- $f_i^{0L} = P_i^0$ 4- Chao-Seader modified Grayson-Streed	$f_i^{0L} = P_i^0$ (not used)
Thermo-user	Gas-liquid partition coefficients and (or) enthalpies calculated by a user model	See chapter 1
Transfer properties	1-Classical methods 2-Ely-Hanley model	Classical methods (not used)

APPENDIX III

Stoichiometric equations describing the compartments of the MELiSSA loop.

<p><u>Consumer compartment</u></p> <p>Diet control</p> <p>Consumption of food</p>	$\text{glucose} + \text{palmitic acid} + \text{biomass} \Rightarrow [\text{C.H.O.N.}]_{\text{FOOD}}$ $\underline{[\text{C.H.O.N.}]_{\text{FOOD}}} + \alpha \text{O}_2$ \Downarrow $\beta [\text{C.H.O.N.}]_{\text{FAECES}} + \delta \text{CO}_2 + \epsilon \text{CH}_4\text{ON}_2 + \zeta \text{H}_2\text{O}$ <p>$\alpha = 0.2975 \text{ ED} - 0.2$ Energy Demand (kcal/d.p.)</p> $[\text{C.H.O.N.}]_{\text{FAECES}} = \text{CH}_{1.649}\text{O}_{0.15}\text{N}_{0.1055}$
<p><u>Liquefying compartment</u></p> <p>Faeces fermentation (mainly proteins, carbohydrates and microorganisms)</p> <p>Urea degradation</p>	$\underline{[\text{C.H.O.N.}]_{\text{FAECES}}} + 0.975 \text{H}_2\text{O}$ \Downarrow $0.25 \text{CO}_2 + 0.89125 \text{H}_2 + 0.25 \text{C}_2\text{H}_4\text{O}_2 + 0.0625 \text{C}_4\text{H}_8\text{O}_2 + 0.1055 \text{NH}_3$ $\underline{\underline{\text{CH}_4\text{ON}_2}} + \text{H}_2\text{O} \Rightarrow \text{CO}_2 + 2 \text{NH}_3$
<p><u>Phototroph compartment</u></p> <p>Biosynthesis of <i>Rh. capsulatus</i> (photoautotroph)</p> <p>Biosynthesis of <i>Rs. rubrum</i> from acetate</p> <p>Biosynthesis of <i>Rs. rubrum</i> from butyrate</p>	$\text{CO}_2 + 0.2022 \text{NH}_3 + 2.1042 \underline{\underline{\text{H}_2}}$ \Downarrow $\text{CH}_{1.6511}\text{O}_{0.4156}\text{N}_{0.2022} + 1.5826 \text{H}_2\text{O}$ $0.5266 \underline{\underline{\text{C}_2\text{H}_4\text{O}_2}} + 0.2022 \text{NH}_3$ \Downarrow $\text{CH}_{1.6511}\text{O}_{0.4156}\text{N}_{0.2022} + 0.5301 \text{H}_2\text{O} + 0.0533 \text{CO}_2$ $0.3063 \text{C}_2\text{H}_4\text{O}_2 + 0.0881 \underline{\underline{\text{C}_4\text{H}_8\text{O}_2}} + 0.2022 \text{NH}_3 + 0.0342 \text{CO}_2$ \Downarrow $\text{CH}_{1.6511}\text{O}_{0.4156}\text{N}_{0.2022} + 0.4418 \text{H}_2\text{O}$
<p><u>Nitrifying compartment</u></p>	$\text{CO}_2 + 4.8 \underline{\underline{\text{NH}_3}} + 8.1435 \text{O}_2$ \Downarrow $\text{CH}_{1.6511}\text{O}_{0.4156}\text{N}_{0.2022} + 4.0763 \text{H}_2\text{O} + 4.5978 \text{HNO}_3$
<p><u>Spirulina compartment</u></p> <p>Proteins biosynthesis (P)</p> <p>Carbohydrates biosynthesis (C)</p> <p>Lipids biosynthesis (L)</p> <p>Exopolysaccharides biosynthesis (E)</p> <p>Nucleic acids biosynthesis (N)</p> <p>Biomass composition</p>	$\text{CO}_2 + 0.6383 \text{H}_2\text{O} + 0.2496 \underline{\underline{\text{HNO}_3}} \Rightarrow \text{CH}_{1.526}\text{O}_{0.327}\text{N}_{0.2496} + 1.5302 \text{O}_2$ $\text{CO}_2 + 0.835 \text{H}_2\text{O} \Rightarrow \text{CH}_{1.670}\text{O}_{0.711} + 1.06225 \text{O}_2$ $\text{CO}_2 + 0.8542 \text{H}_2\text{O} \Rightarrow \text{CH}_{1.714}\text{O}_{0.204} + 1.3251 \text{O}_2$ $\text{CO}_2 + 0.825 \text{H}_2\text{O} \Rightarrow \text{CH}_{1.65}\text{O}_{0.950} + 0.9375 \text{O}_2$ $\text{CO}_2 + 0.44 \text{H}_2\text{O} + 0.393 \underline{\underline{\text{HNO}_3}} \Rightarrow \text{CH}_{1.273}\text{O}_{0.710}\text{N}_{0.393} + 1.4545 \text{O}_2$ $\text{Biomass} = \% \text{P} + \% \text{C} + \% \text{L} + \% \text{E} + \% \text{N}$