ENERGY

SUSTAINABILITY

RESEARCH & DEVELOPMENT CENTER

Modeling and simulation of the microalgae derived hydrogen process in compact photobioreactors

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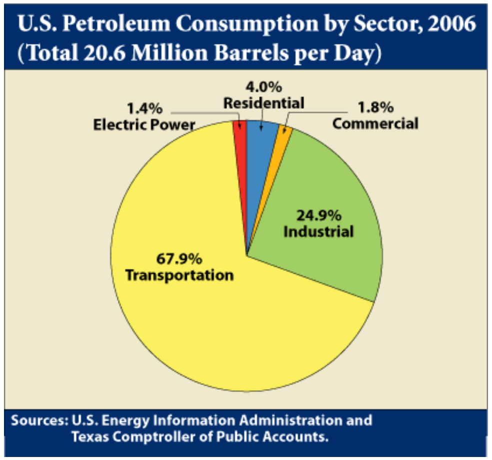
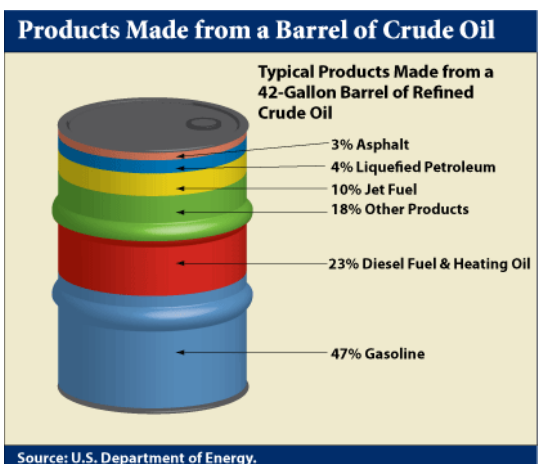
OUTLINE

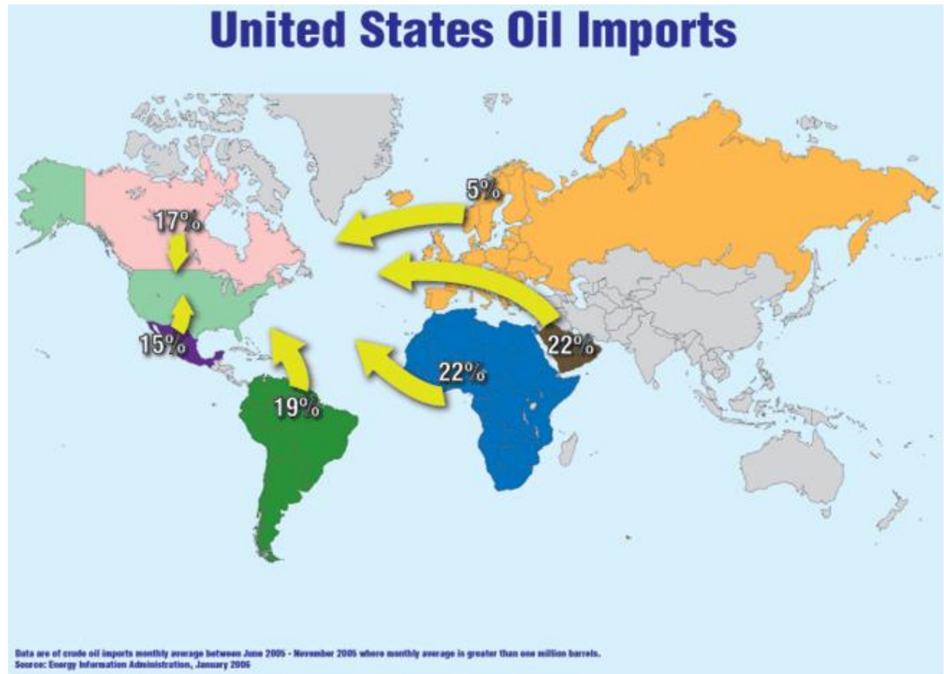
1. Introduction
2. Bibliographic Review
3. Materials and methods
4. Results and Discussion
5. Conclusions
6. Suggestions

US OIL USE

The USA currently imports more than 60% of its petroleum.







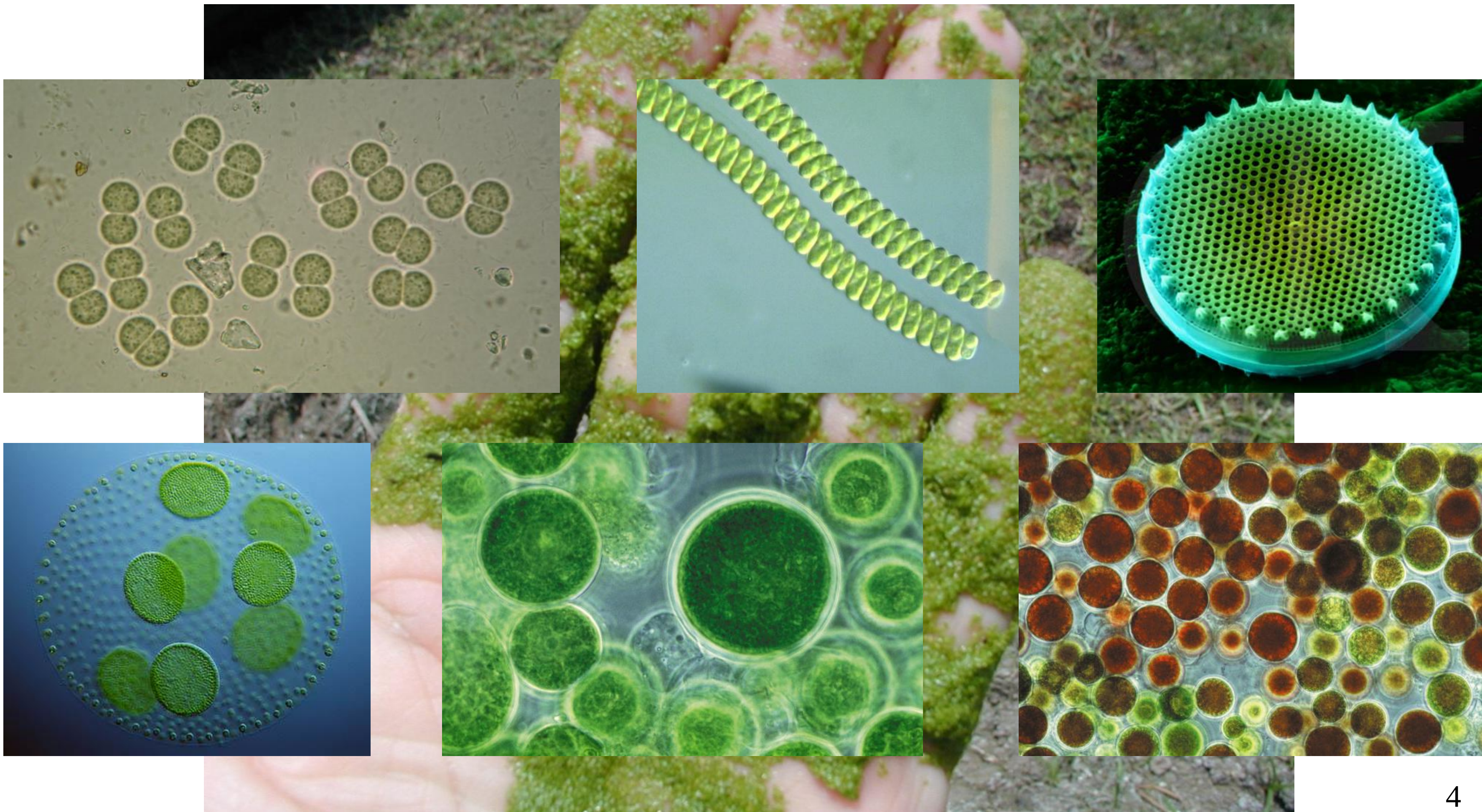
2/3 of it go to transportation fuels

140×10^9 gallons of gasoline/year

44×10^9 gallons of diesel/year

WHAT ARE MICROALGAE?

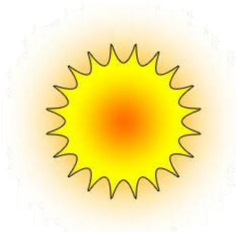
MICROALGAE are the unicelular algae with great photosynthetic capability and rapid growth due to their simple structure.



MICROALGAE ROLES IN NATURE?

MICROALGAE comprise the ***phytoplankton*** and are the basis of the aquatic food chain.

AUTOTROPHIC – are energy primary producers



$CO_2 + H_2O$ → $C_6H_{12}O_6$

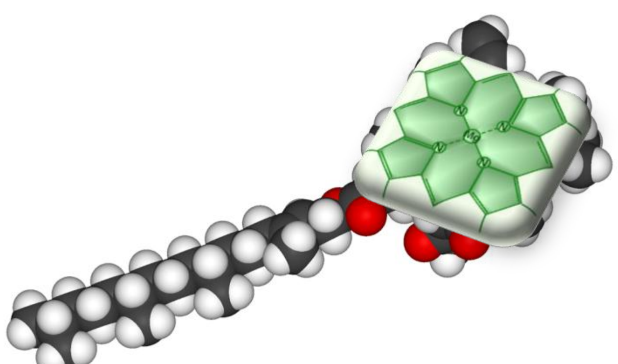
Chlorophyll + mineral salts

O_2

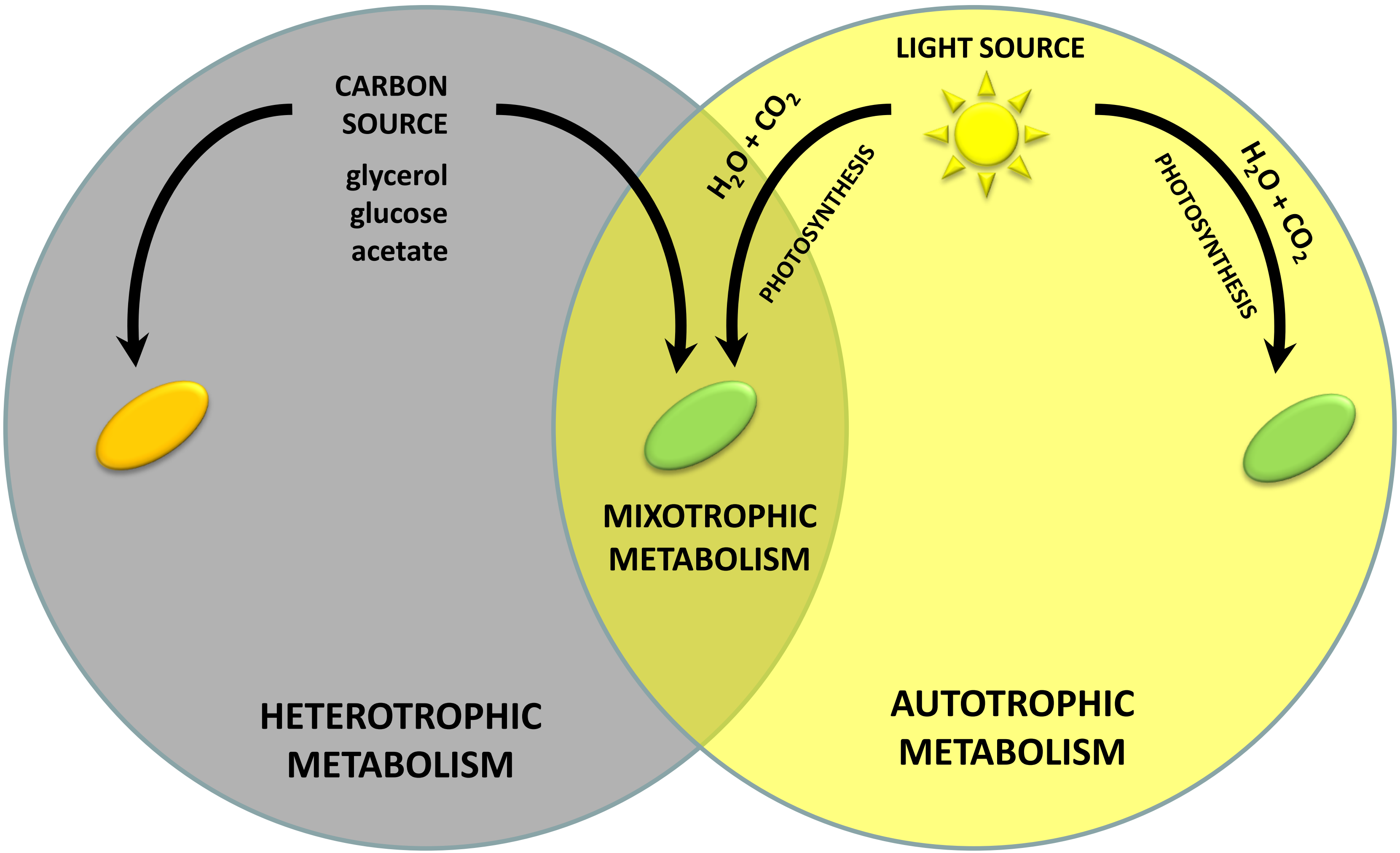
Lipids

Proteins

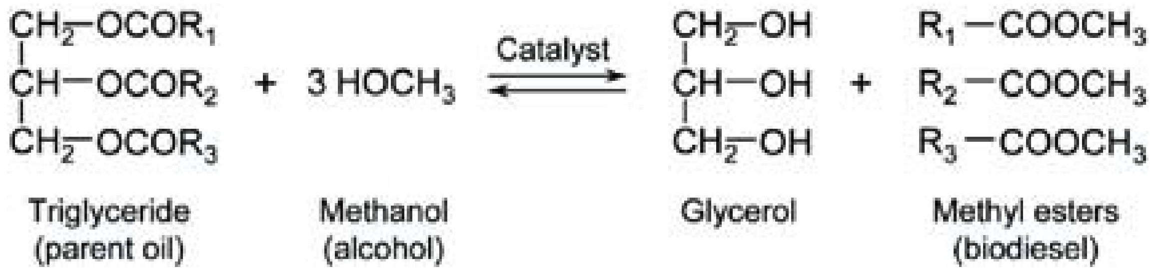
DNA, RNA, etc



MICROALGAE METABOLISM



Biodiesel production



- Triglycerides are converted first to diglycerides, monoglycerides and then to glycerol
- The equilibrium reaction requires 3 mol of alchohol per mol of triglyceride. Industrial processes use excess alcohol to ensure it is in the direction of the methyl esteres
- The reaction is catalyzed by using acids and alkali. Alkali catalyzed transesterification is 4000 times faster (sodium and potassium hydroxide). Sodium-methoxide.
- T= 60^{o}C
- Reaction takes place in about 90 minutes

EFFICIENCIES

ENERGIA AUTO-SUSTENTÁVEL
NÚCLEO DE PESQUISA E DESENVOLVIMENTO

CROP	OIL (L/ha)	LAND AREA NEEDED (M ha)	PERCENT OF EXISTING US CROPPING AREA[a]
Corn	172	1540	846
Soybean	446	594	326
Canola	1190	223	122
Coconut	2689	99	54
Palm oil	5950	45	24

[a] For meeting 50% of all transport needs of the US

(Chisti, 2007 e Chisti, 2009)

MICROALGAE CULTIVATION

Raceway ponds

Inexpensive operation

Simple construction

- High losses via evaporation

- Problems of contamination

Photobioreactors

-More expensive construction (~10x)

- More engineering

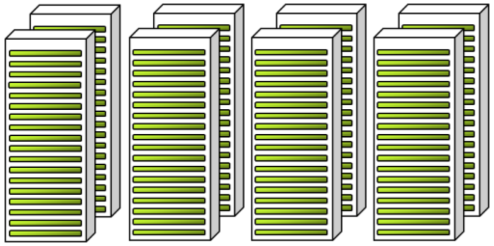
- Less evaporation

- Better CO_2 use

-Better mixing

-higher biomass concentration (easier harvesting)

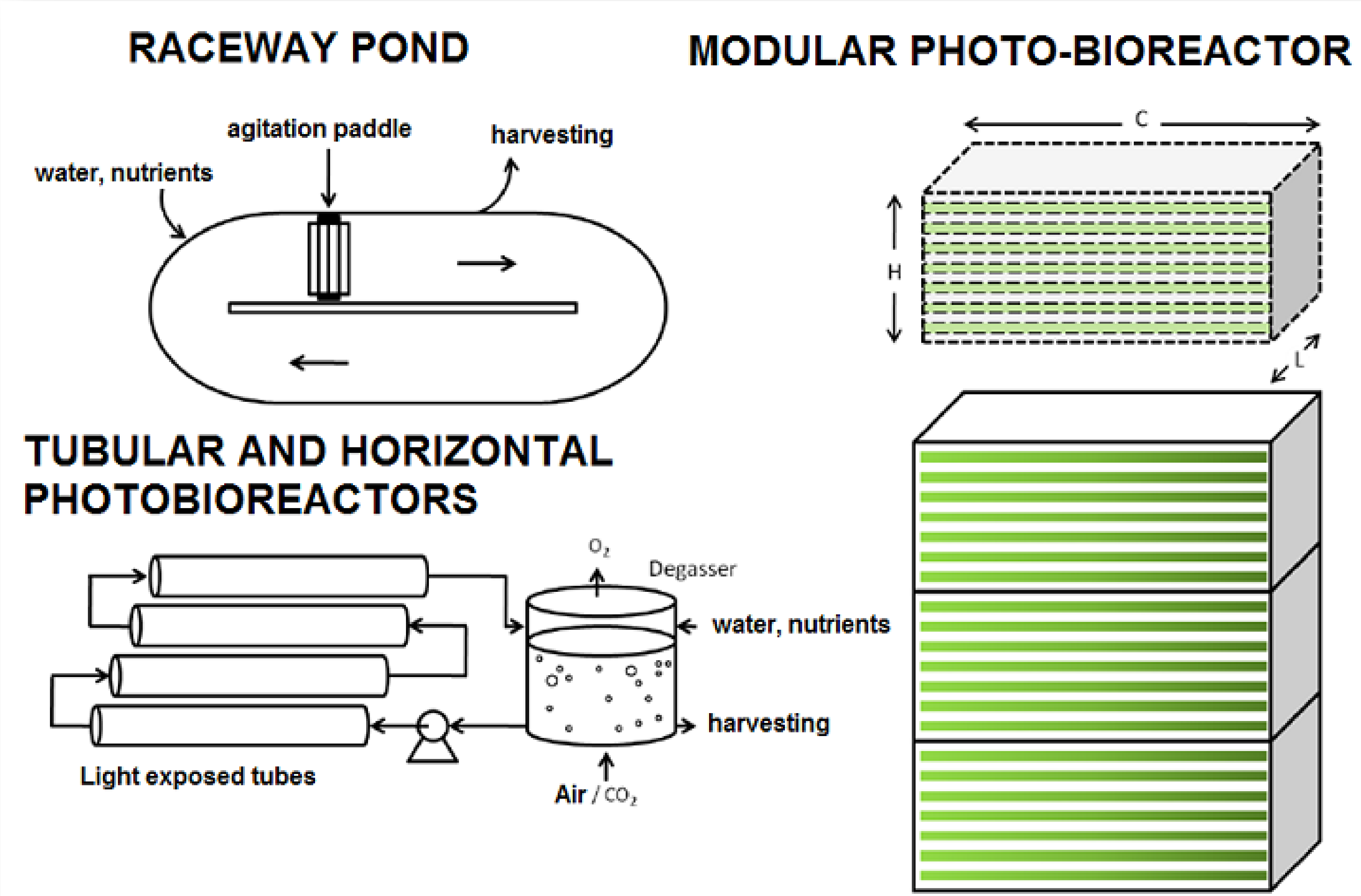
-volumetric biomass productivity (~13 x)



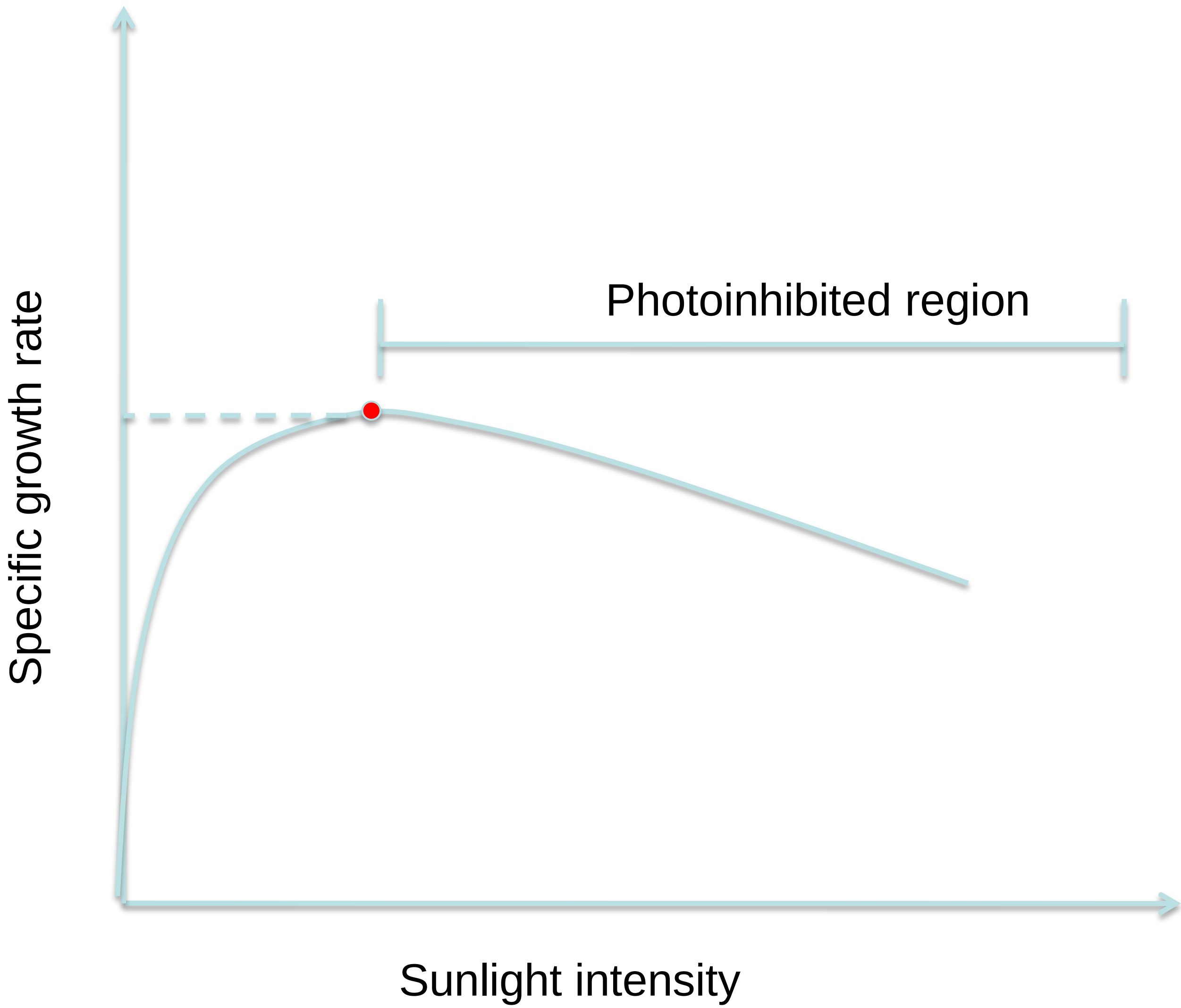
PROJECT LOCATION IN BRAZIL

NPDEAS LAY-OUT

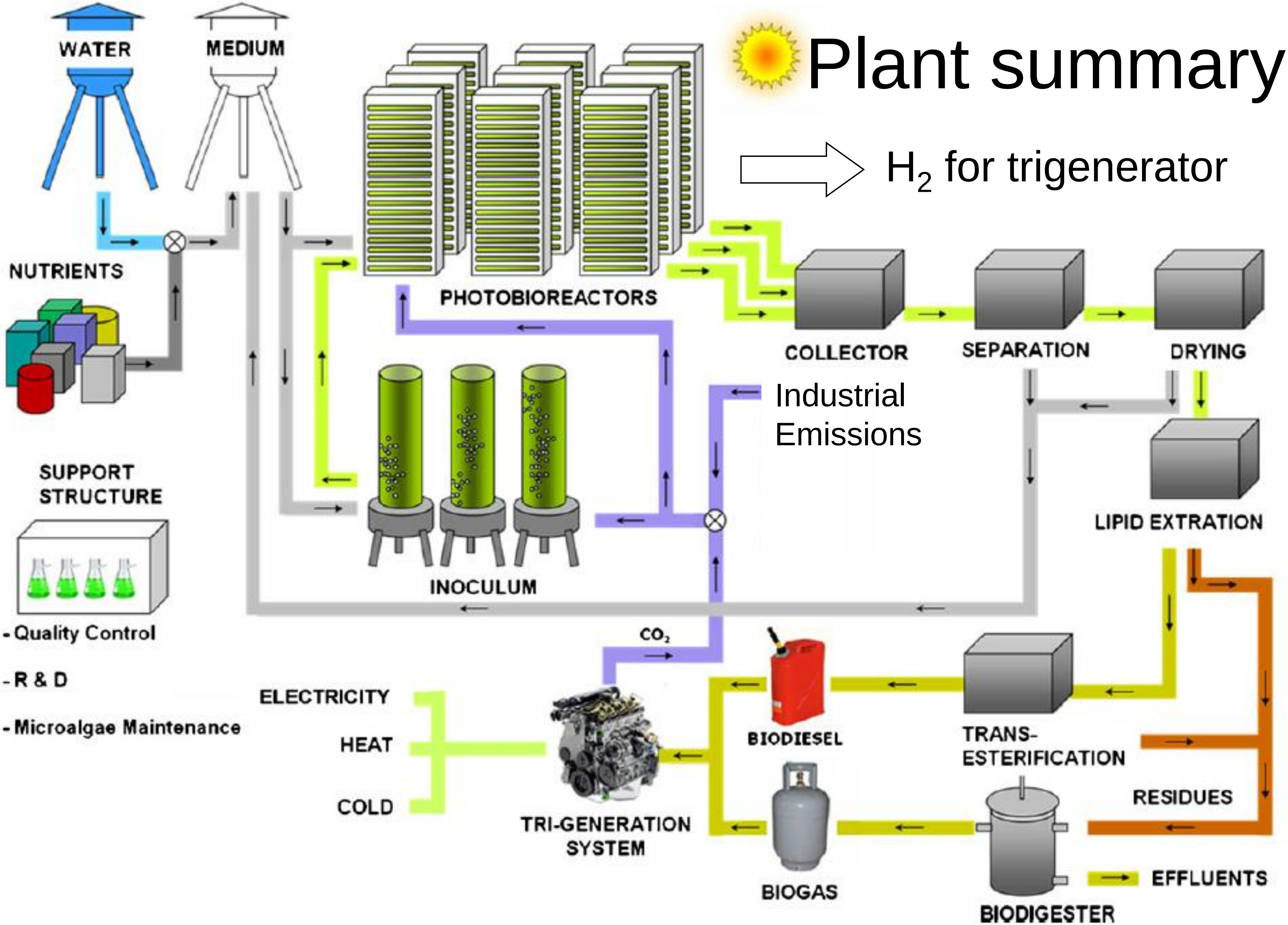
CULTIVATION IN PHOTOBIOREACTORS

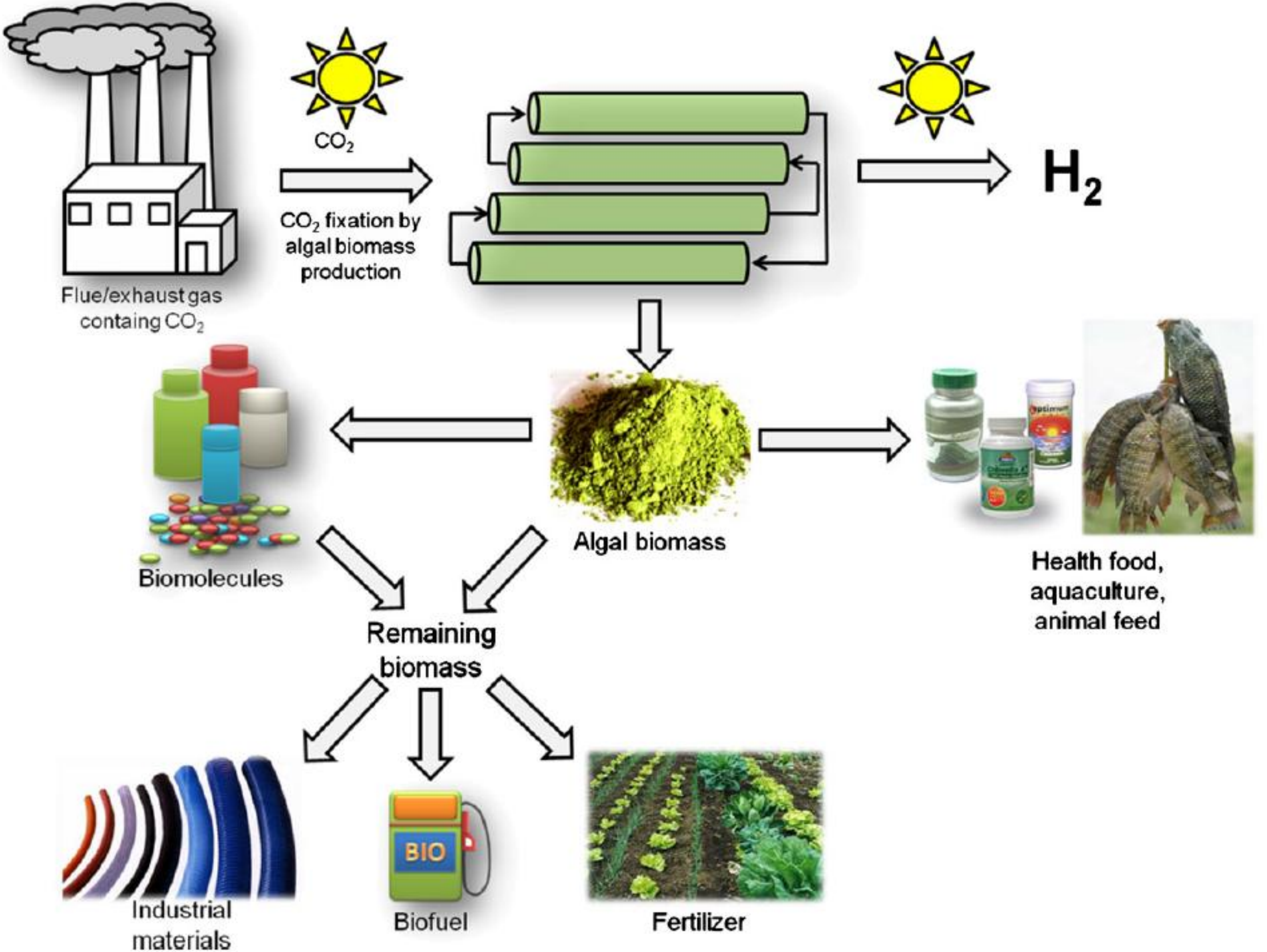


Photoinhibition



Plant summary





CO_2
CO_2 fixation by algal biomass production
Flue/exhaust gas containg CO_2
H_2
Biomolecules
Algal biomass
Health food, aquaculture, animal feed
Remaining biomass
Industrial materials
BIO
Biofuel
Fertilizer

Hydrogen

Combustível:	Valor do Poder Calorífico Superior (a 25ºC e 1 atm)	Valor do Poder Calorífico Inferior (a 25ºC e 1 atm)
Hidrogénio	141,86 KJ/g	119,93 KJ/g
Metano	55,53 KJ/g	50,02 KJ/g
Propano	50,36 KJ/g	45,6 KJ/g
Gasolina	47,5 KJ/g	44,5 KJ/g
Gasóleo	44,8 KJ/g	42,5 KJ/g
Metanol	19,96 KJ/g	18,05 KJ/g

Biohydrogen

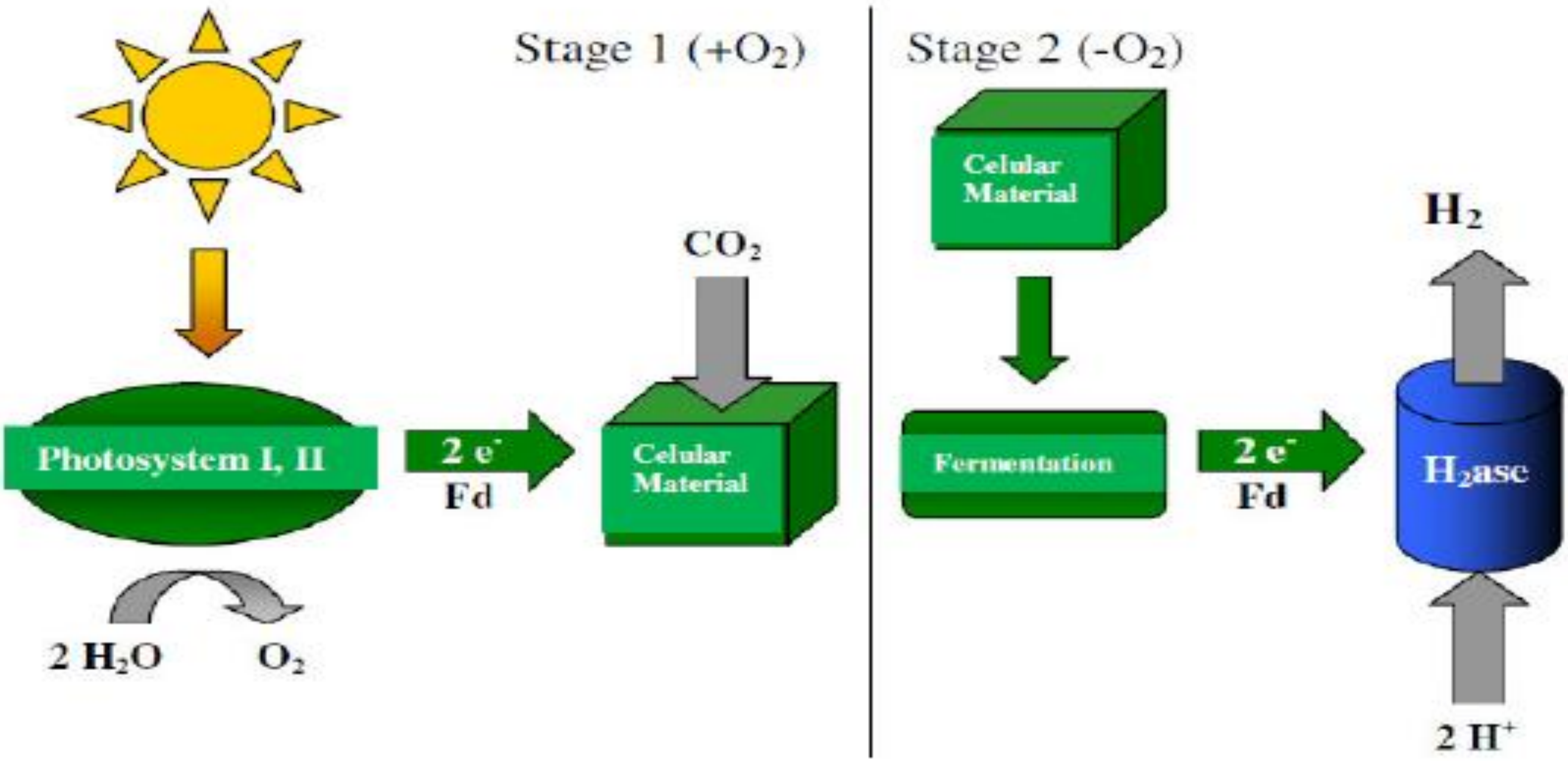
1. Direct Biophotolysis
2. Indirect Biophotolysis
3. Photofermentation
4. Dark fermentation
5. Hybrid systems

(stage 1 – aerobic)

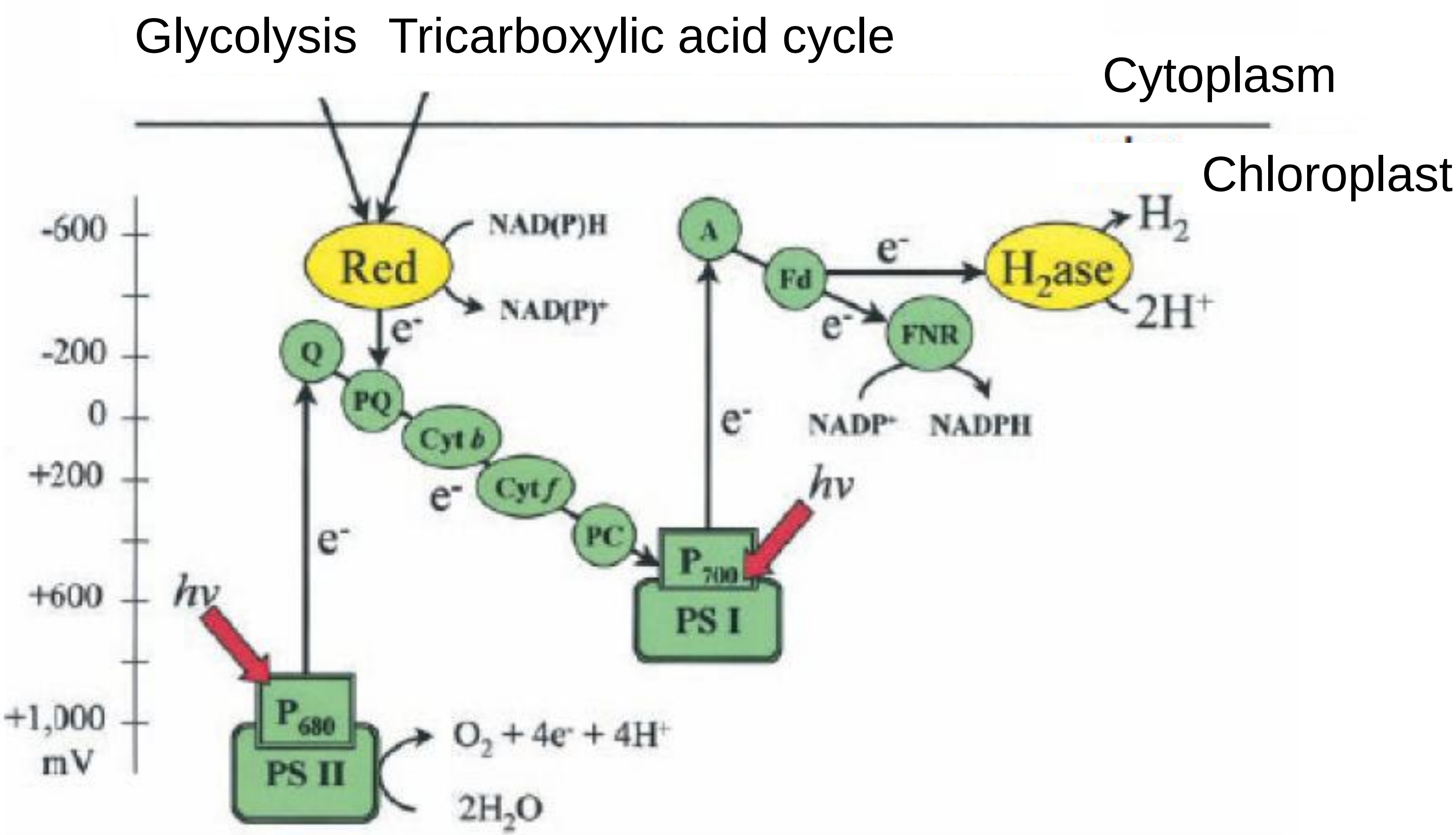
$$12\ H_2O + 6\ CO_2 + \text{light energy} \mapsto C_6H_{12}O_6 + 6\ O_2 \quad (1)$$

(stage 2 – anaerobic)

$$C_6H_{12}O_6 + 6\ H_2O + \text{light energy} \mapsto 12\ H_2 + 6\ CO_2 \quad (2)$$



2. BIBLIOGRAPHIC REVIEW



Electron transport pathways related to hydrogenase in green algae.
The electrons could originate in the water photolysis or in the plastoquinone through cellular substrates oxidation via glycolysis or in the Krebs cycle. (MELIS and HAPPE, 2001).

ENERGIA AUTO-SUSTENTÁVEL
NÚCLEO DE PESQUISA E DESENVOLVIMENTO

Challenges:

1. **Low hydrogen generation rate**
2. **High cost**
3. **GMO**
4. **Engineering – PBR; contamination; purification, separation**
5. **Sensitivity to oxygen**
6. **Co-products (e.g., biodiesel)**
7. **Mathematical modeling**

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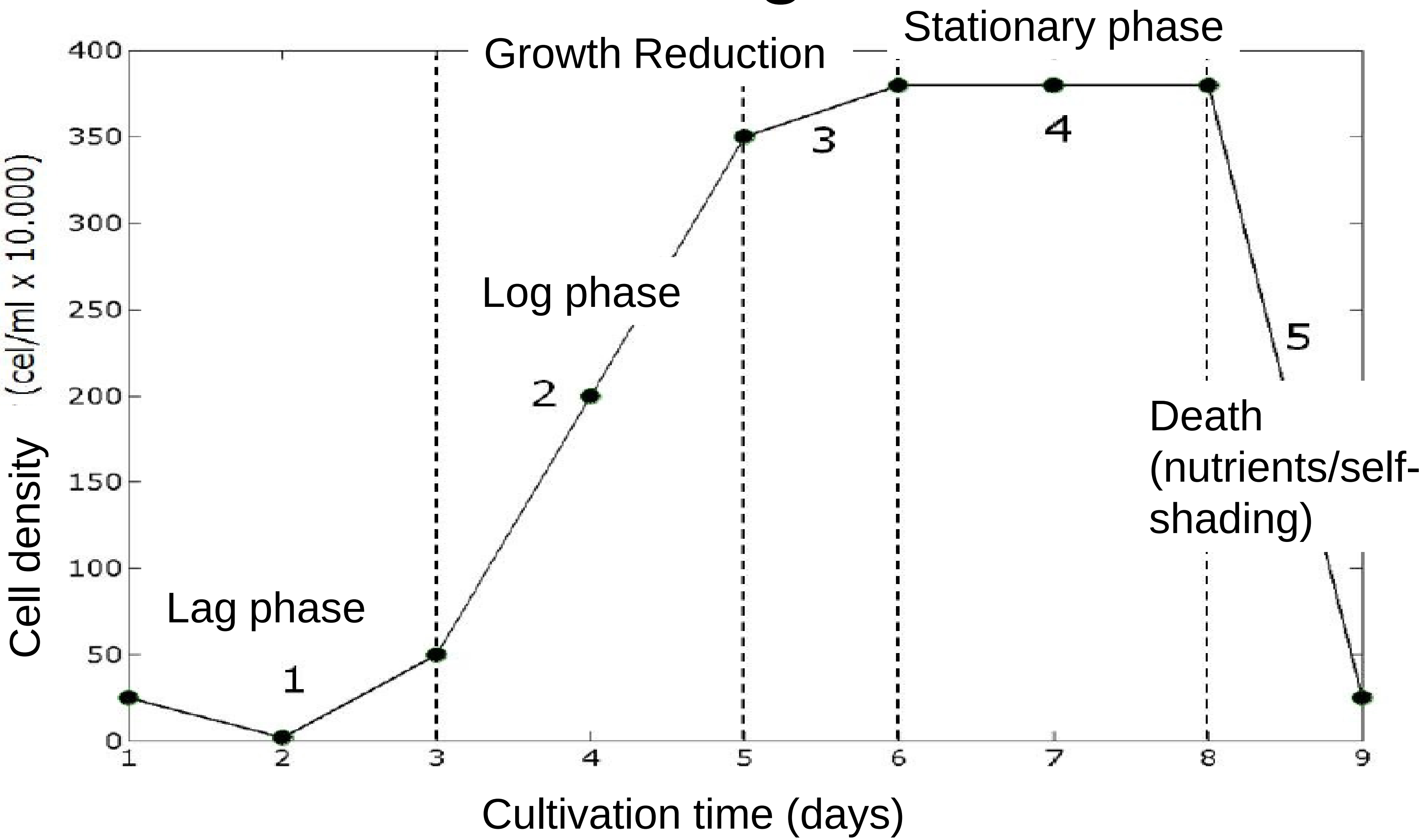
General objective:

H_2 **production mathematical modeling**

Specific objectives:

1. **Mathematical model**
2. **Low computational time**
3. **Experimental comparison**
4. **Case study**

Mathematical modeling



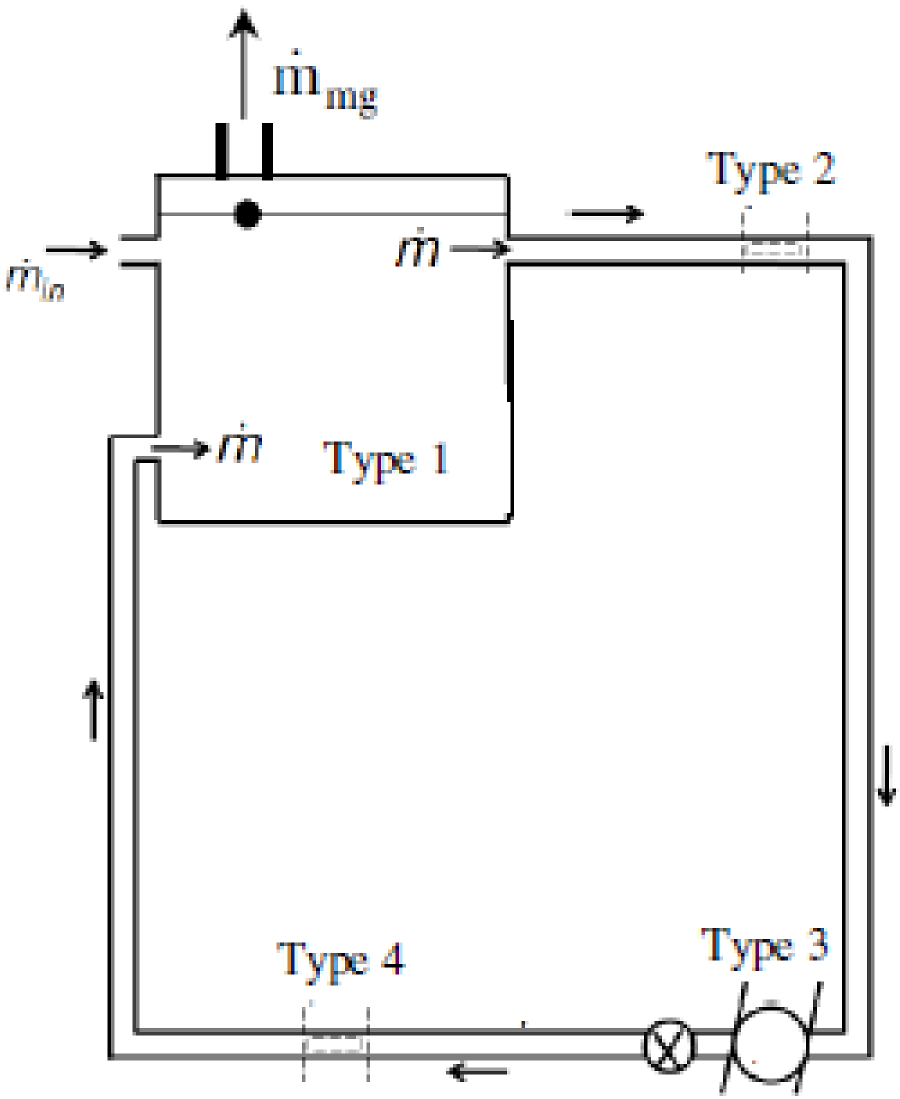
Mathematical modeling

Molina Grima, 1996

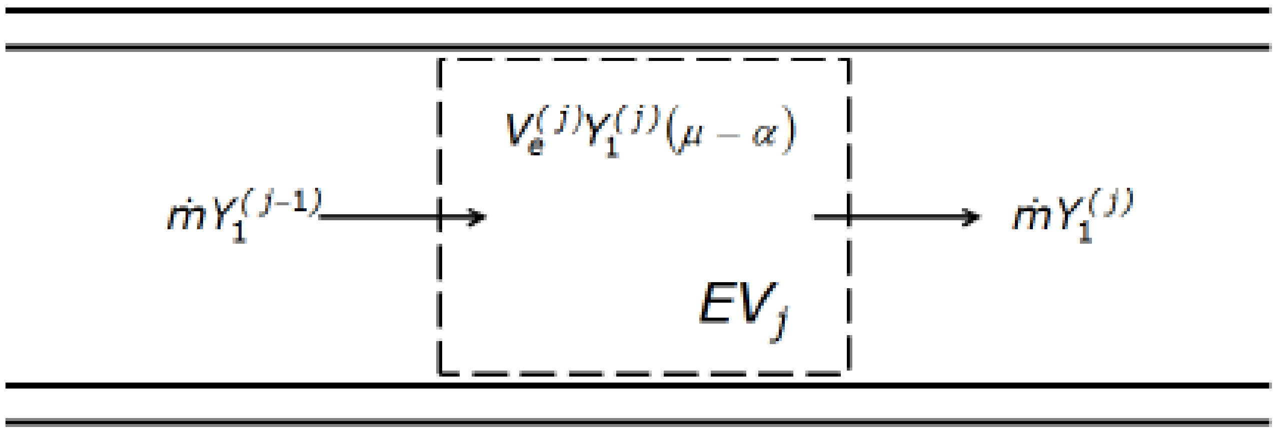
iya et al. (1953)

$$\mu = \frac{\mu_{max} I_{av}^{\,b+\frac{c}{I_0}}}{I_{av}^{\,b+\frac{c}{I_0}} + \left(I_K \left(1 + \left(\frac{I_0}{K_i} \right)^{a} \right) \right)^{b+\frac{c}{I_0}}}$$

3. MATERIALS AND METHODS



3. MATERIALS AND METHODS



$$V^{(j)} \frac{dy_{alga}^{(j)}}{dt} = \frac{\dot{m}}{\rho} \left(y_{alga}^{(j-1)} - y_{alga}^{(j)} \right) + V^{(j)} y_{alga}^{(j)} (\mu - \alpha)$$

$$V^{(j)} \frac{dy_{CO_2}^{(j)}}{dt} = \frac{\dot{m}}{\rho} \left(y_{CO_2}^{(j-1)} - y_{CO_2}^{(j)} \right) - V^{(j)} y_{alga}^{(j)} R_{y_{CO_2}/y_{alga}} (\mu - \alpha)$$

3. MATERIALS AND METHODS

ENERGIA AUTO-SUSTENTÁVEL
NÚCLEO DE PESQUISA E DESENVOLVIMENTO

$$V^{(j)} \frac{dy_{O_2}^{(j)}}{dt} = \frac{\dot{m}}{\rho}\left(y_{O_2}^{(j-1)} - y_{O_2}^{(j)}\right) + V^{(j)} y_{alga}^{(j)} R_{y_{O_2}/y_{alga}} (\mu - \alpha)$$

alga *Scenedesmus almeriensis* (SÁNCHEZ et al., 2008)

$$\mu = \frac{\left(A_1 e^{\left(\frac{-E_{a1}}{RT}\right)} - A_2 e^{\left(\frac{-E_{a2}}{RT}\right)}\right) I_{avg}^n}{\left(\frac{I_{k,max} I_0}{I'_k + I_0}\right)^n + I_{avg}^n}$$

$$I_{avg} = I_0 . e^{-d.C.K_a}$$

3. MATERIALS AND METHODS

$$V^{(j)} \frac{dy_{H_2}^{(j)}}{dt} = \frac{\dot{m}}{\rho}\left(y_{H_2}^{(j-1)} - y_{H_2}^{(j)}\right) + V^{(j)}\, y_{H_2}^{(j)} \left(\mu_{H_2} - \alpha_{H_2}\right) e^{-y_{O_2}/y_{O_2,sat}}$$

Dilution

$$\mu_{H_2} = \frac{\mu_{max}\, I_{avg}}{I_k + I_{avg}}$$

3. MATERIALS AND METHODS

Martínez and Casas [26]

$$\frac{dy_i}{dt} = \frac{27 v_{meio} D_i u_i}{2 g r_0^4} \left(y_{i,sat} - y_i \right)$$

$$y_i(t_d) = y_{i,sat} \left\{ 1 - \left(1 - e^{-K t_d} \right) \right\}$$

$$K = \frac{27 v_{medium} D_i u_i}{2 g r_0^4} \; ; \; t_d = \frac{L_{tdg}}{u_b} \; ; \; u_b = \frac{2 g r_0^2}{9 v_{medium}} \qquad A_{tdg} = \frac{\dot{m}_{CO_2} t_d}{y_{CO_2} \rho_{meio} L_{tdg}}$$

3. MATERIALS AND METHODS

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$$pH = -\log\left(\frac{-k_a + \sqrt{k_a^2 + 4k_a[CO_2]}}{2}\right)$$

$$T_\infty = T_{min} + \frac{\Delta T}{2} - \frac{\Delta T}{2}\cos\left[\frac{\pi(t - t_0)}{43200}\right]$$

$$\varepsilon_{mesh,i} = \frac{\left| \|y_i\|_{mesh,j} - \|y_i\|_{mesh,j+1} \right|}{\|y_i\|_{mesh,j}} \leq 0.01$$

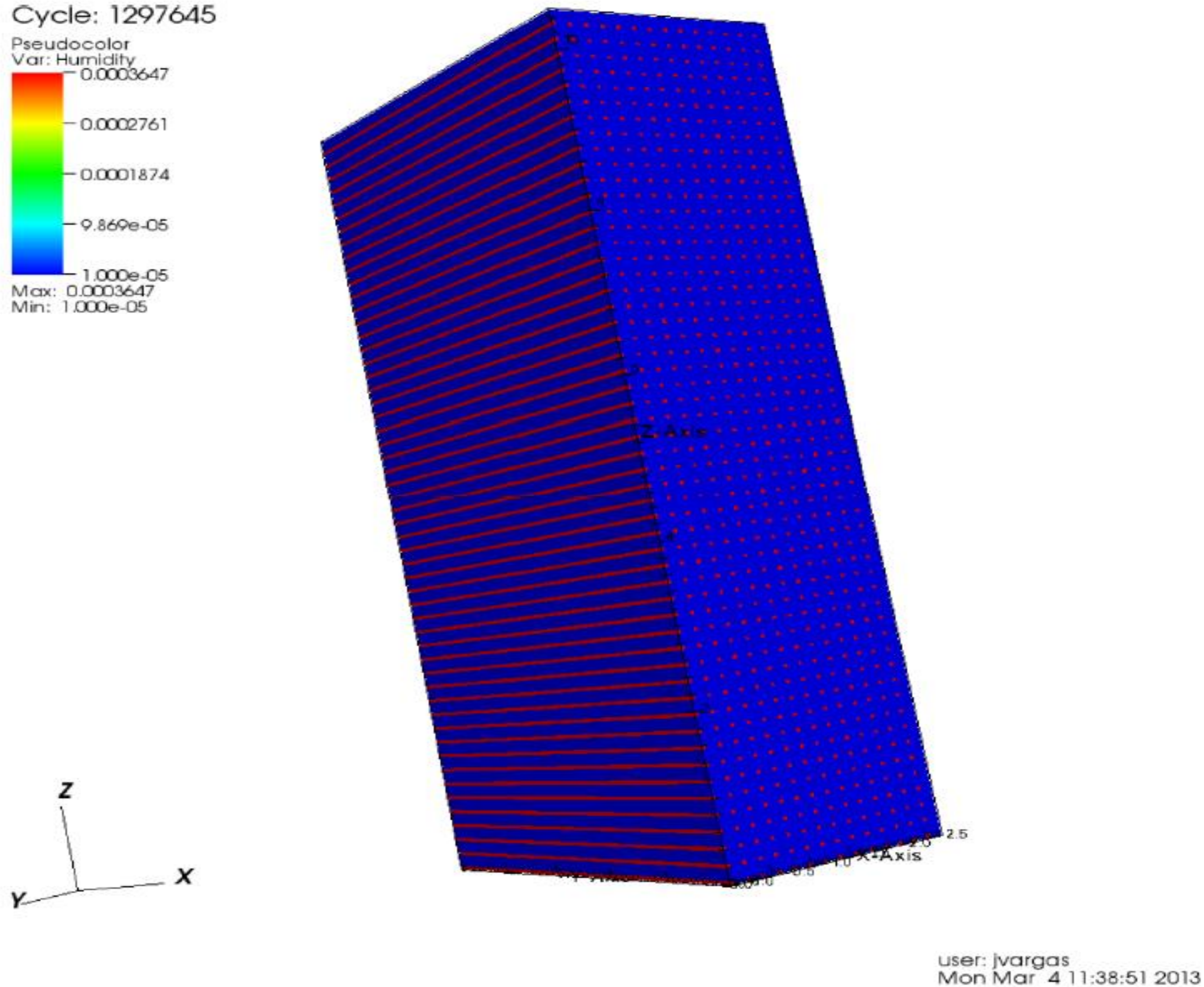
3. RESULTS AND DISCUSSION

A. *Mesh and boundary conditions*

The PBR measures $(5\,\mathrm{m} \times 2\,\mathrm{m} \times 8\,\mathrm{m})$. The converged mesh according to Eq. (21) had a total of 6048 VEs.

The conditions for the cases considered in this work were:

1. Average sun irradiation: 500 W m^{-2} (day) and 0 W m^{-2} (night);
2. Side wind through one of the faces as desired. In this work, the wind flow was assumed from east to west: 5 m/s;
3. PBR temperature regime: between T_{min} = 283 and T_{max} = 303 K, and
4. Two simulation periods: 15 e 17 days, always beginning at 5 AM.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Pseudocolor
Var: Humidity
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0.0002761
0.0001874
9.869e-05
1.000e-05
Max: 0.0003647
Min: 1.000e-05
Z-Axis
X-Axis
Z
X
Y
user: jvargas
Mon Mar 4 11:38:51 2013

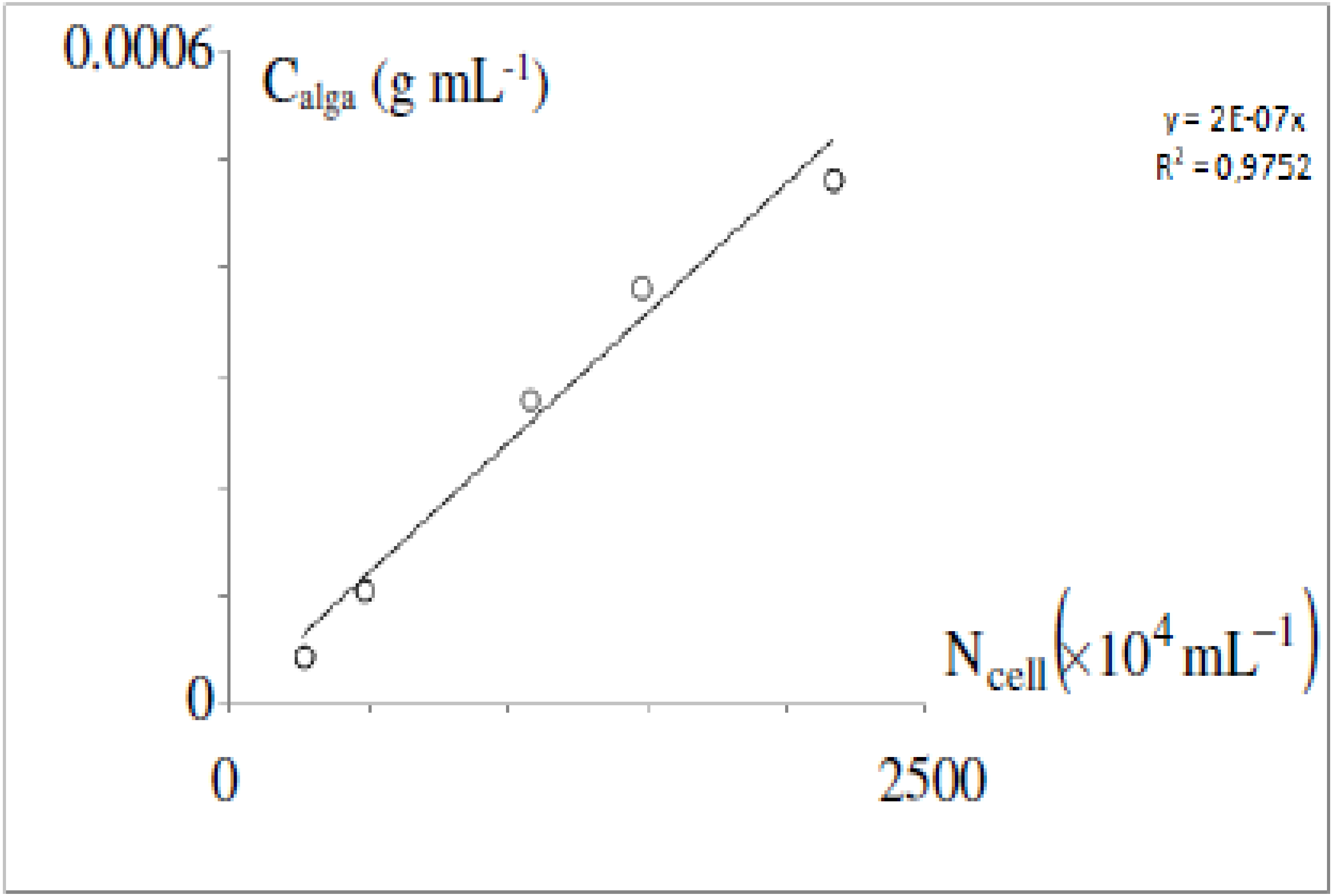

Fig. 5. Dry biomass versus cell number correlation.

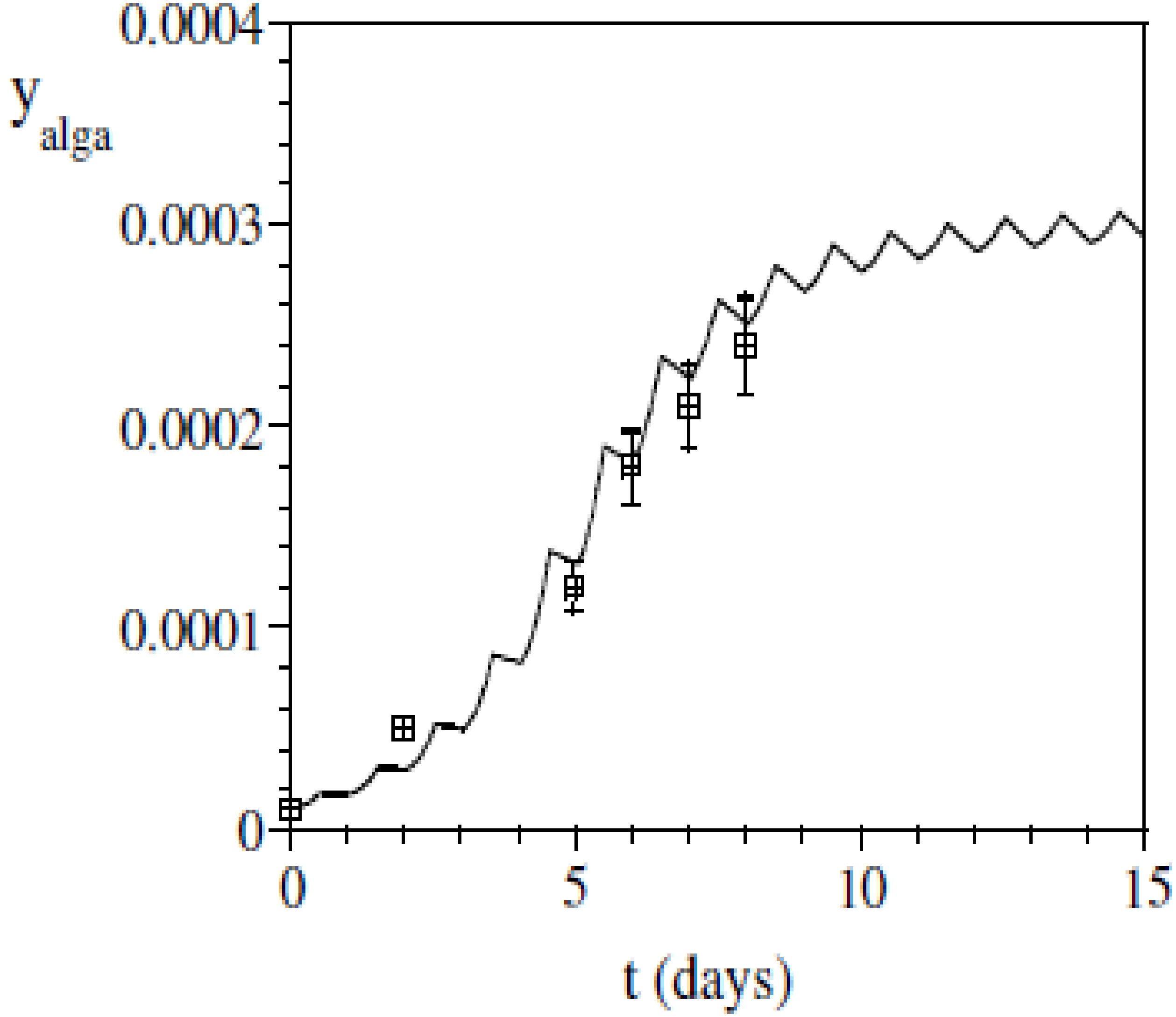

Fig. 6. The comparison between numerical and experimental results for PBR microalgae growth.

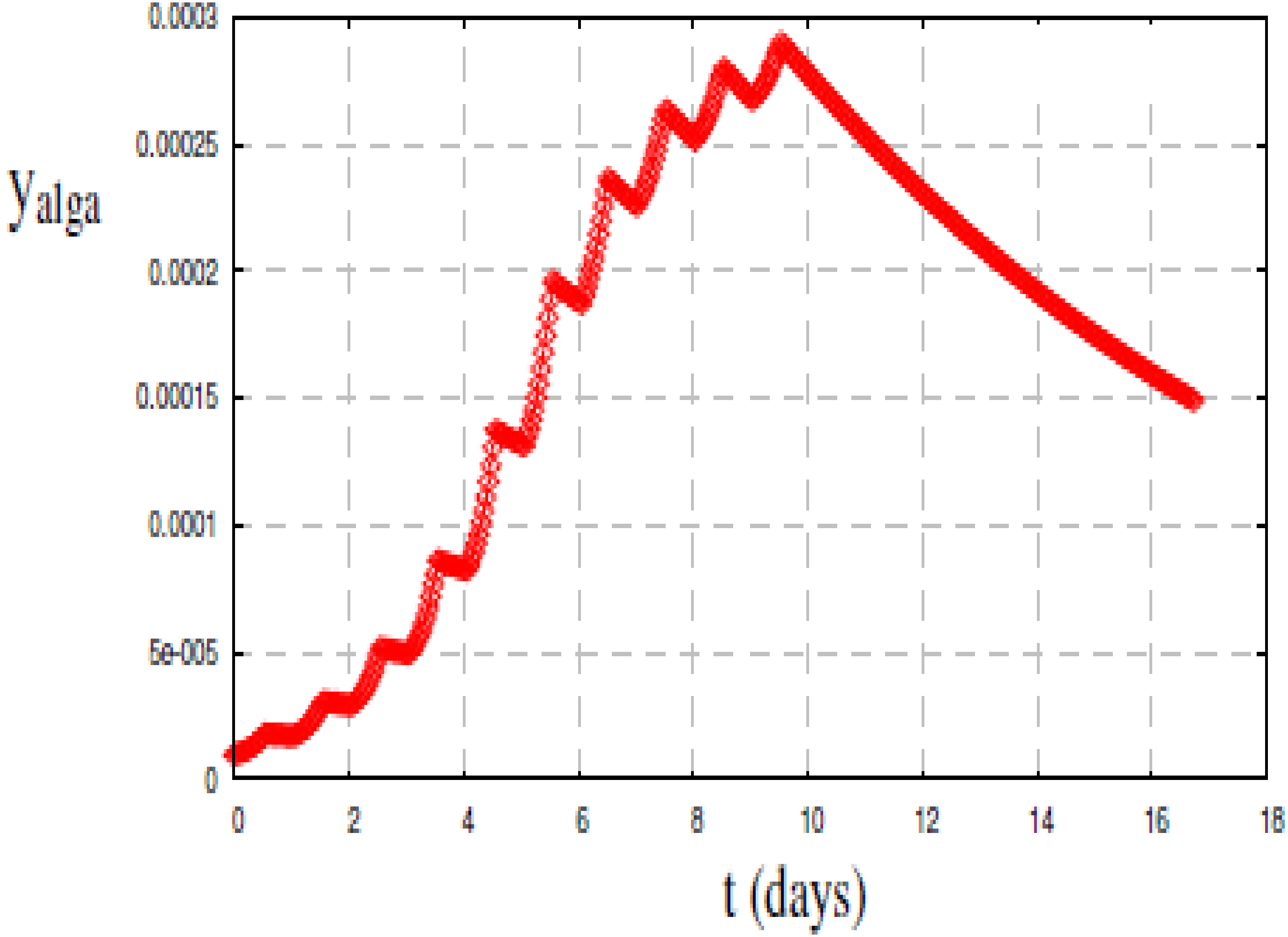

Fig. 7. PBR microalgae mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.

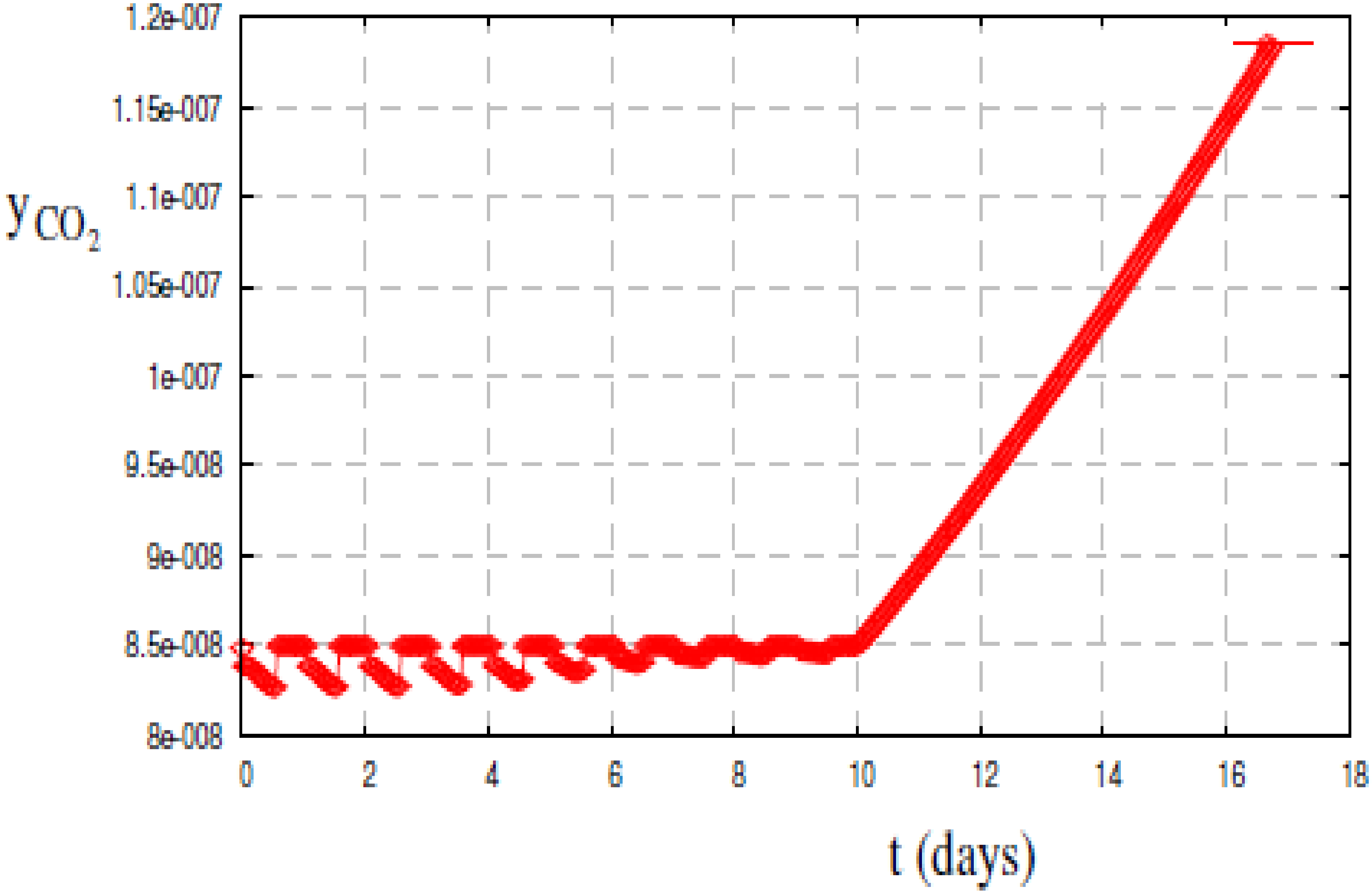

Fig. 8. PBR CO_2 mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.

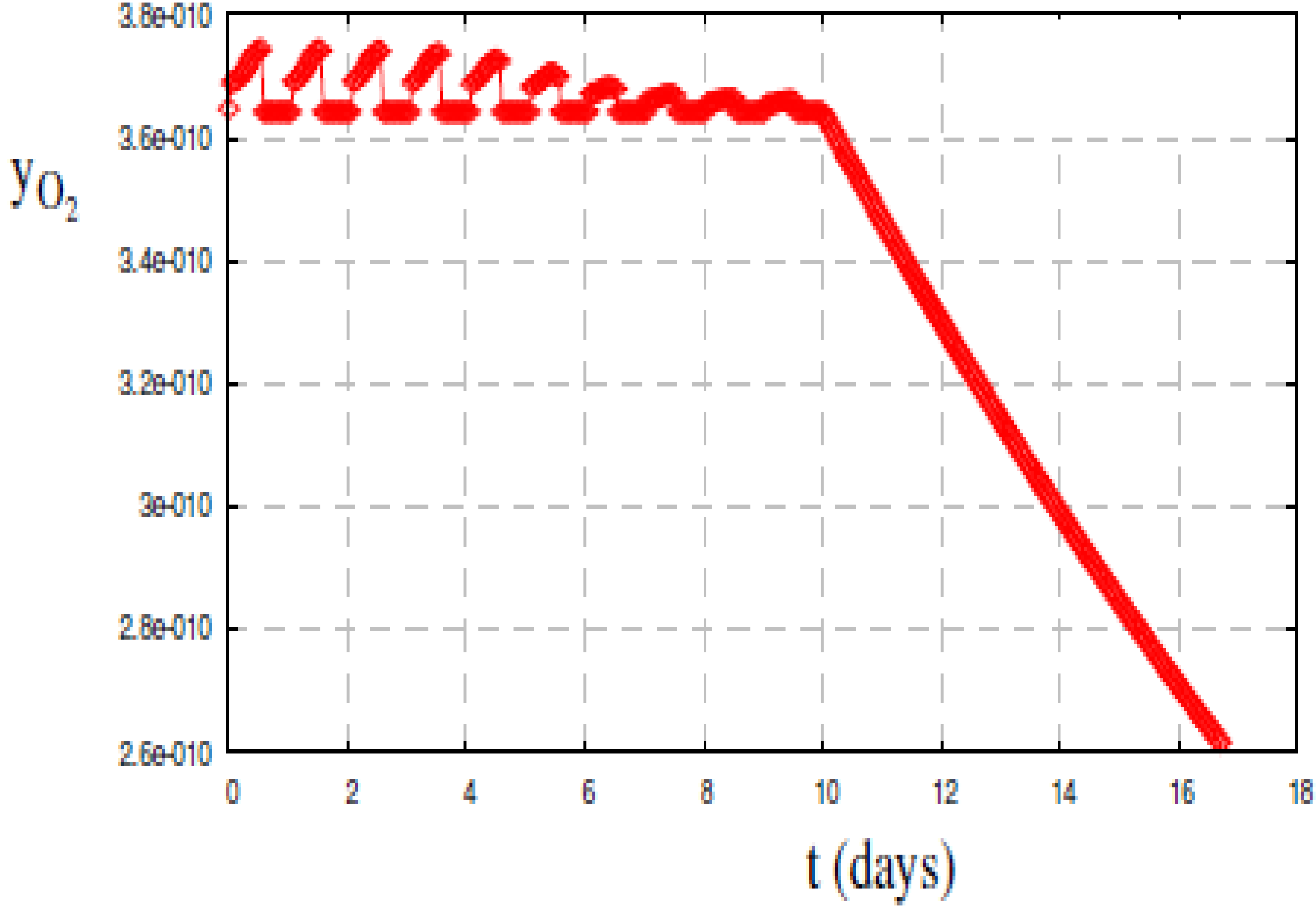

Fig. 9. PBR O_2 mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.

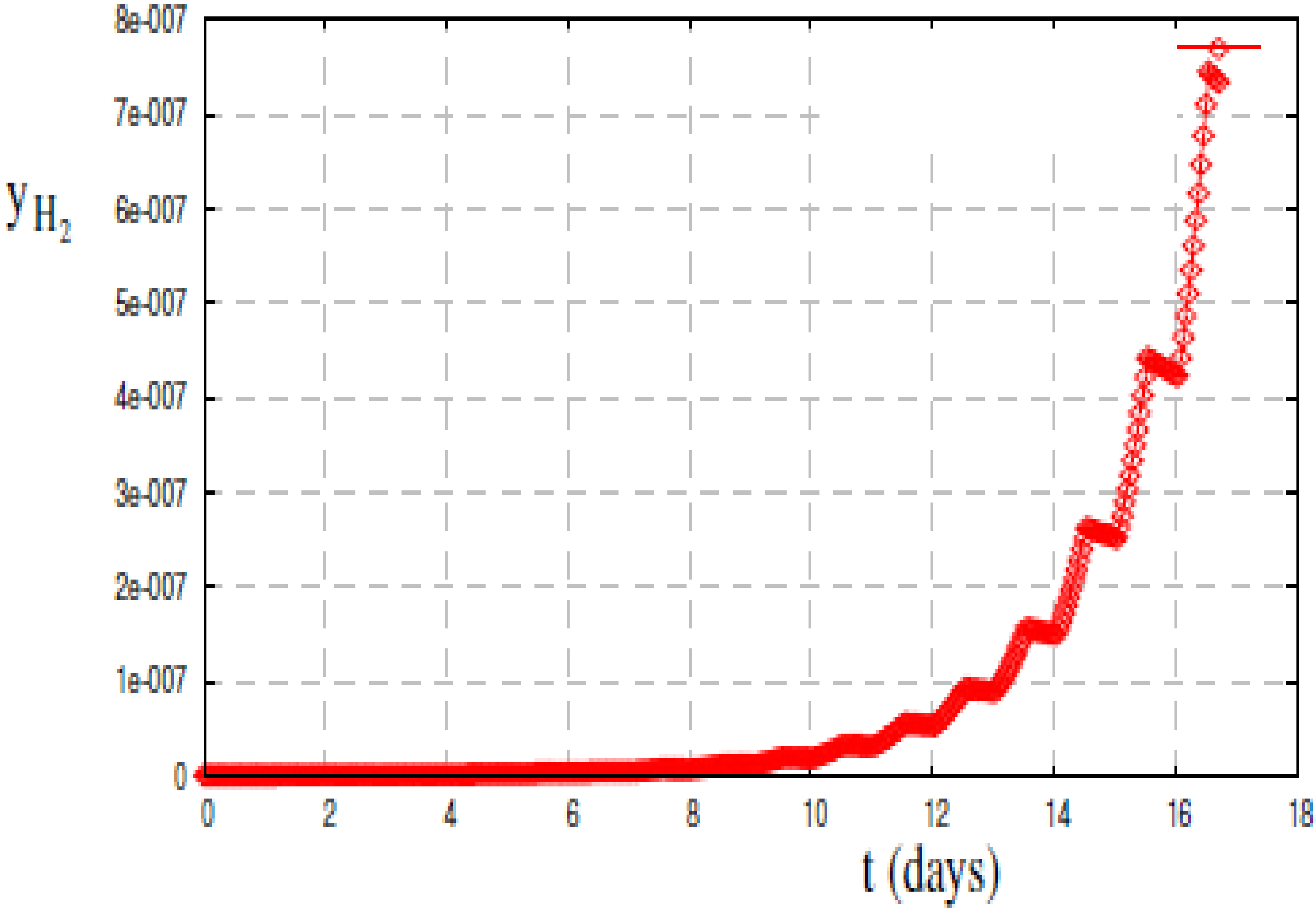

Fig. 10. PBR H_2 mass fraction time evolution for 17 simulation days with aerobic (10 days) and anaerobic (7 days) stages.

5. CONCLUSIONS

1. Indirect photolysis mathematical model has been developed
2. Low computational time application
3. Experimental validation for microalgae growth
4. Case study – expected trends have been observed

6. SUGGESTIONS

1. Prototype (HGP – “Hydrogen Generation Photobioreactor”)
2. Different green algae species for hydrogen generation
3. Complete characterization of the obtained fuel (e.g., purity)
4. Mathematical model improvement and experimental validation
5. Process thermodynamic optimization (numerical)


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