



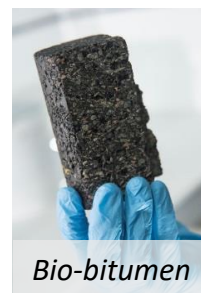
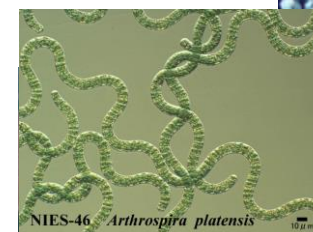
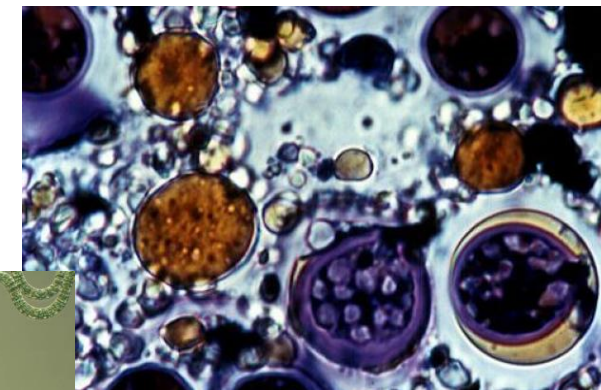
Biological valorization of CO₂ by microalgae
Valorisation biologique du CO₂ par microalgues

Pr. Jeremy PRUVOST
Nantes University, France

Why microalgae?

	Microalgae	C4 vegetals (corn,...)
Maximal areal productivity (T.ha⁻¹.year⁻¹)	100	60
Actual areal productivity (T.ha⁻¹.year⁻¹)	50-70	10-30

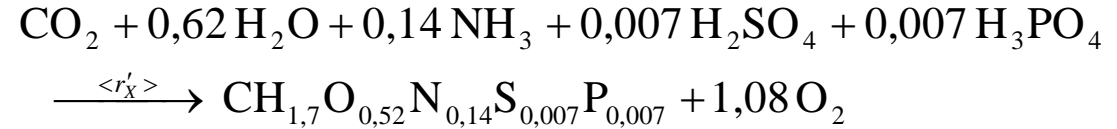
- Highest photosynthetic production rate
- Basis for sustainable processes (water recycling, negligible impact on soils...)
- Numerous applications: food/feed, healthcare, biofuels...
- Industrial ecology concept: possible use of industrial effluents (CO₂, waste water...)



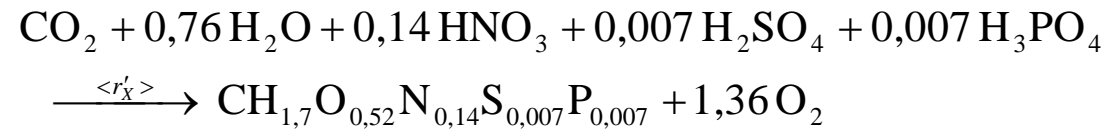
Nutrients for microalgae growth

Stoichiometric growth equation

Culture on ammonium



Culture on nitrate



Yield of consumption (mineral nutrients)

NO_3^-	$Y_{\text{NO}_3/\text{C}_x} = 400\text{g/kg}$ of dry biomass
SO_4^{2-}	$Y_{\text{SO}_4/\text{X}} = 60\text{g/kg}$ of dry biomass
PO_4^{3-}	$Y_{\text{PO}_4/\text{X}} = 50\text{g/kg}$ of dry biomass

Yield of consumption (CO₂)

CO_2	$Y_{\text{CO}_2/\text{C}_x} = 1600\text{-}1900\text{g/kg}$ of dry biomass
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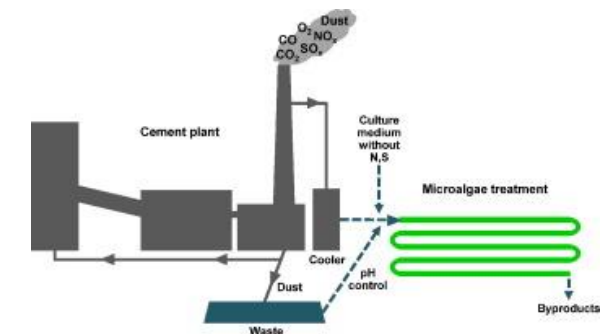
C/N ratio in the range 4,2-7,8

Waste-water can be used as a nutrient source

- Urban wastewater : Nurdogan et Oswald, 1995
- Porc liver, Zhou et al., 2012
- Anaerobic digestion effluents



Peterborough (Australia, Flinders Univ.)



CO₂ from flue gas can also be used

Feasibility of microalgae culture on CO₂ flue gas

In-site implantation of a mini-lab with direct connection to an emitting cyclone tower (coll. with Ciment Calcia) 2011-2012



Cyclone tower of the Gargenville's cement plant



Experimental platform



Sampling line connected to chimney stack



13% of CO₂ + various compounds

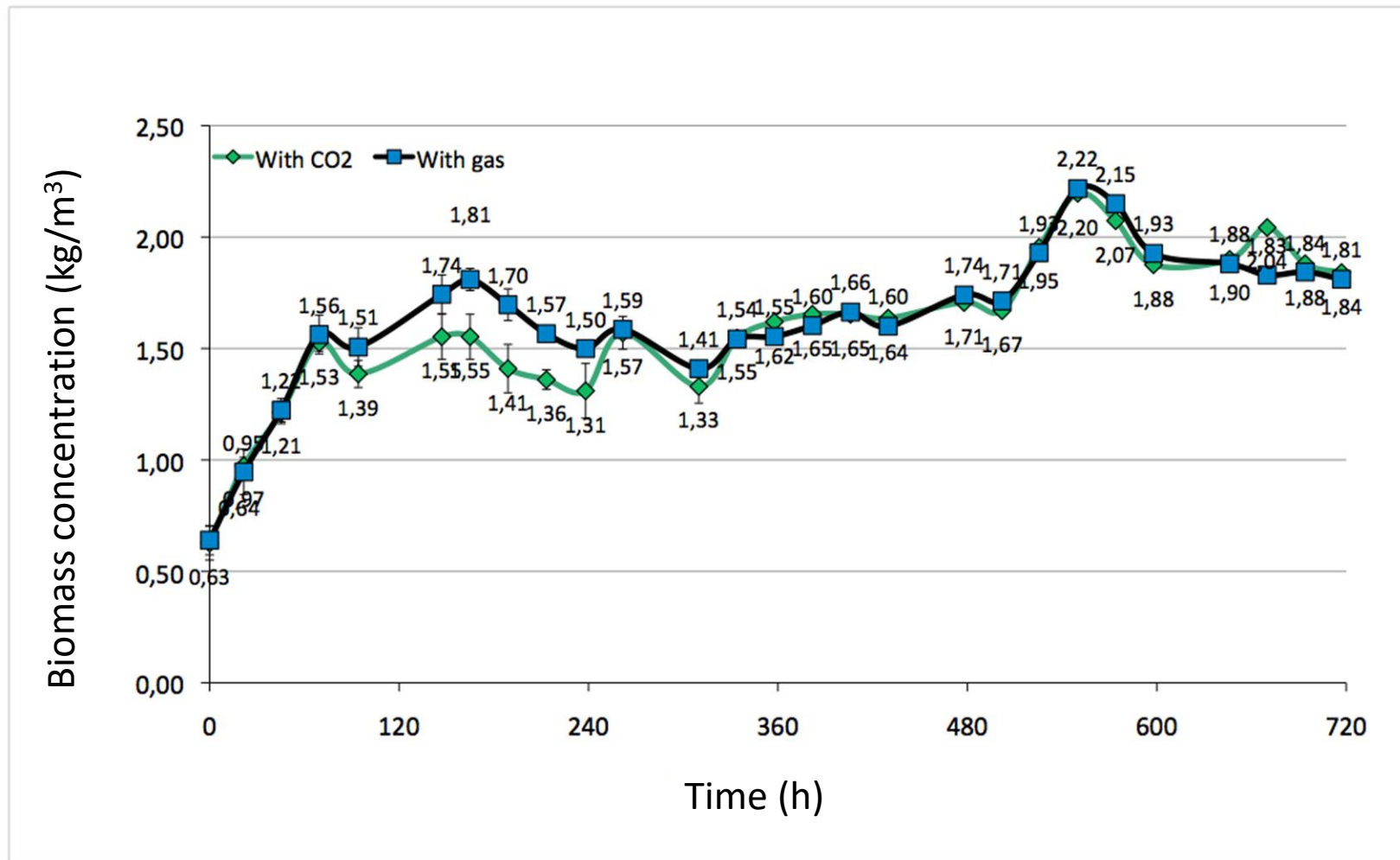


Photobioreactor (small scale studies)

Feasibility of microalgae culture on CO₂ flue gas

Long-term culture of A.platensis with appropriate flue-gas feeding strategy (results obtained in the cement plant)

2011-2012



What is the potential ?

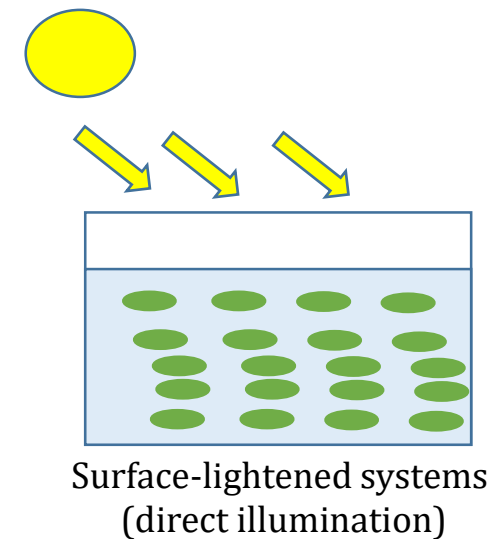
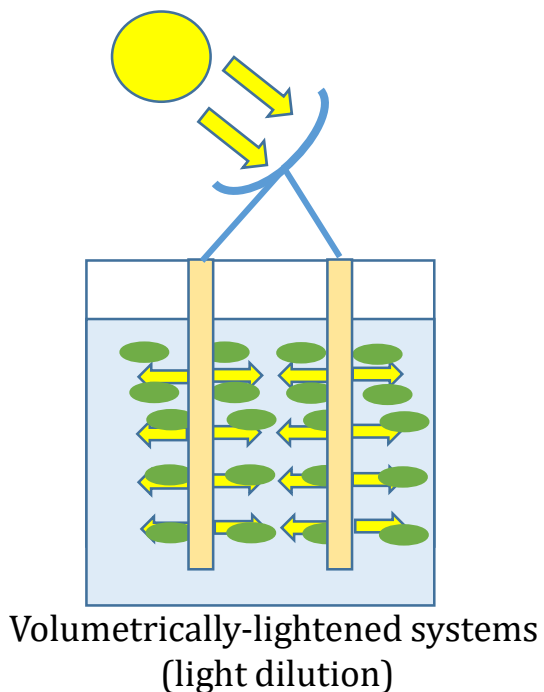
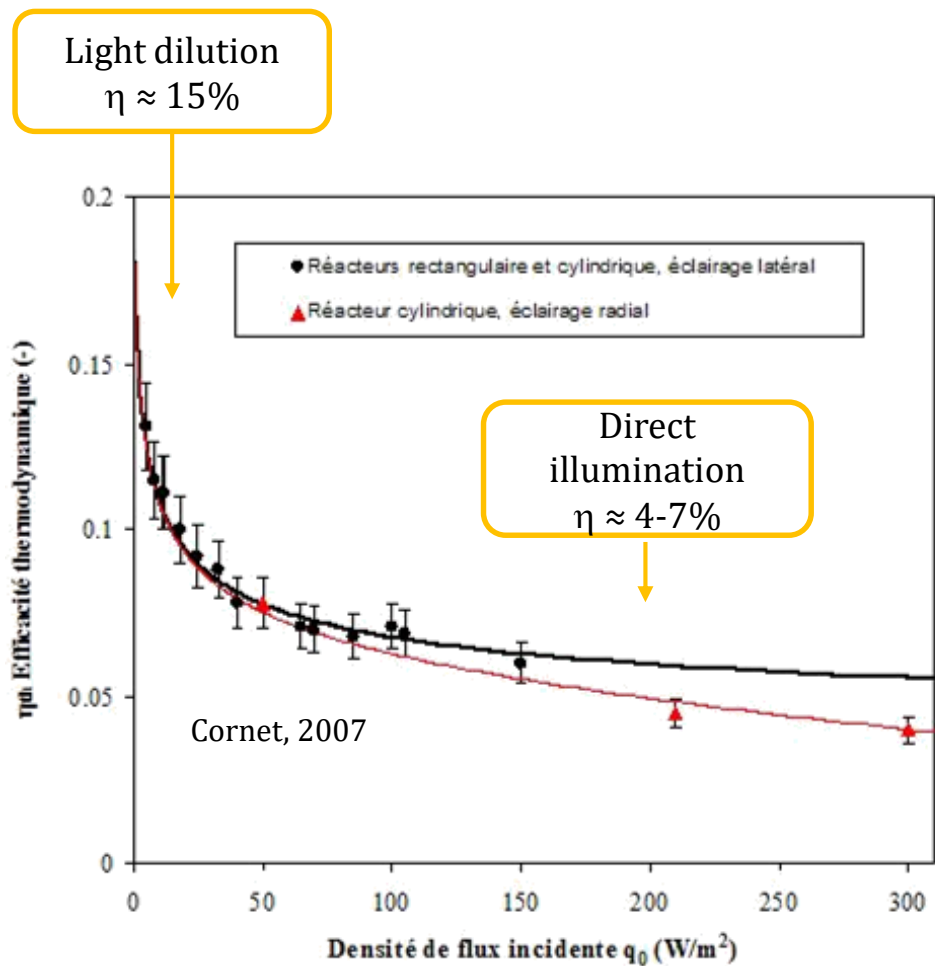
Biomass productivities of microalgae culture systems

Areal productivities (g/m²/day or t/ha/year)

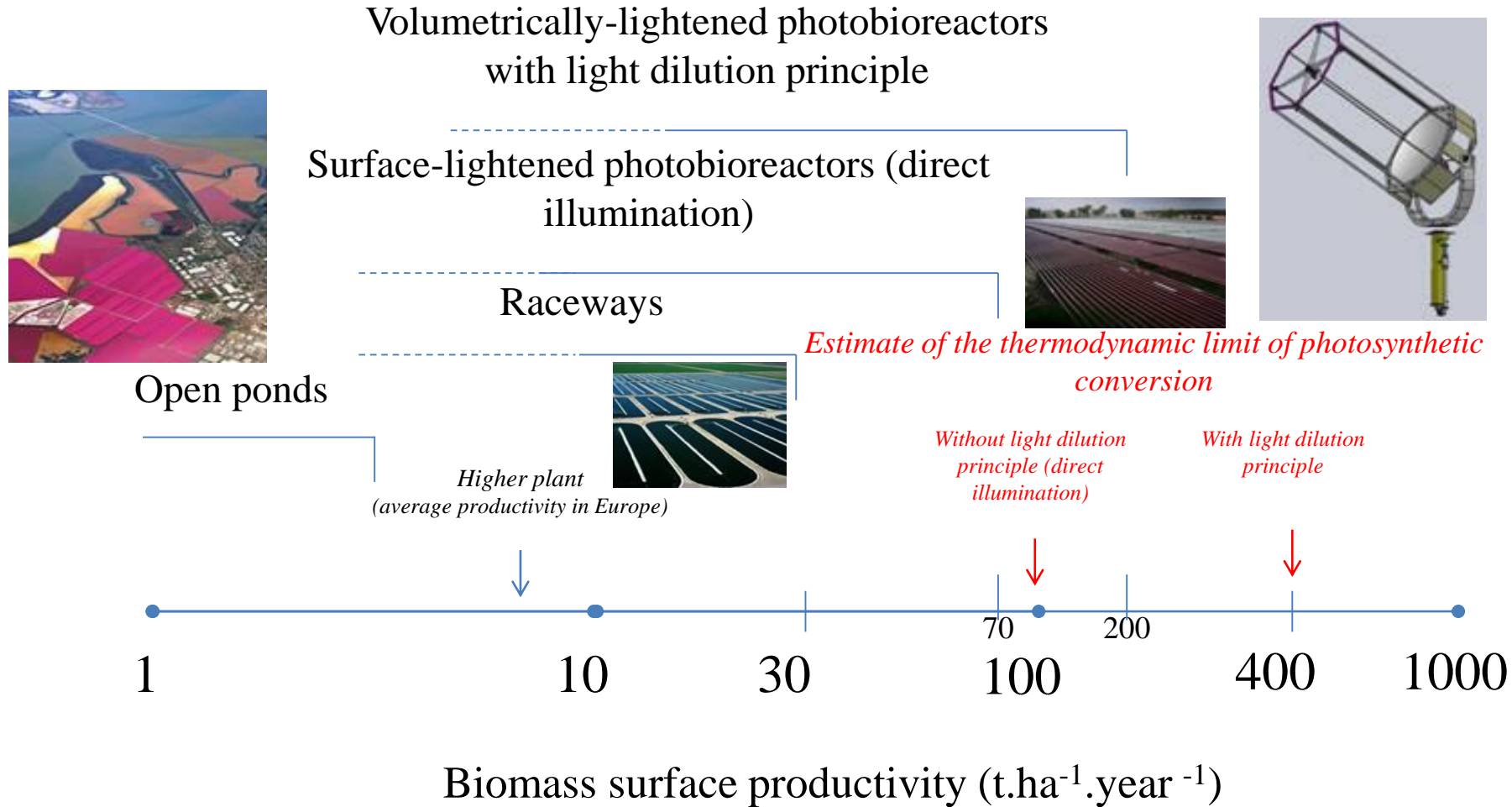
$$\langle P_S \rangle_{max} \propto \ln\left(1 + \frac{q}{K}\right)$$

Fix the area requested for a given production

- Function of the photosynthetic conversion yield (and so of the PFD)
- Can only be increased by using light dilution principle



Areal biomass productivity



10t/ha/year : 2.7g/m²/day
 100t/ha/year : 27g/m²/day
 400t/ha/year : 110g/m²/day

The potential of microalgal culture for CO₂ mitigation

Example for the mitigation of 1ton of CO₂ per day

Production system	q _o (μmoles photons/m ² .s)	V (m ³)	S (ha)
Plants (agricultural field – European average)	400	--	37
Microalgae (state-of-the-art PBR)	400	2500	2,5
Thermodynamic limit (maximum photosynthetic conversion yield)	400	--	0,5-0.6

3 000 t of CO₂ per day (1 000 000 t/year*)

S (ha)
111 000**
7 500***
1500 - 1800

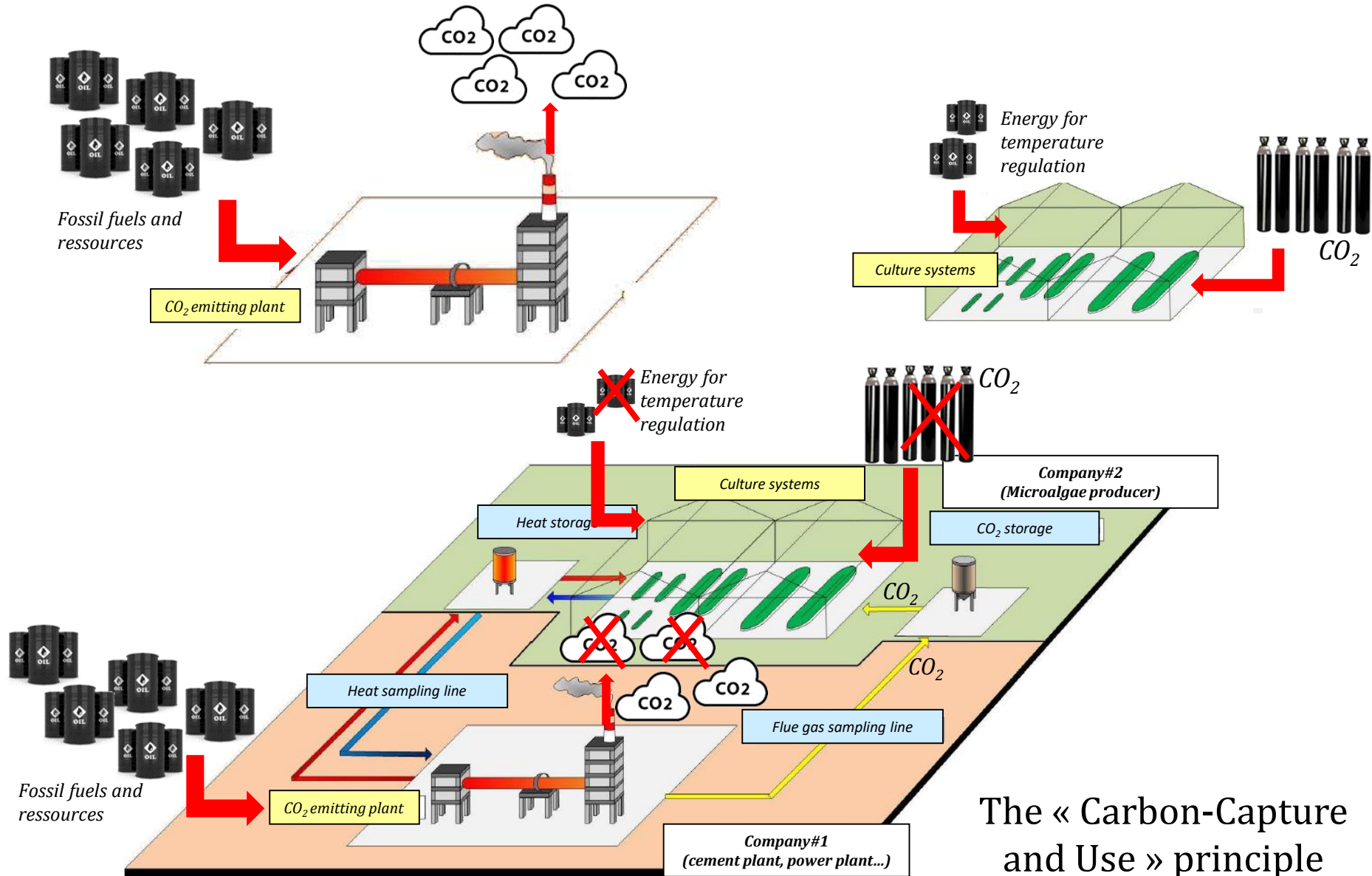
*Middle size oil refinery emission (Donges, Feyzin,)

** 16% of Loire Atlantique area or 160 000 soccer fields

*** 1% of Loire Atlantique area or 11 000 soccer fields

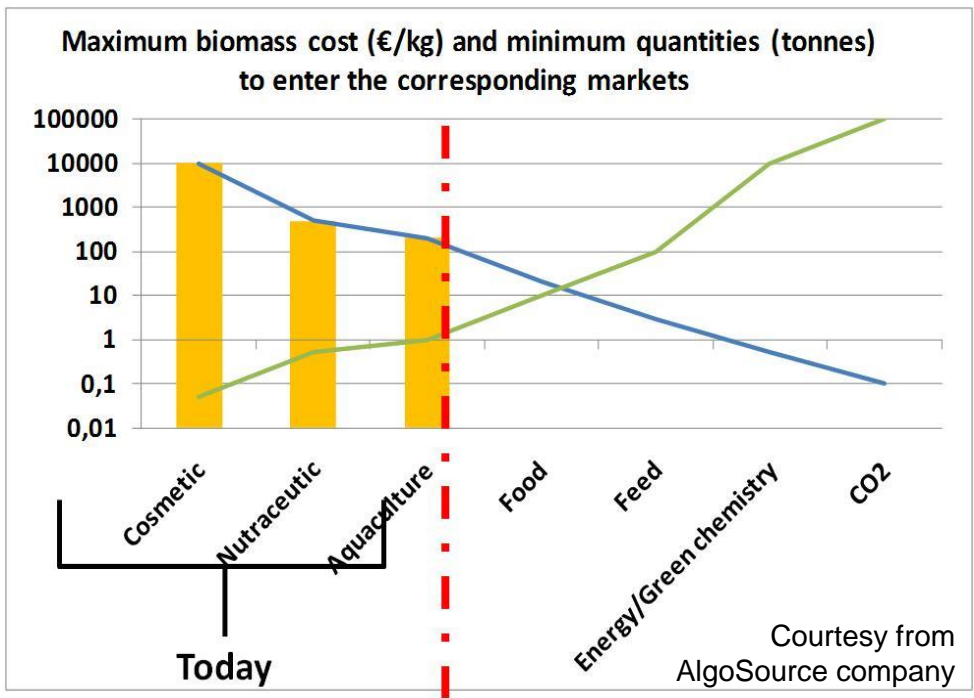
- Microalgae allows achieving highest yields (but at best, 2 orders of magnitude are covered)
- Mitigation of CO₂ industrial emission by biological means involves huge surface (because emissions are huge!)
- The main interest of microalgae is for biological CO₂ valorisation (in the perspective of alternative petro-based products)

Microalgae in circular economy (« waste-to-value » approach)



The « Carbon-Capture and Use » principle

Industrial exploitation of microalgae – the cost/scale issue



« Scientists study the world as it is,
engineers create the world that never has been »
Theodore von Karman

- Main issues of the algae industry:
- Cost of production
 - Scale-up issues
 - Robustness of industrial production
 - Available technologies
 - Identification of new markets and applications
 - Regulation

Potential uses in various sectors... but moderate industrial exploitation (worldwide production around 20-30 kT/year → the current cereals production obtained in 4 minutes!)

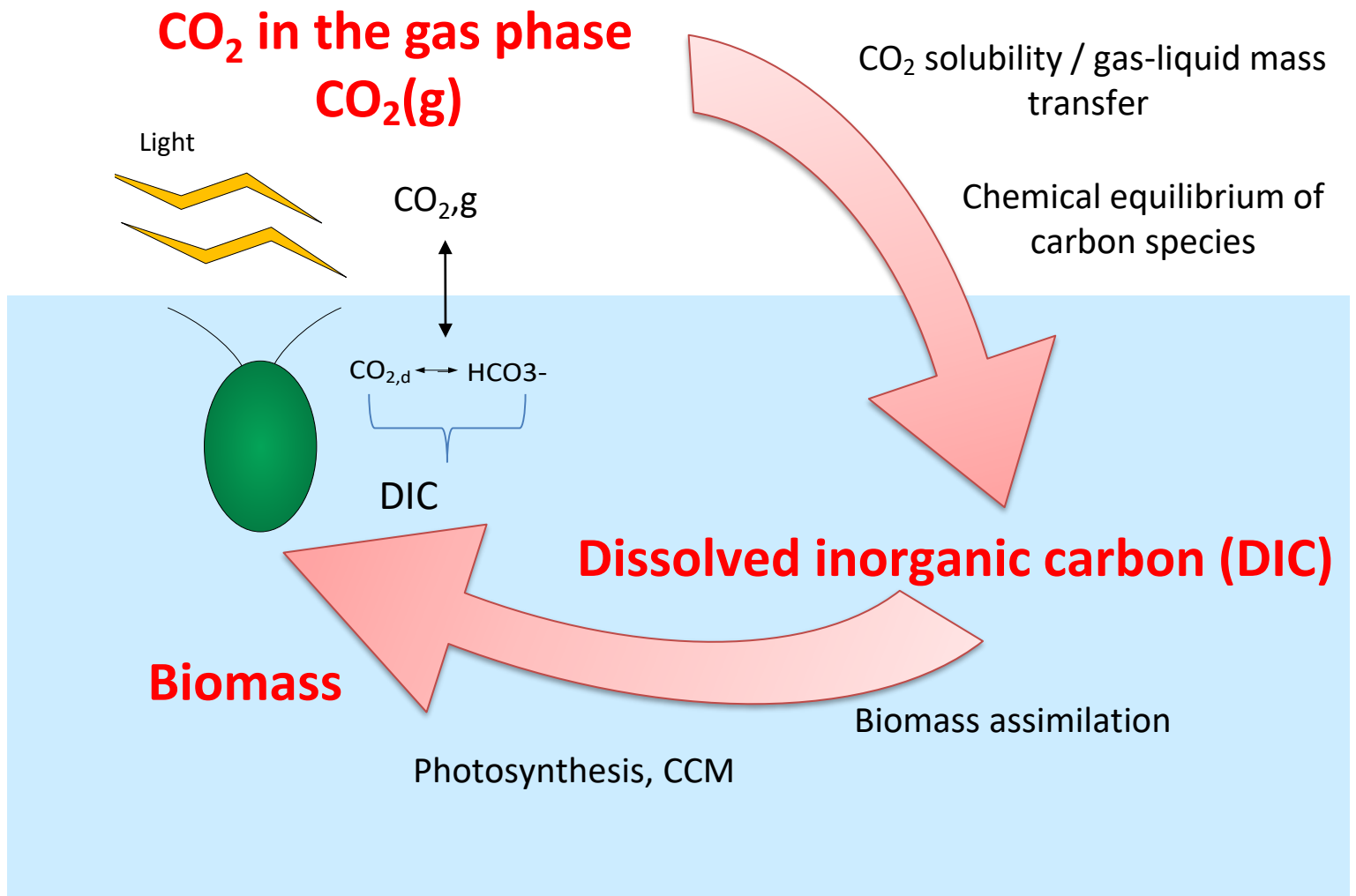
In practice ?

Carbon assimilation by microalgae : main aspects

An important remark:
Only dissolved carbon is assimilated (aqueous micro-organisms)

↓

Dissolved inorganic carbon (DIC) is the main parameter (and not %CO₂ in the gas phase)

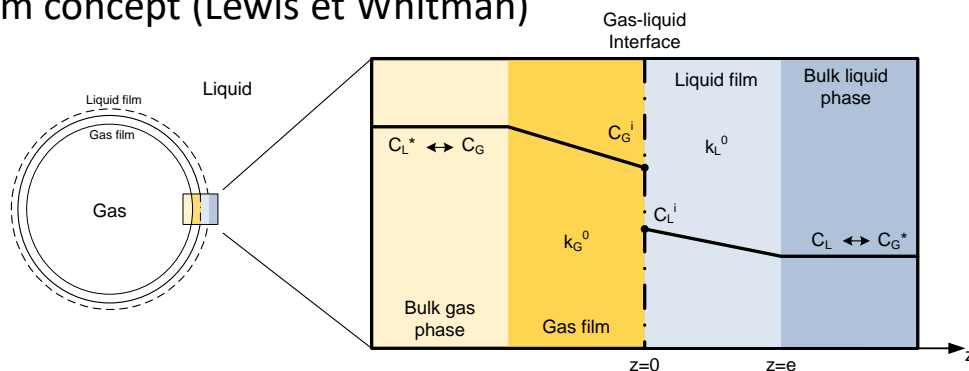


Carbon assimilation by microalgae : main aspects

CO₂ gas-liquid mass transfer

Gas-liquid mass transfer

Two-film concept (Lewis et Whitman)



CO₂ poorly soluble in water



Diffusion of CO₂ in liquid is 4 orders of magnitude slower than in the air

$$a \cdot N_A = k_L a \cdot (\Delta C)$$

Mass transfer coefficient

Driving force

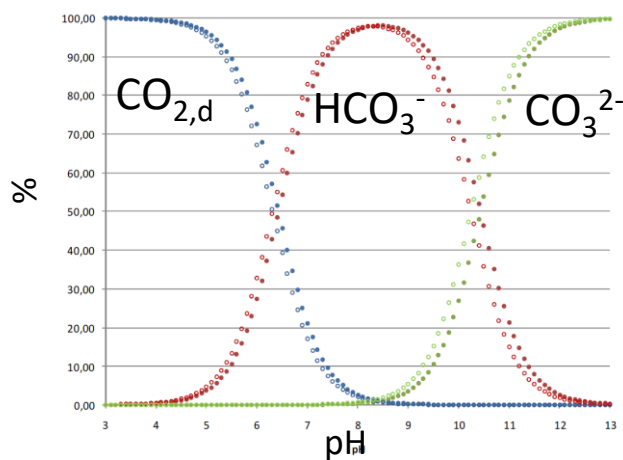


Function of the cultivation system/injection device

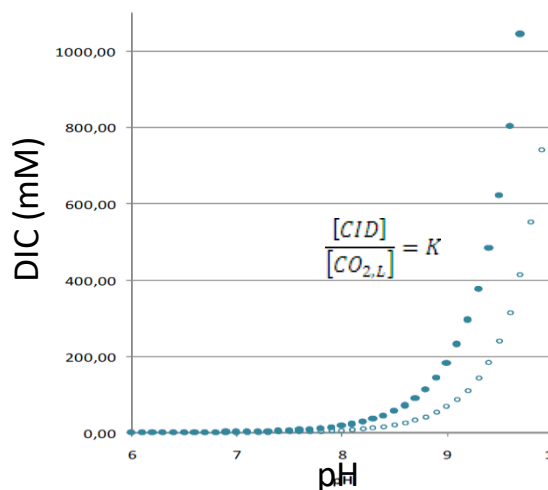


Influenced by %CO₂ and DIC

Carbon dissociation in liquid phase



Carbon species evolution as a function of pH value



Total DIC evolution as a function of pH value

The pH value is a key parameter of available DIC

Carbon assimilation by microalgae : main aspects

Mass balance in the gaseous phase

$$a \cdot N_{CO_2} = \frac{G}{V_L} \cdot \Delta y_{CO_2}$$

$$\Delta y_{CO_2} = y_{CO_2}^i - y_{CO_2}^o$$

Gas-liquid mass transfer

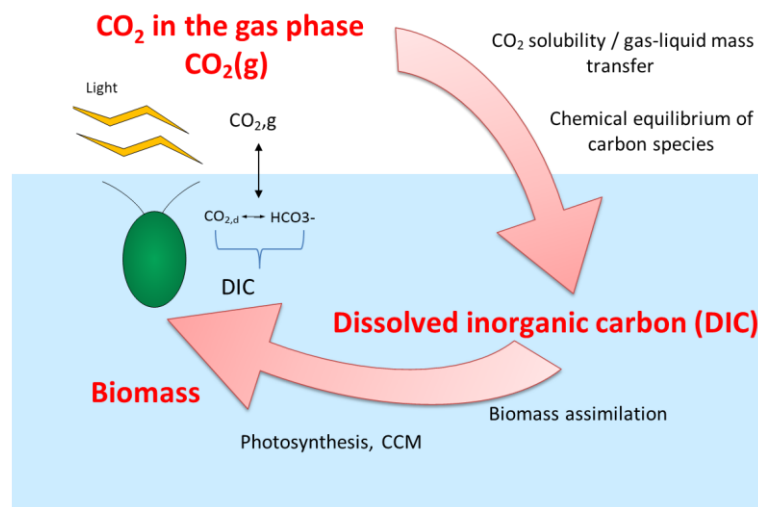
$$a \cdot N_{CO_2} = k_L a \left(C_{CO_2,L}^* - \frac{C_T}{K} \right)$$

$$C_{CO_2,L}^* = \frac{y_{CO_2}^o \cdot P}{H}$$

pH evolution

$$\text{pH} = -\log(C_{H^+})$$

$$\sum z_i C_{cations} = \sum z_j C_{anions}$$



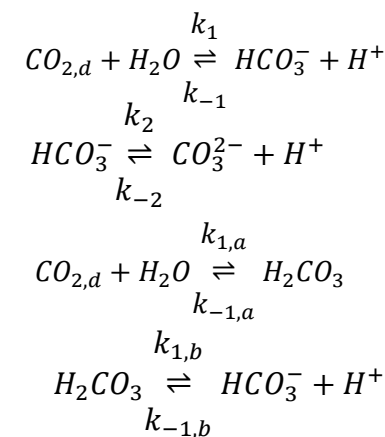
Mass balance in the liquid phase

$$\frac{dC_T}{dt} = a \cdot N_{CO_2} + \frac{(C_T^i - C_T)}{\tau_p}$$

without biological fixation
(i.e. carbonatation)

$$\frac{dC_T}{dt} = k_L a \left(C_{CO_2,L}^* - \frac{C_T}{K} \right) - \langle r_{CO_2} \rangle + \frac{(C_T^i - C_T)}{\tau_p}$$

with biological fixation



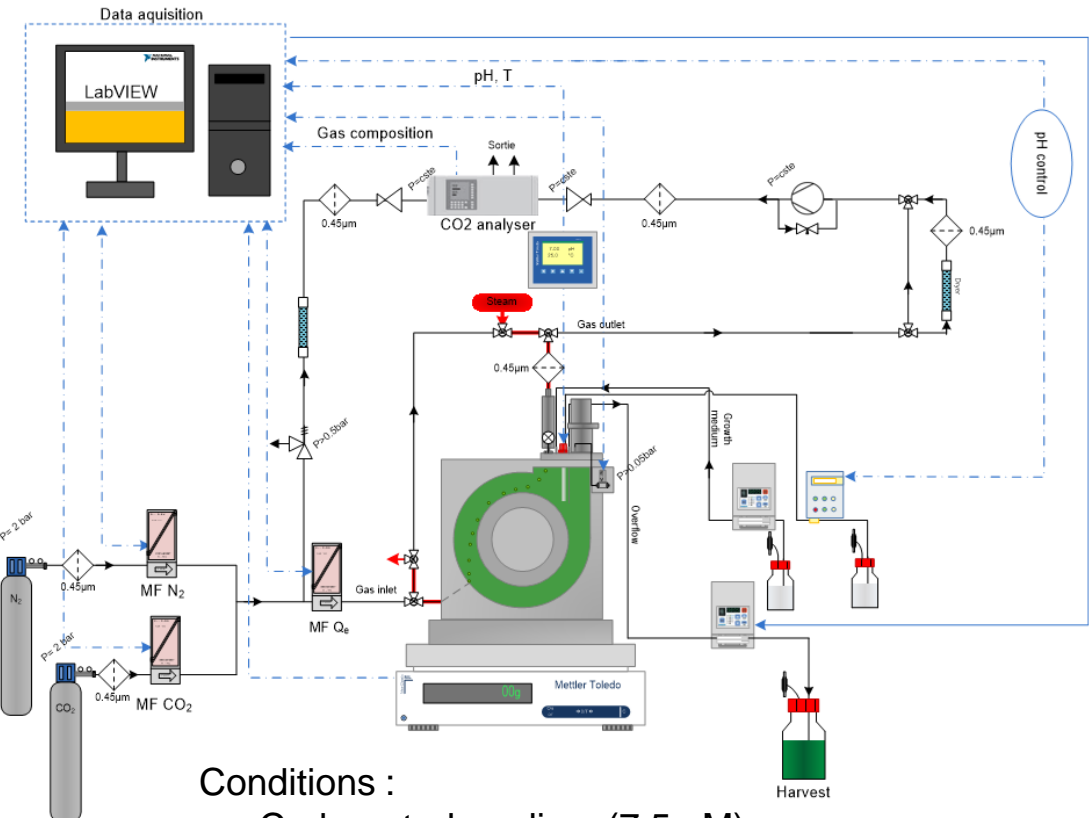
$$C_T = C_{CO_2,L} + C_{HCO_3^-} + C_{CO_3^{2-}}$$

$$C_T = K \cdot C_{CO_2,L}$$

$$K = 1 + \frac{K_1}{C_{H^+}} + \frac{K_1 \cdot K_2}{C_{H^+}^2}$$

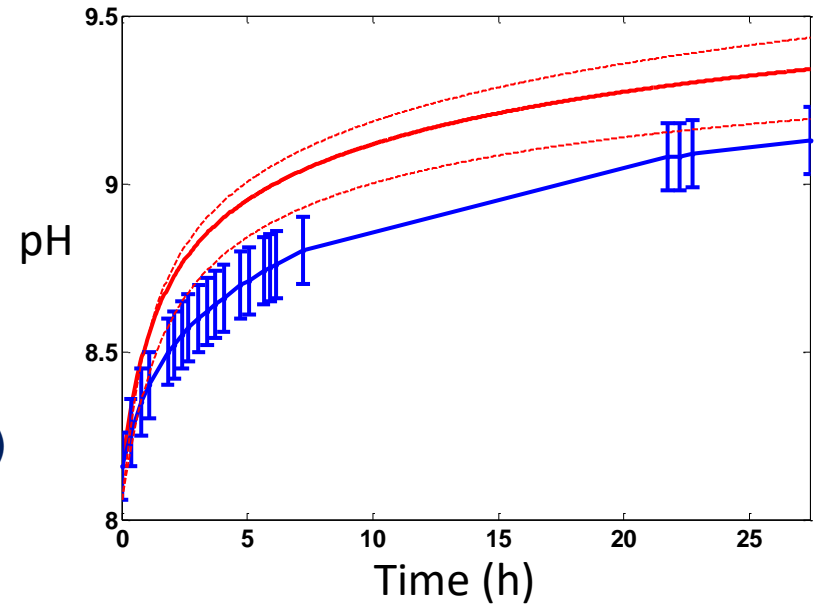
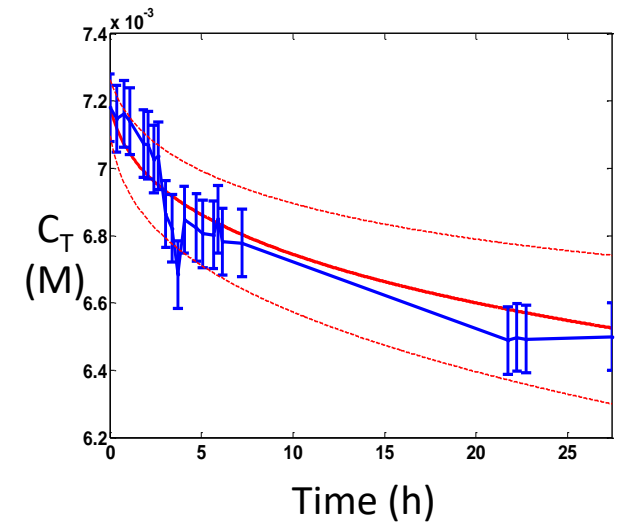
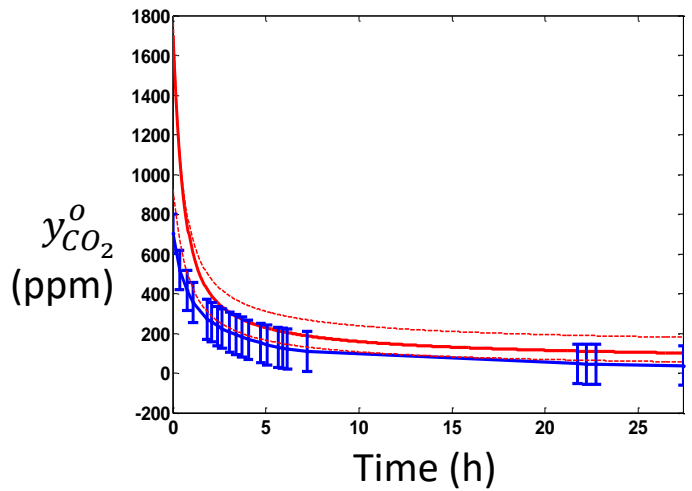
$$\begin{cases} \frac{dC_{CO_2,L}}{dt} = \frac{1}{K} \cdot a \cdot N_{CO_2} \\ C_{HCO_3^-} = \frac{K_1 \cdot C_{CO_2,L}}{C_{H^+}} \\ C_{CO_3^{2-}} = \frac{K_2 \cdot C_{HCO_3^-}}{C_{H^+}} \end{cases}$$

Carbon desorption without pH regulation in photobioreactor



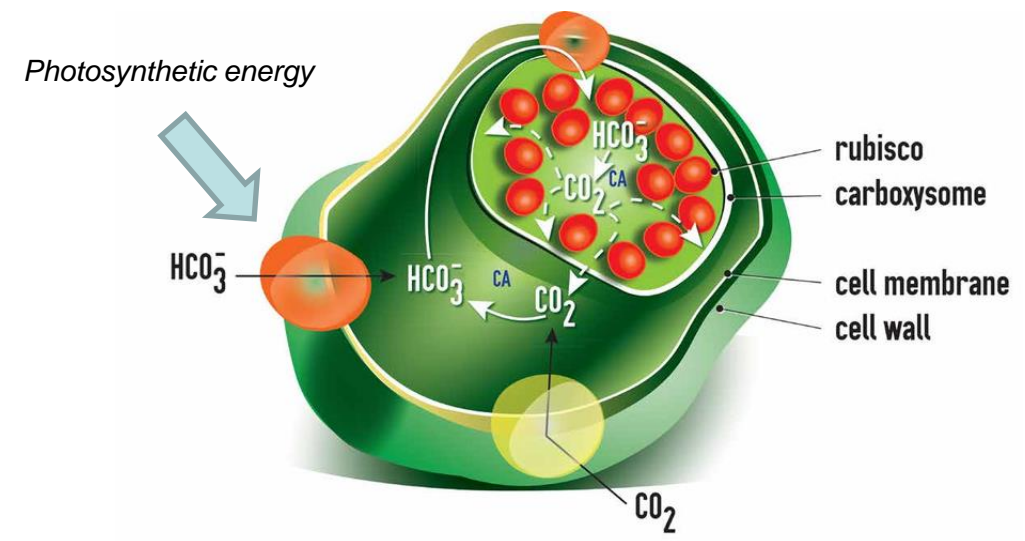
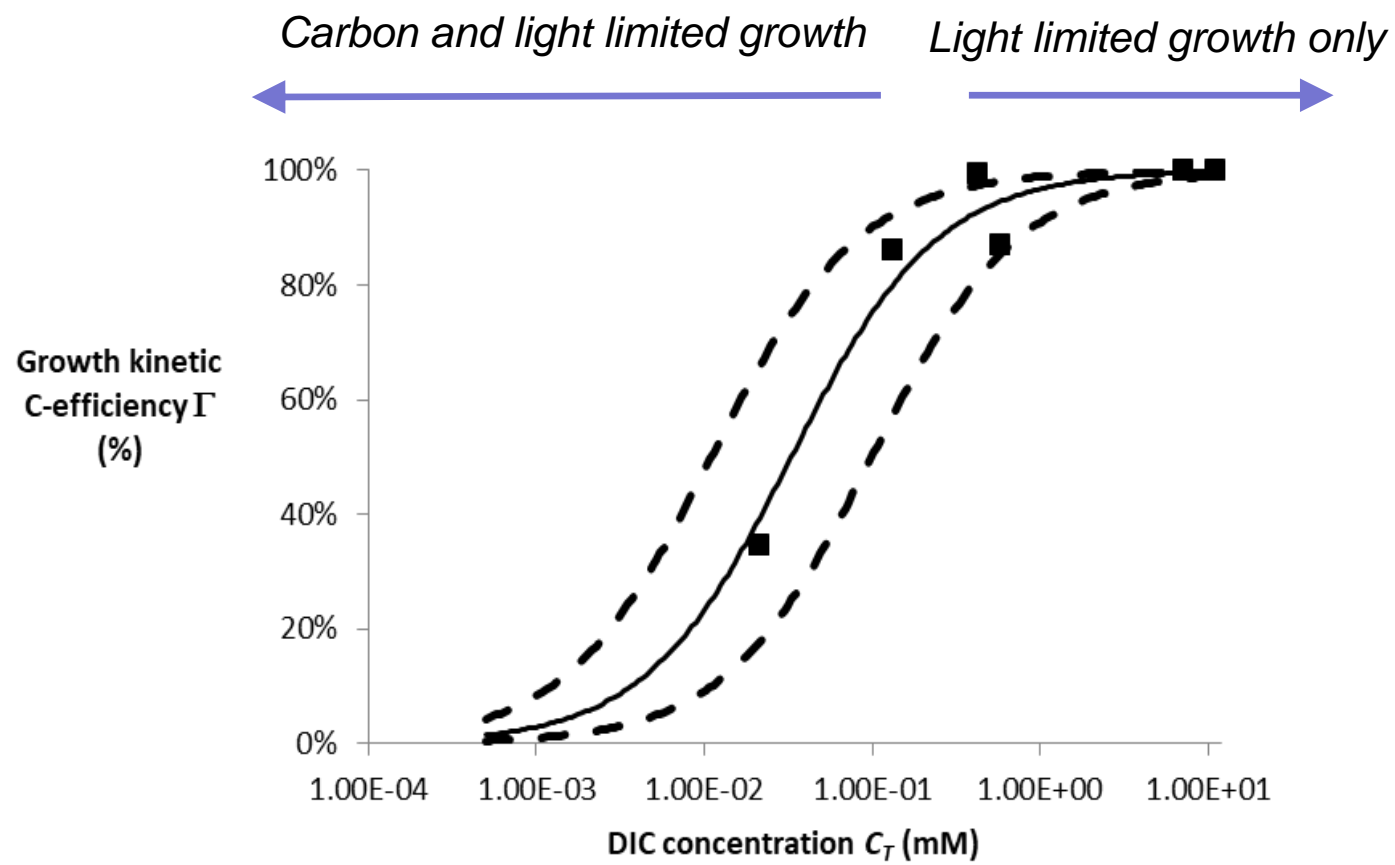
Conditions :

- Carbonated medium (7.5mM)
- Air bubbling (0.07vvm), no pH regulation (similar to flask conditions)



- Bubbling air in a photobioreactor leads to a quick rise in pH value (pH>9)
- Carbon desorption occurs (but at a lower kinetics)
- Conditions can be predicted with accuracy by the model (small deviation for pH, but pH is usually regulated in practice)

Carbon-limited growth (cellular level)



Carbon concentrating mechanism (CCM)

Can be represented by Monod-type relation (in first instance)

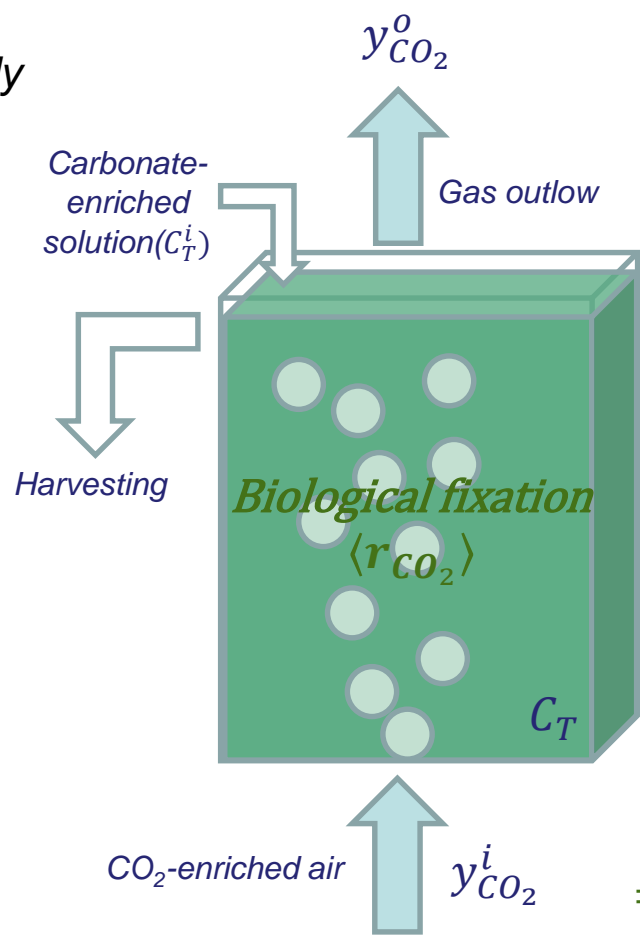
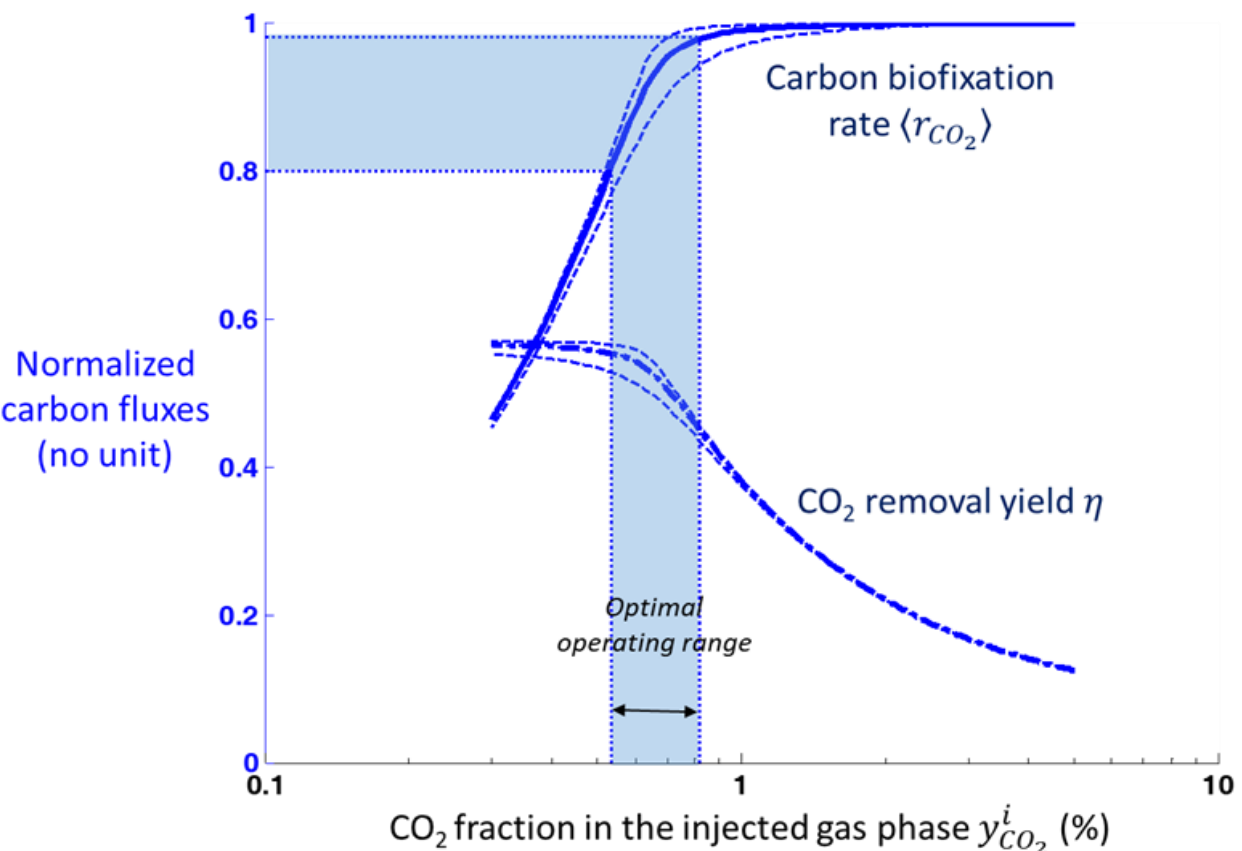
$$\langle r'_X \rangle = \langle r'^{LL}_X \rangle \left(\frac{C_T}{C_T + K_{DIC}} \right)$$

Resulting growth rate Growth rate for light-limited condition (only)

Carbon limitation

Carbon-limited growth (bioprocess level)

Carbon and light limited growth Light limited growth only



Removal yield η :

$$\eta = \frac{y_{CO_2}^i - y_{CO_2}^o}{y_{CO_2}^i} = \frac{\Delta y_{CO_2}}{y_{CO_2}^i}$$

% of gaseous CO₂ transferred into the culture system for either biomass synthesis or accumulation in the liquid phase

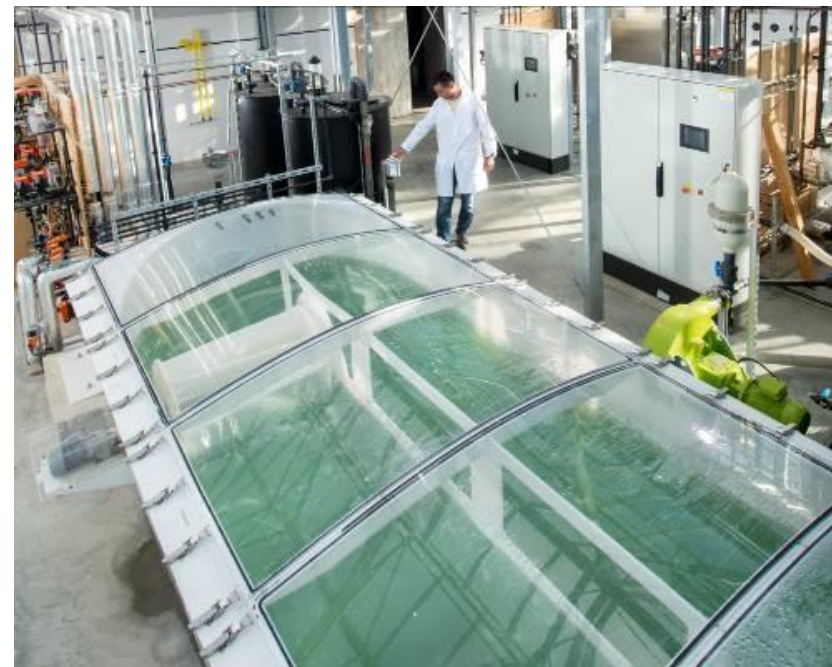
CO₂ biofixation rate $\langle r_{CO_2} \rangle$:

$$\begin{aligned} \langle r_{CO_2} \rangle &= \frac{Y_{CO_2/X}}{M_{CO_2}} \langle r'_X \rangle \\ &= \frac{G}{V_L} \cdot (y_{CO_2}^i - y_{CO_2}^o) + \frac{(C_T^i - C_T)}{\tau_p} \end{aligned}$$

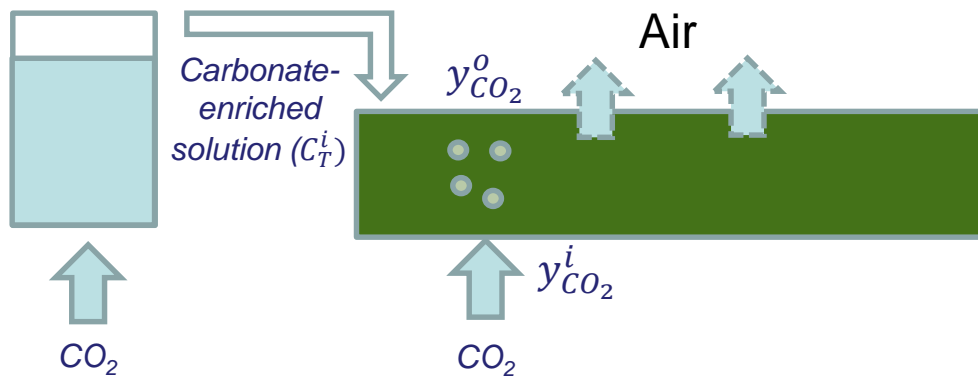
- CO₂ natural air content is in most cases not sufficient to avoid growth limitation by the carbon source
- Increasing the CO₂ supply avoid from growth limitation up to limit of biofixation rate which is light-limited.....then CO₂ removal yield decreases...

Optimal operating range: maximisation of CO₂ removal yield with carbon biofixation close to maximal value

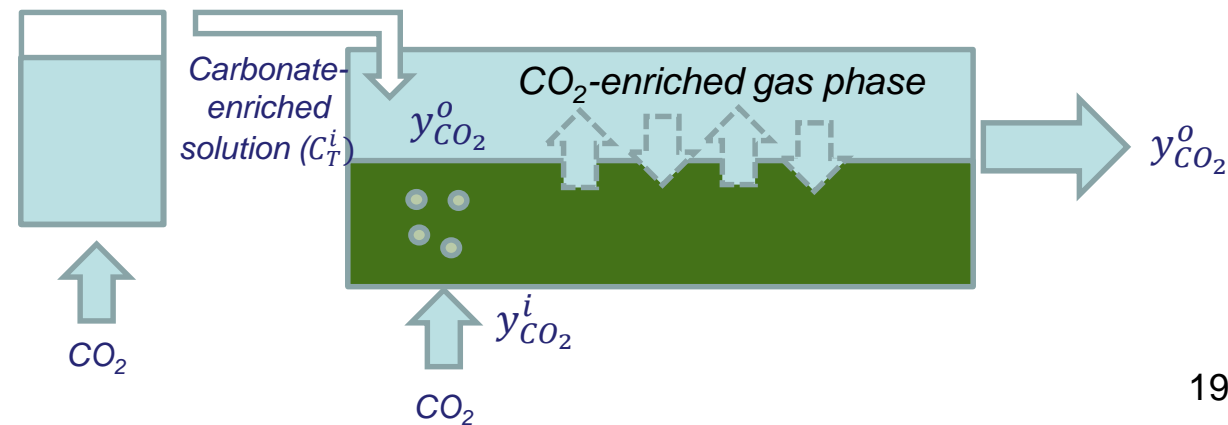
Open vs covered raceways



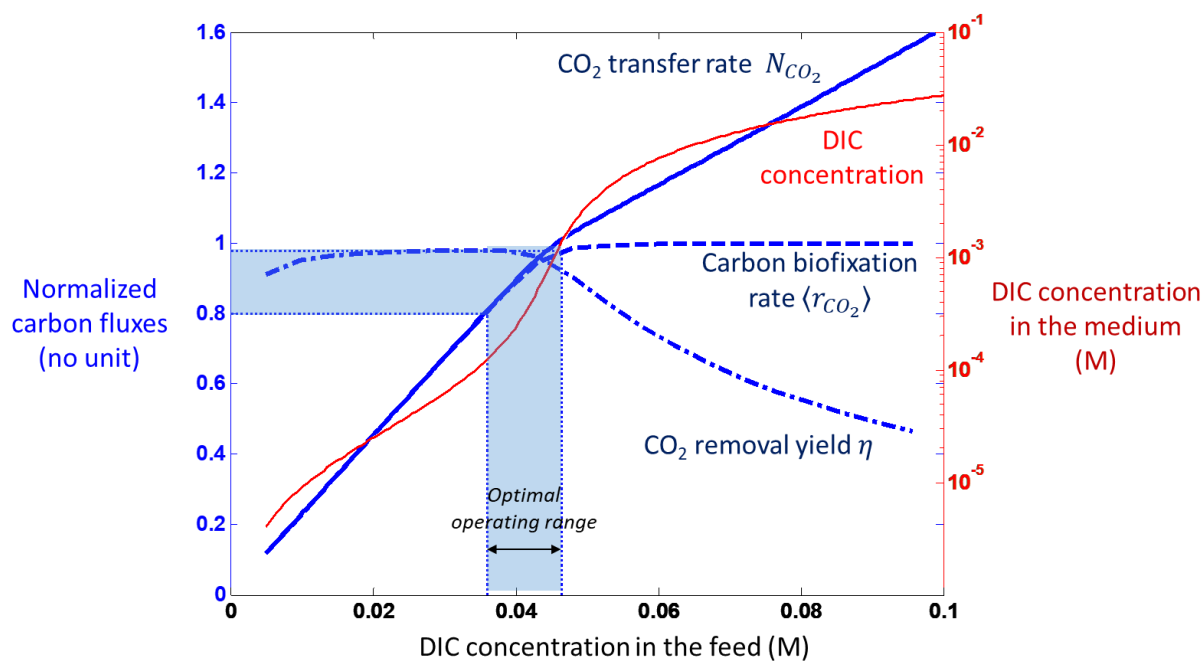
Open system fed with air (0.38% CO₂)



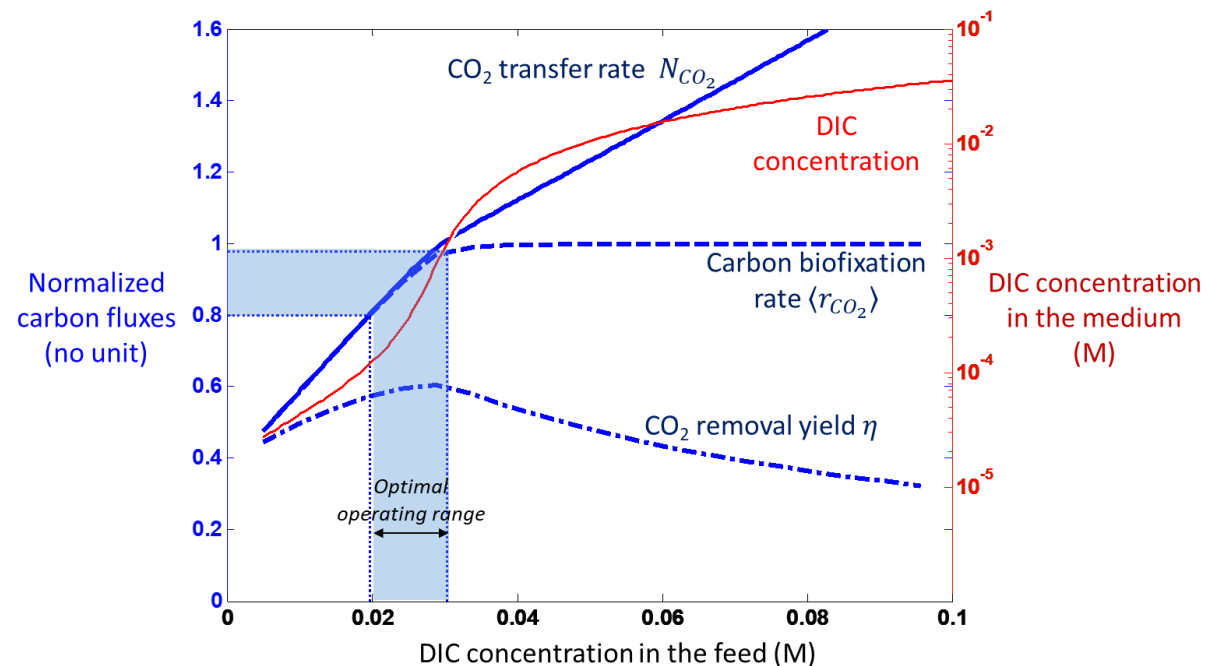
Covered raceway fed with CO₂-enriched gas (2%)



Open vs covered raceways



Open system fed with air (0.38% CO₂)



Covered raceway fed with CO₂-enriched gas (2%)

Benefits of covered raceways:

- Greater performance in CO₂ removal yield (60-80%) compared to airlift PBR (10 - 40%)
98% in CO₂ removal yield with an open system but with the need of precarbonatation to avoid from strong growth limitation
- Lower need in precarbonatation compared to open raceway (10 mM with 4% CO₂ in the gas phase vs 40mM)
Without pre-carbonation, the injection of a gas enriched with CO₂ at a minimum rate of 5.7% needed to achieve non-limiting growth conditions in a covered raceway ($k_L a = 0.5 \text{ h}^{-1}$)

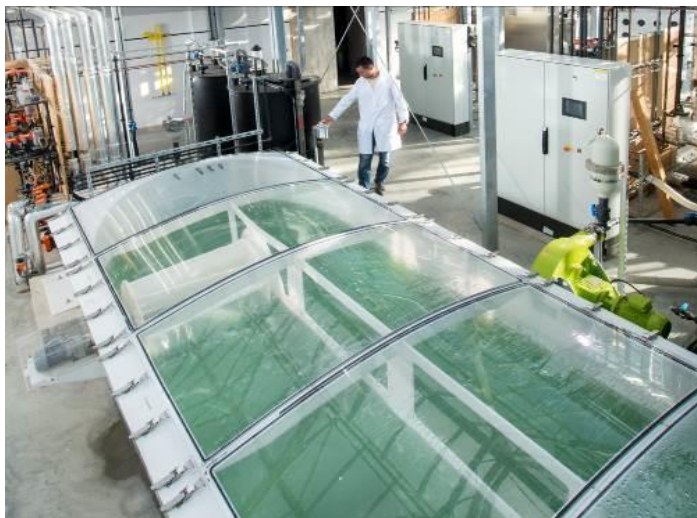
Strategies for the optimization of biological valorisation of CO₂ flue gas

Case study: Covered raceway

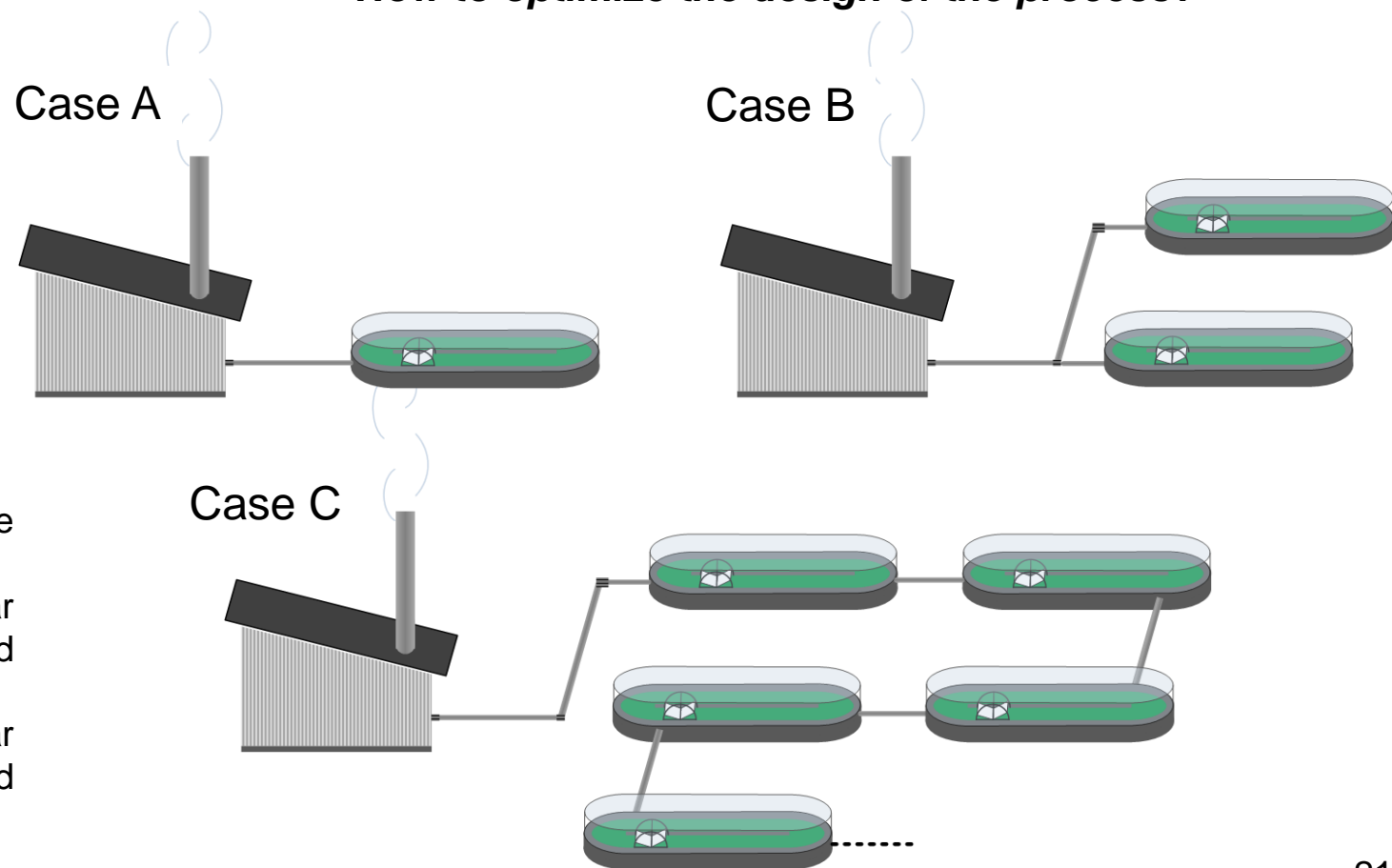
Flue gas flow rate 1000 L.min⁻¹,

16% CO₂, $k_La = 0.5 \text{ h}^{-1}$

A 16% of CO₂ enrichment (typical CO₂ content in flue gas) leads to a DIC concentration of around 80 mM at equilibrium, which is very large compared to biological growth limitation (<10mM)



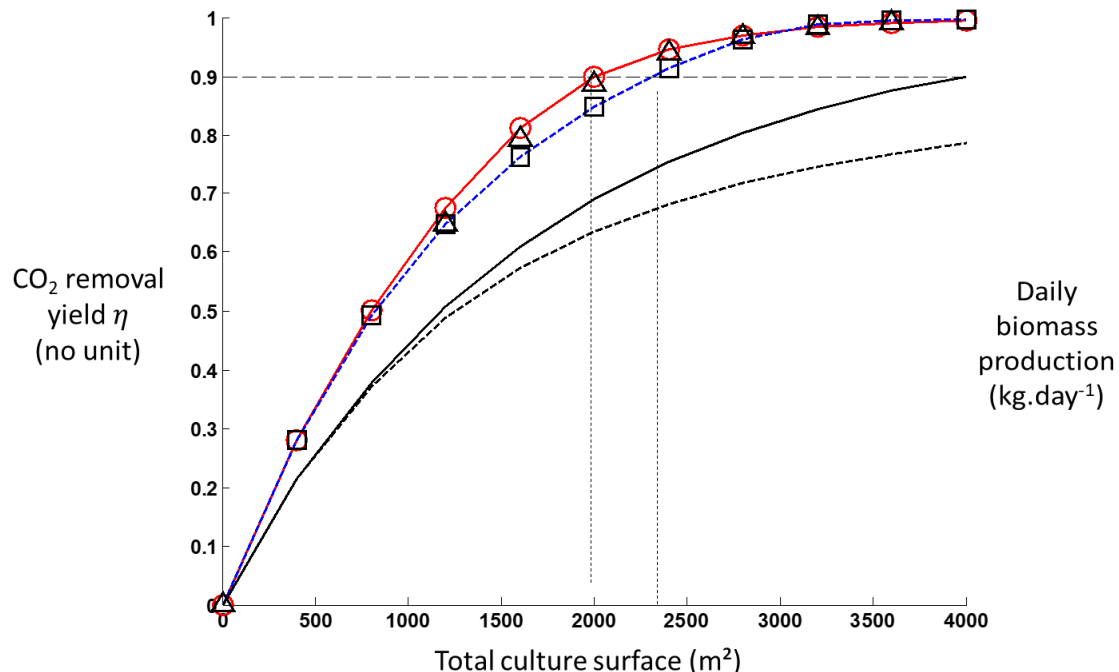
How to optimize the design of the process?



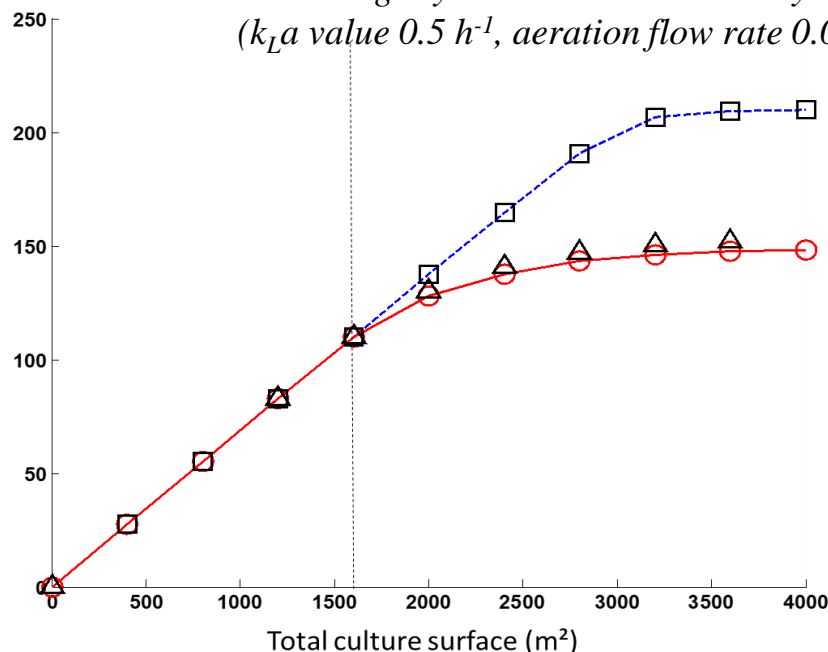
Scenarios investigated:

- Case A - Normal single-system configuration (the reference scenario)
- Case B - Multi-stage system comprising a similar culture system (area 400 m², volume 80 m³) connected in series
- Case C - Multi-stage system comprising a similar culture system (area 400 m², volume 80m³) connected in parallel

Strategies for the optimization of biological valorisation of CO₂ flue gas



Multi-stage systems: covered raceway of 400 m²
($k_L a$ value 0.5 h⁻¹, aeration flow rate 0.025 vvm, total volume 80 m³).



- Single system (dashed blue line)
- Multi-stage system comprising covered raceways connected in series (solid red line) and in parallel (black squares).
- Systems without biological fixation (i.e. no algae) (solid black line for the multi-stage system in series; dashed black line for the single system).

Multi-stage system in parallel vs single system :

- Same performances but with benefits in terms of operation for multi-stage system in parallel

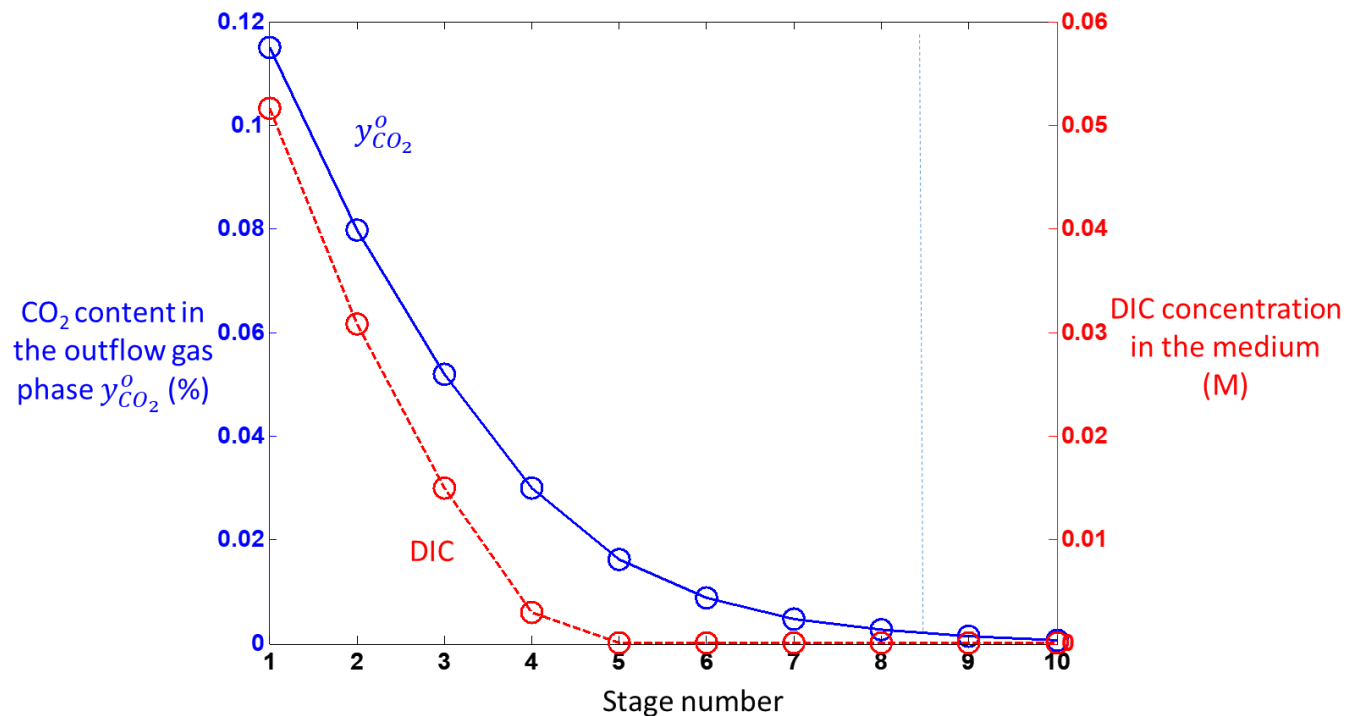
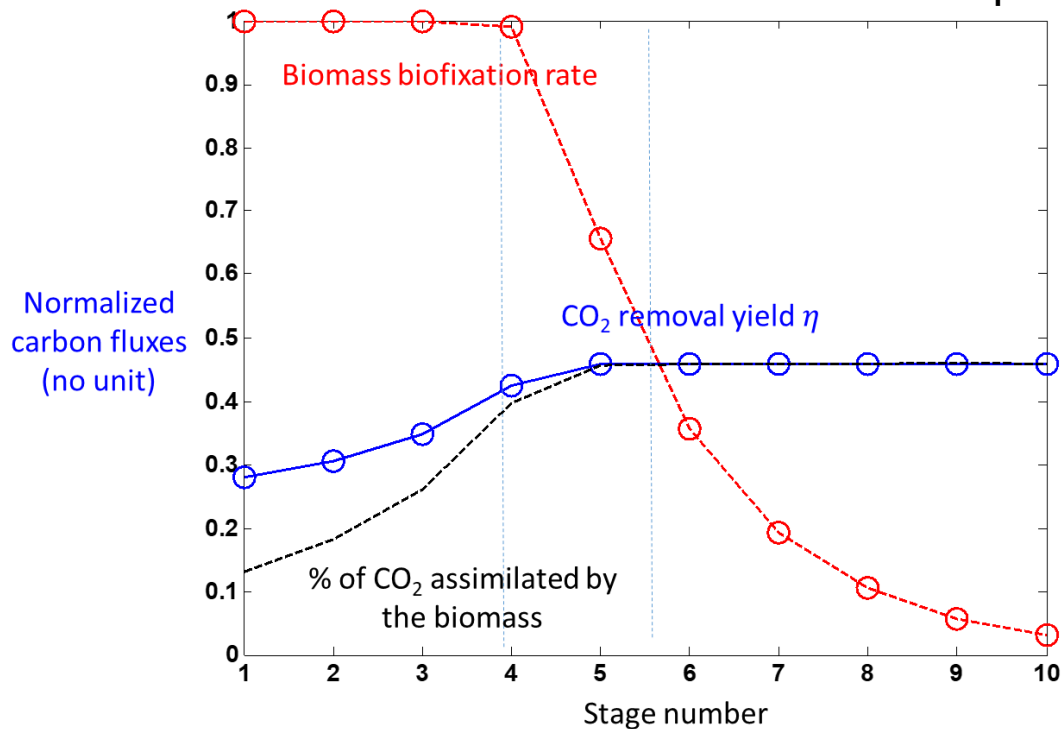
Multi-stage system in series vs single system:

- Less surface needed for 90% removal, less biomass produced
- More advantageous for limited surface only (<1600m² here)

Culture system	Surface for 90% CO ₂ removal	Maximum daily biomass production
Single-stage system	2400m ²	210 kg.day ⁻¹ with 3600 m ²
Multi-stage system in series	2000m ² (-16%)	140 kg.day ⁻¹ (-33%) with 2000m ² (-44%)
Without microalgae	4000m ² (multi-stage) >10000m ² (single stage)	No biomass produced

In-depth analysis of CO₂ use in multi-stage system

Individual performance of each stage

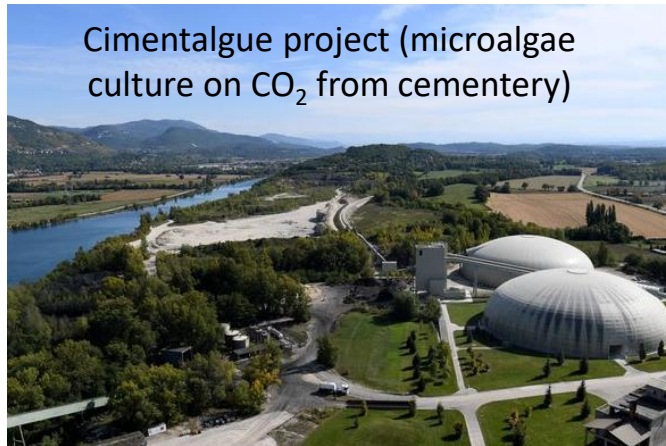


- First three stages : Optimal biomass growth conditions but with low removal yield (28% for Stage #1)
- Stages #5 to #10: Maximum CO₂ removal yield at each stage, allowing further CO₂ euration of the gas phase
But beginning of growth limitationstrong growth limitation but

Four-stage culture system (1600m² total) : Total CO₂ removal yield around 90% with biomass production close to maximum allowed by the 1600m² surface of culture

Integration of microalgal culture in CO₂ emitting sites

The « waste-to-value » approach helps to develop the microalgal industrial production



Cimentalgue project (microalgae culture on CO₂ from cementery)



IN_VIVO _ Paris 13e
Concours Réinventer Paris 2015
BPD Marignan | SNI
XTU architects | MU architecture
Retenu en finale du concours

ALGO_PILOT
CSTB _ Champs-sur-Marne
Pilote industriel de biofaçades
XTU architects | Consortium SymBIO₂
En chantier | Mise en service début 2016



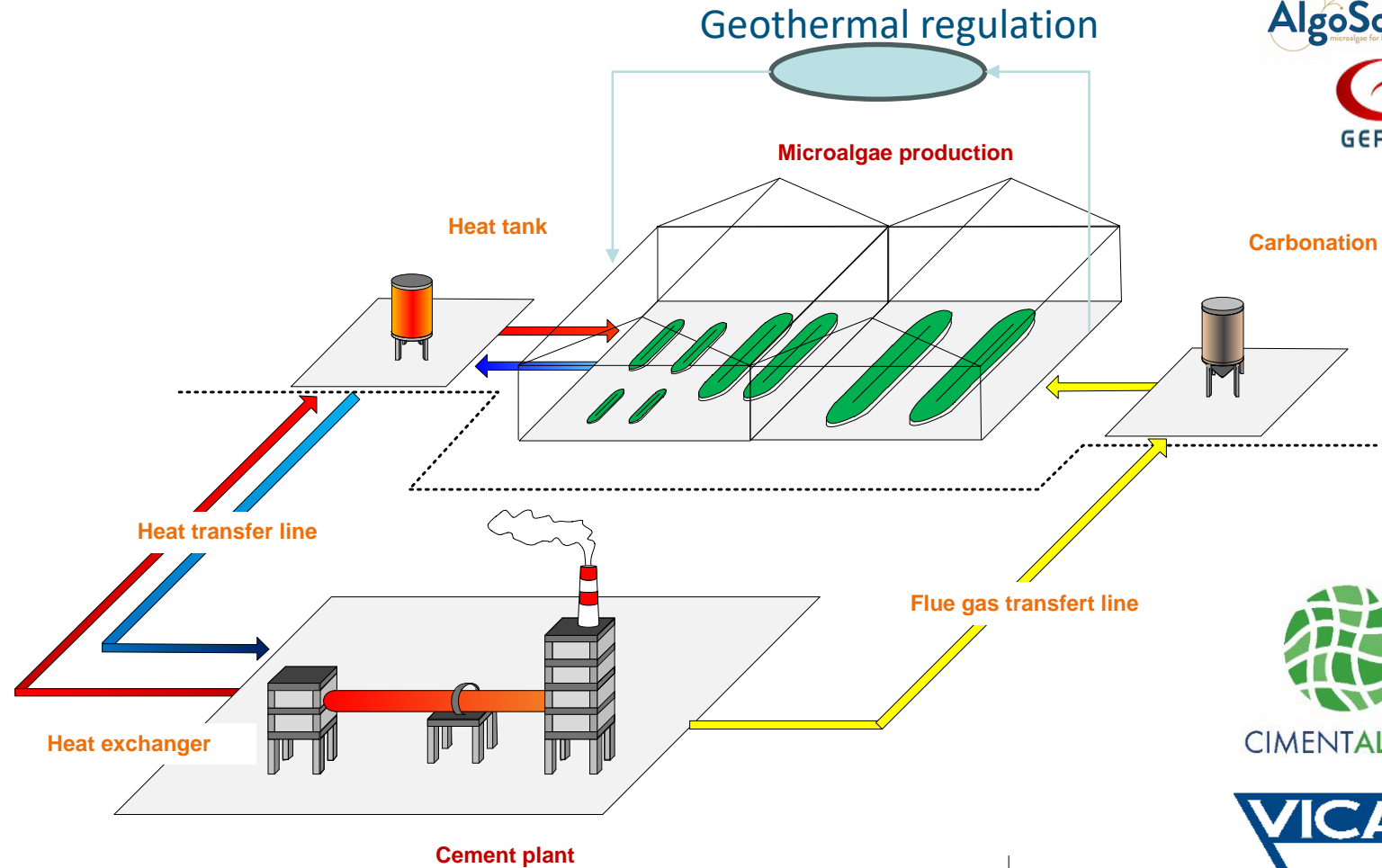
SAVANE project (funding by french ADEME grant PIA3 "Bioéconomie et Protection de l'Environnement")



Develop the microalgae sector in the DOM-TOMs

An industrial ecology project : CIMENTALGUE

- Co-valorization of heat and CO₂
- 800 m² greenhouse



Sustainability of microalgae cultivation

Implementation



Ciment plant Oven



Demonstration unit

Cimenterie VICAT in Montalieu-Vercieu, France



CIMENTALGUE



Uptake of fumes and heat



Projet ADEME « CIMENTALGUE » »



Transfert pipelines
(heat and fumes)





5 open raceways

PBR



closed raceway



Laboratories

- 5 open raceways
- 1 closed raceway
- 1 tubular
- 1 AlgoFilm

Sustainability of microalgae cultivation



- The biological valorization of CO₂ from microalgae should be considered in a circular economy logic, to convert an effluent into a product of interest
- Commodity products (biofuels, bio-based chemistry...) will in principle impose large surface areas
→ the biological valorization of CO₂ is a lever for the expected change in scale of microalgae production
- The cultivation of microalgae on gaseous effluents does not pose a major problem
- The simultaneous optimization of purification and biofixation requires determining specific operating parameters in terms of CO₂ feeding
- Modeling combining chemistry, physics and biology appears to be a relevant tool for developing decision support tools:
 - *Optimization of the operation of culture systems (%CO₂, pre-carbonation, mixing mode)*
 - *Simulations of different installation configurations for gases rich in CO₂*
 - *Simulation of different strains, taking into account implementation conditions (weather, etc.)...*

Links and more infos

About the author (J.Pruvost) :

[Open science \(HAL\)](#) :

[Google Scholar](#)

[Research Gate](#)

[CV \(Nantes University\)](#)

About the lab :

[GEPEA](#)

[AlgoSolis](#)

About education:

[Ecole d'Ingénieurs Polytech Nantes \(dept. Génie des Procédés et Bioprocédés\)](#)

[International Master Degree in Microalgae Bioprocess Engineering](#)

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- AlgoSolis facility : [LinkedIn](#)
- J.Pruvost : [LinkedIn](#)





Atlantic ocean

La Baule

Saint-Nazaire



GEPEA lab. (CRTT)



Polytech'Nantes
Graduate school of the University of Nantes
Process and Bioprocess Engineering



Thank you for your attention.

CO₂ emissions for a microalgae culture: some figures

Example: Production of 1kg of dry Spirulina in France (West)

Source O.Lépine + J.Pruvost
Conf. AlgaEurope 2021

A total of **15 kg CO₂ per kg of Spirulina is emitted*** :

- Electricity: 3 kg CO₂/kg of Spirulina
- Infrastructure and maintenance : 5 kg CO₂/kg of Spirulina
- Nutrients and cleaning products : 7 kg CO₂/kg of Spirulina

* Cultivation from April to October, without thermal regulation, in basins, optimal cultivation conditions, without drying or freezing



For comparison: 1 kg of greenhouse tomatoes in France → **12.5 kg eq. CO₂**

Data for a French electric mix: 0.12 kg eq. CO₂/electric kWh

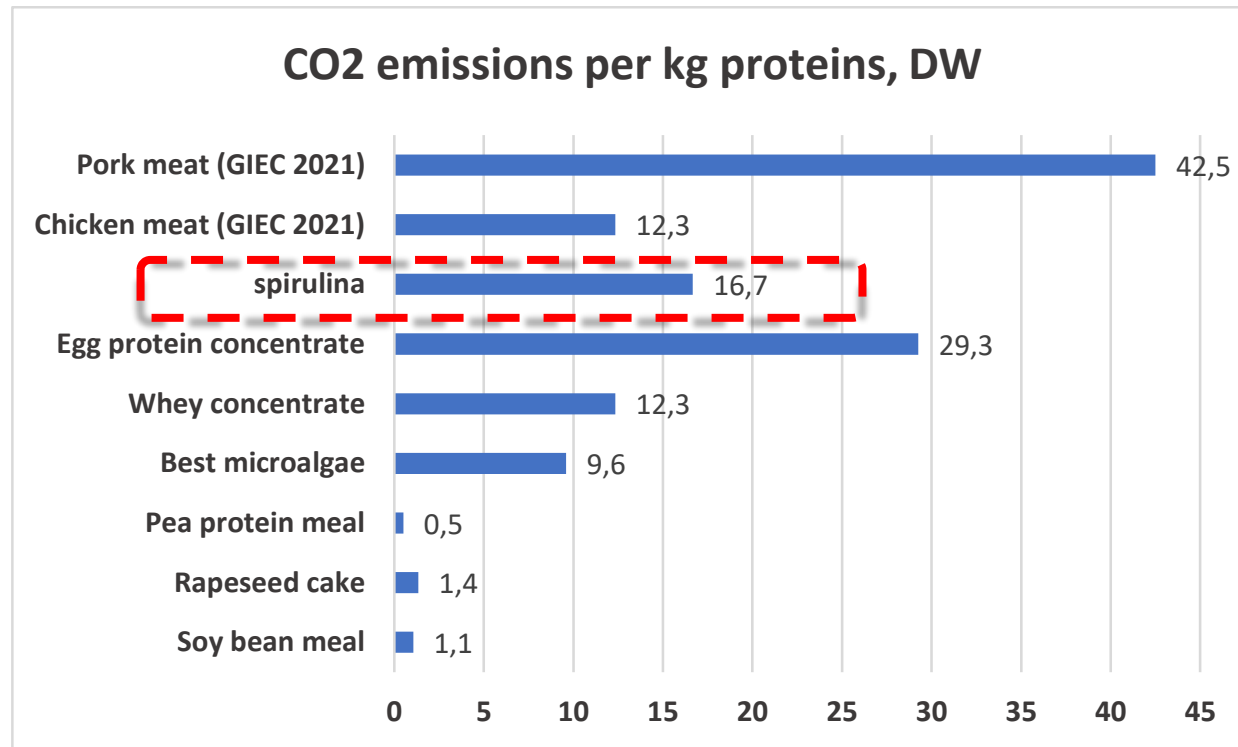
- With the Chinese mix (0.766 kg eq. CO₂/kWh) : 30 kg CO₂/kg of Spirulina
(18 only for electricity)
- With the German mix : 23 kg CO₂/kg of Spirulina

*Note : in artificial light, 1kg of microalgae will need at best 110 kWh of electricity or 12 kg of CO₂ in France
(and not including cooling, equivalent to the electrical energy supplied !)*

An example: CO₂ emissions per kg of protein

One of the challenges of the industrial food transition: **the production of proteins**

Spirulina is one of the biomasses with the highest protein content (60-70%) and is produced by photosynthesis (**1kg of biomass biologically consumes 1.6-1.8kg of CO₂**)



Source O.Lépine + J.Pruvost
Conf. AlgaEurope 2021

The life cycle analysis (LCA) shows that microalgae are not necessarily the best solution... (at the moment)

Algal culture in Qatar: the « Food Security issue »



But this is not the only criterion: issues of land use, in particular non-arable, and security of supply (desert countries):

2 concepts not taken into account in the LCA

Example: Production of 1kg of dry Spirulina in France (West) with industrial ecology

2 major levers:

- **Intensification** makes it possible to reduce the energy requirement by a factor of approximately 100
- **Industrial ecology** makes it possible to use the CO₂ resulting from industrial flue gas and to extend the culture to the whole year (valorization of fatal heat)



A total of **5.3 kg CO₂ per kg of Spirulina is emitted*** (-70% compared to conventional ponds):

- Electricity: 0.3 kg CO₂/kg of Spirulina (-90% / to conventional ponds)
- Infrastructure and maintenance: 2 kg CO₂/kg of Spirulina (-60% / to conventional ponds)
- Nutrients and cleaning products: 3 kg CO₂/kg of Spirulina (-60% / in classic ponds)

* This saves 10 kg CO₂/kg of Spirulina

But, in the end, about 200 tons of CO₂ emitted/ha/year

→ 5 times more than the CO₂ captured in biomass (1.8 kg/kg)

Source O.Lépine + J.Pruvost
Conf. AlgaEurope 2021

Note : Nitrogen becomes the main emitter → use of nitrogen from industrial effluent? → **circular economy concept**