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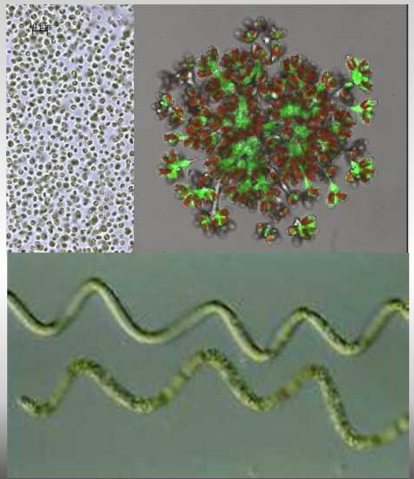
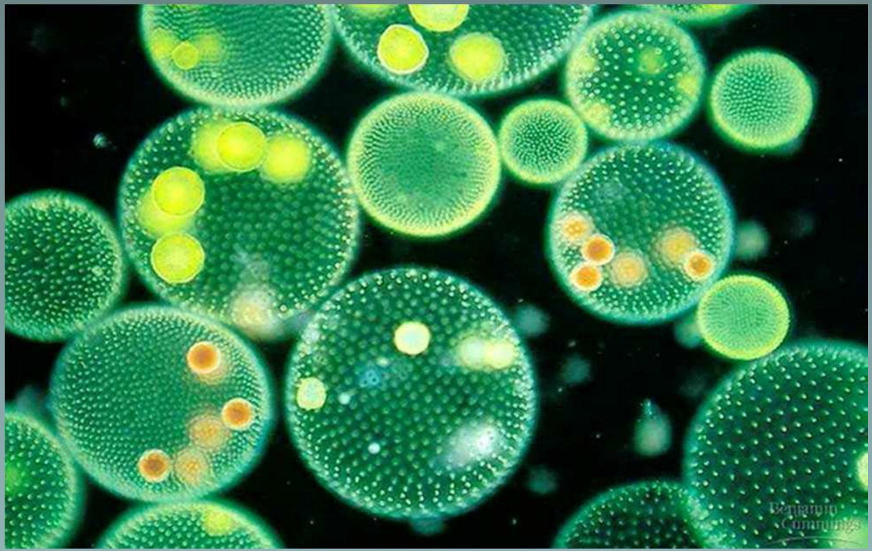
Microalgues et biocarburants : potentiel et enjeux actuels



$$r_X = \rho\phi A - \mu s \frac{K_r}{K_r + G} X = \rho\phi A - \frac{J_{NADH_2} M_X}{\upsilon_{NADH_2 - X}} \frac{K_r}{K_r + G} X$$

Jack LEGRAND, Jérémy PRUVOST



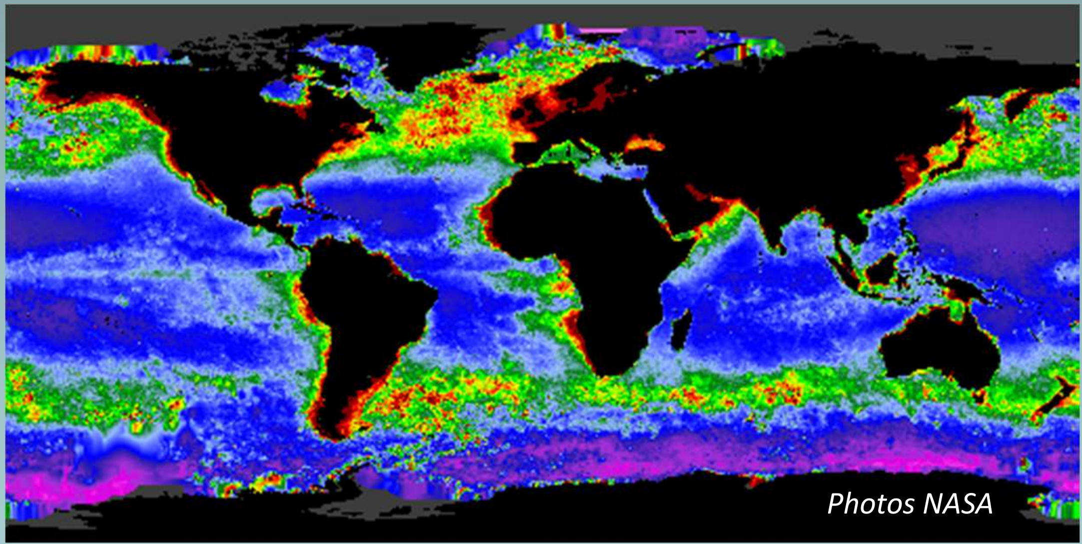
Microalgues, Cyanobacteries

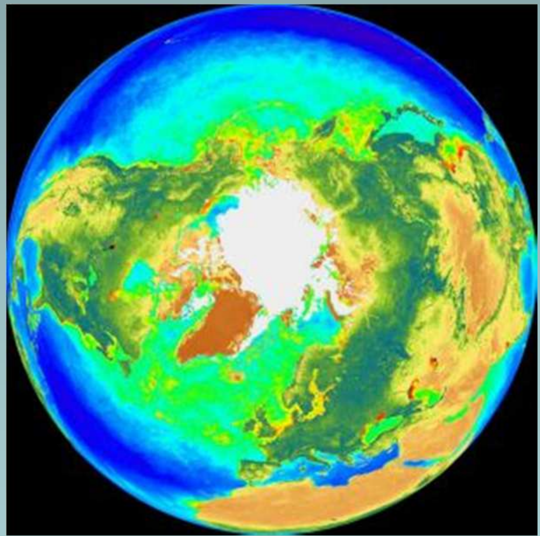
Croissance par photosynthèse :

Milieu entièrement minéral, sans apport d'un substrat organique (organismes autotrophes), par absorption en milieu aqueux des minéraux nécessaires et du **carbone inorganique** environnant grâce à la **lumière captée** .

Les micro-algues et les cyanobactéries

… une biodiversité à peine explorée :
30 000 espèces décrites
200 000 à 1 million estimées

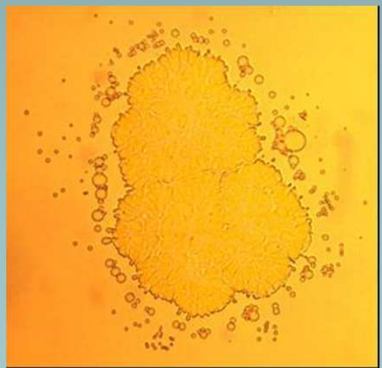




Photosynthèse : - fixation du CO_2
- production d'O_2

Biodiversité

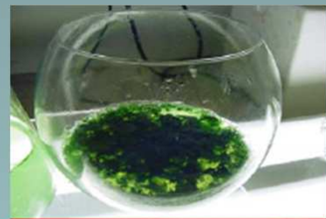
▶ précurseurs de la vie sur terre



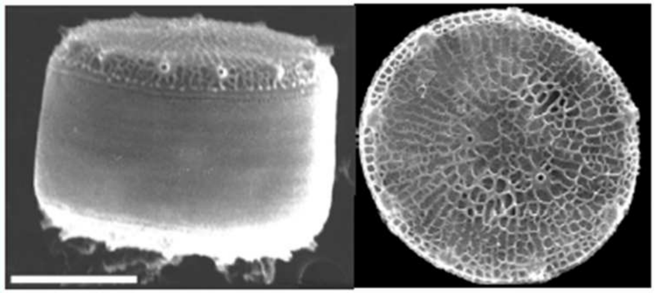
Botryococcus Braunii

Euglena

Cyanobacteria

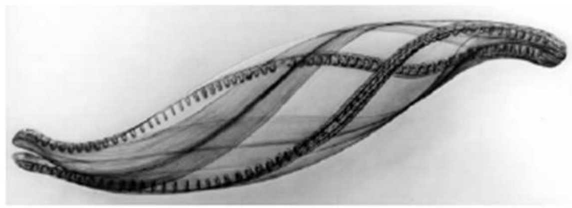


Cyanobacteria



Thalassiosira pseudonana

Phaeodactylum tricornutum



Cylindrotheca fusiformis

Photosynthèse

- Grande diversité (longue évolution)
- Biochimie très variée
- Vitesse de croissance élevée

- Teneur élevée en **protéines**
- **Carbohydrates** : amidon, sucres, glucose, polysaccharides
- **Lipides** : Glycérols, acides gras saturés ou pas (w_3, w_6) (de 1 à 70% de la matières sèche)

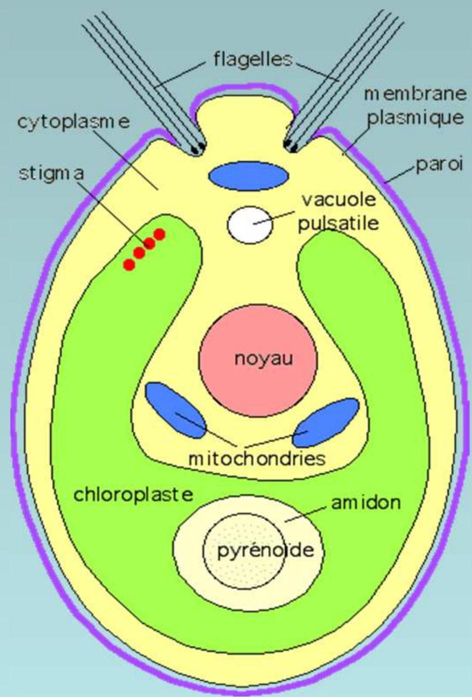
- **Pigments** : caroténoïdes, phycobiliprotéines

Photosynthèse

$$CO_2 + 0.512H_2O + 0.0063MgSO_4 + 0.181NH_4Cl + 0.0213K_2HPO_4 \xrightarrow{h\upsilon} CH_{1.77}O_{0.472}N_{0.181}S_{0.063}P_{0.0213} + 1.0752O_2 + 0.0063Mg + 0.181Cl + 0.0426K$$

1 kg CO_2 ——> 0.6 kg biomasse

Photosynthèse : chloroplaste
Respiration : mitochondrie
Absorption de la lumière : pigments = Chlorophylle + Caroténoïdes)



Systèmes de production

Lumière

Microalgues

Nutriments (chimiques, gaz)

Photobioréacteur

Produits

<u>Paramètres</u> :

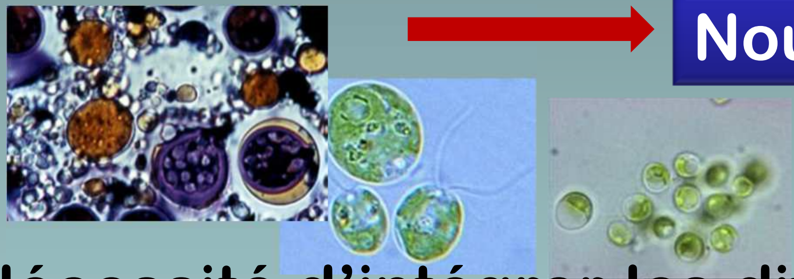
Cinétiques

- **<u>physique</u> : rayonnement, transfert gaz/liquide**
- **<u>chimique</u> : incorporation cellulaire des nutriments**
- **<u>biologique</u> : photosynthèse, métabolisme**

~30 000 tonnes de microalgues sont commercialisées par an

Valorisation industrielle des microalgues

- Biomasse spécifique : milieux aqueux



→ Nouvelle ressource

- Nécessité d'intégrer les différentes étapes

Souches

O_2

Production → Récolte → Biomasse → Extraction → Products

CO_2, nutriments

Effluents

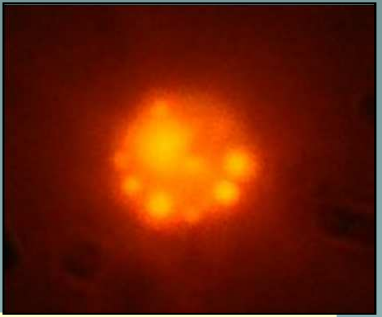
Effluents

Recyclage

Valorisation energétique des microalgues

<u>Différents vecteurs énergétiques</u> :

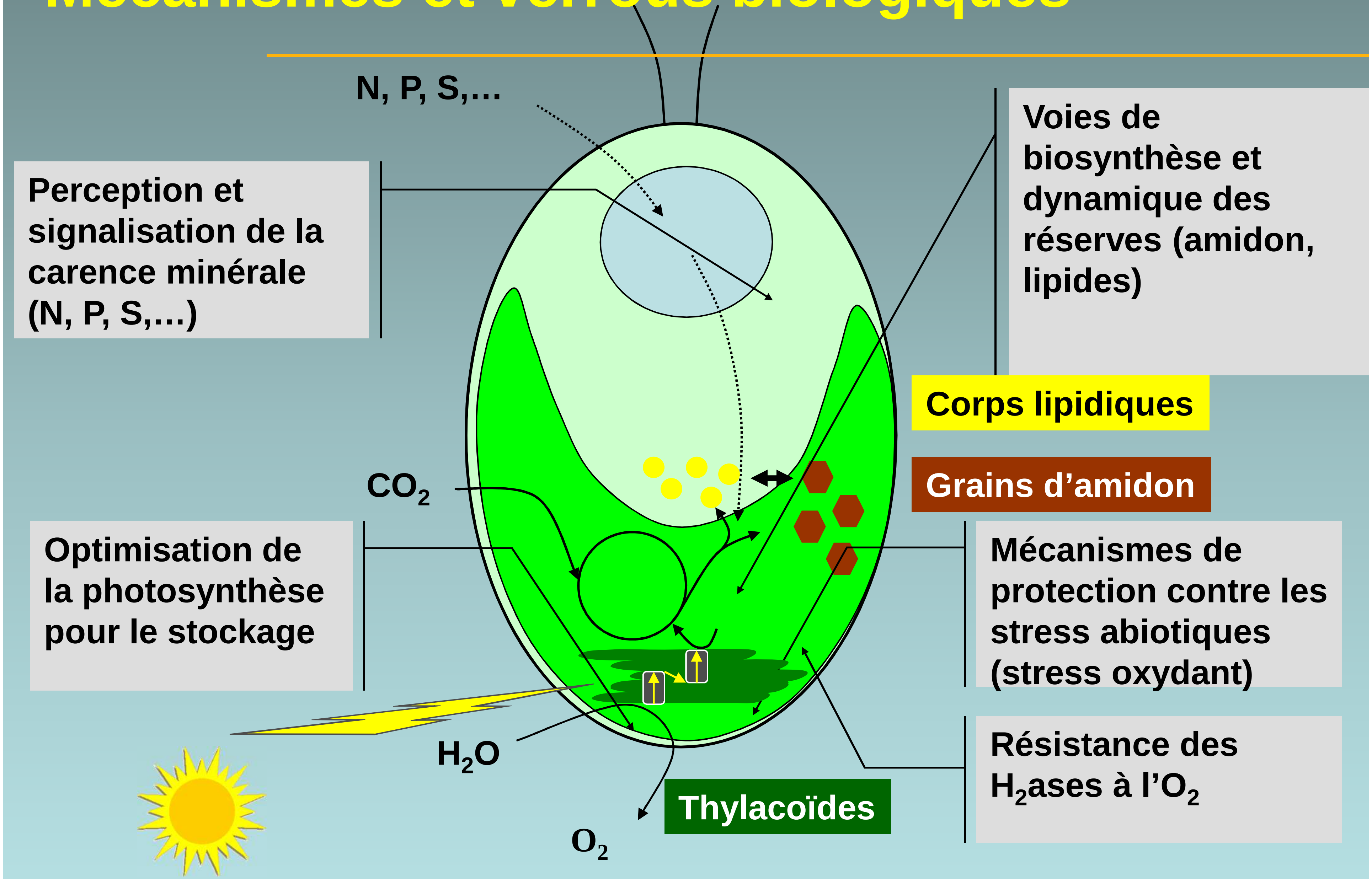
H_2 (photolyse de l'eau), lipides (biodiesel), polysaccharides (bioethanol), fermentation (méthane)



- Production sans gaz à effet de serre
- Production contrôlée dans des systèmes clos : pas de relargage de fertilisants, recyclage de l'eau,
- Pas de compétition avec l'alimentation

Production solaire de masse

Mécanismes et verrous biologiques



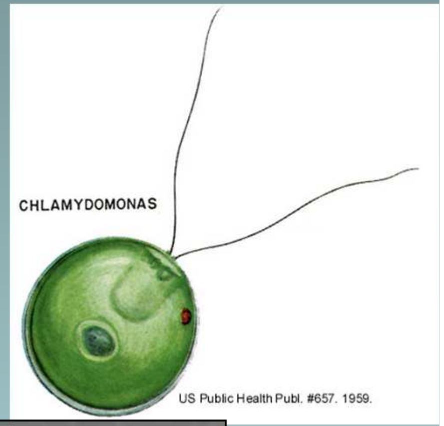
Production d’hydrogène par voie biologique

Chlamydomonas reinhardtii

Algue verte unicellulaire; bi flagellée; ordre des Volvocales

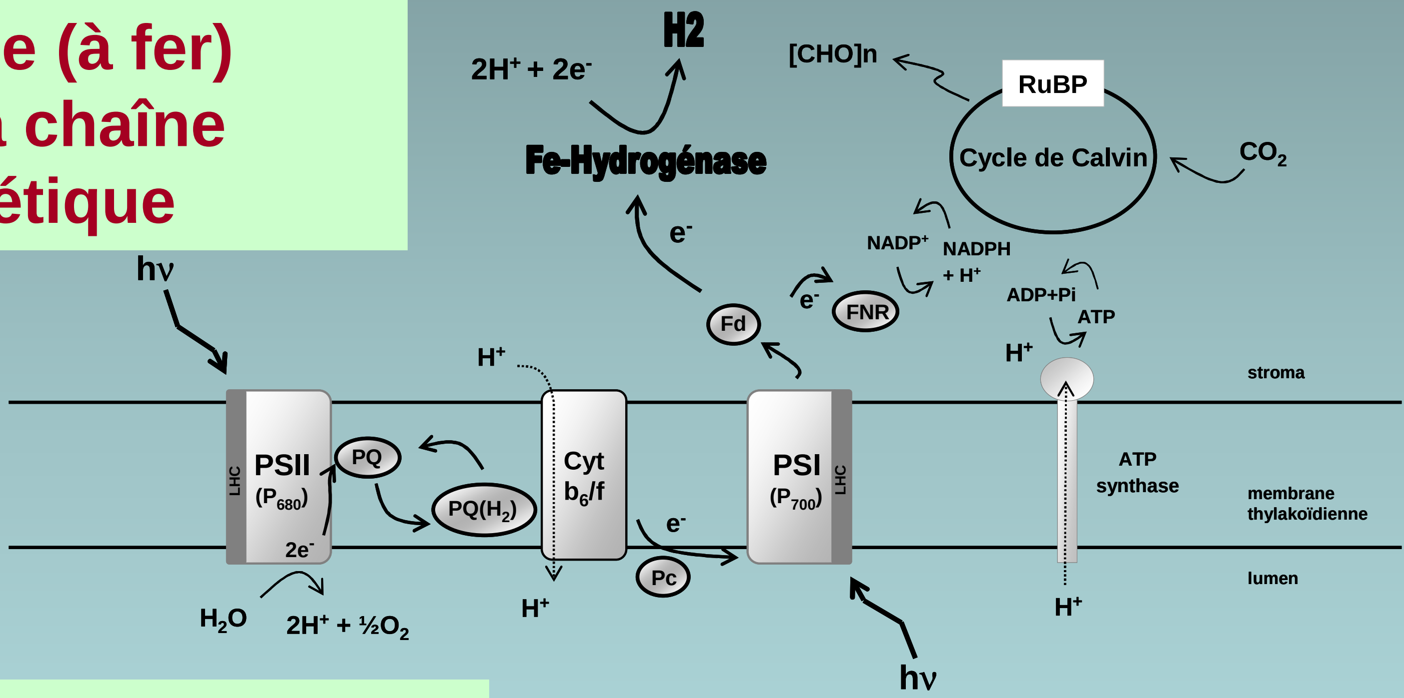
. Organisme modèle : facilement cultivable

. Production H_2 : hydrogénase à forte activité spécifique



Métabolisme de l'H_2 chez *Chlamydomonas reinhardtii*

Existence d'une hydrogénase (à fer) couplée à la chaîne photosynthétique



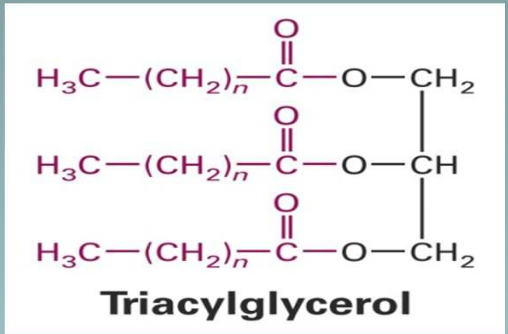
Dégagement transitoire d'H_2 (mécanisme de protection)

Facteur limitant la production d'H_2 : la sensibilité de l'hydrogénase à l'O_2

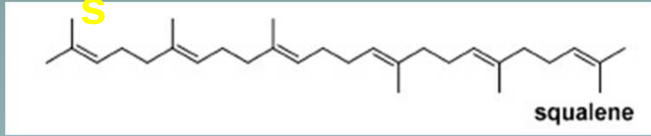
Production de lipides par les microalgues

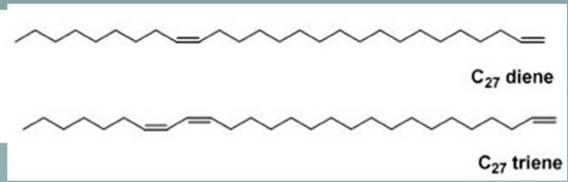
Différents types de lipides (dépendant des souches)

Lipide neutres (stockage)

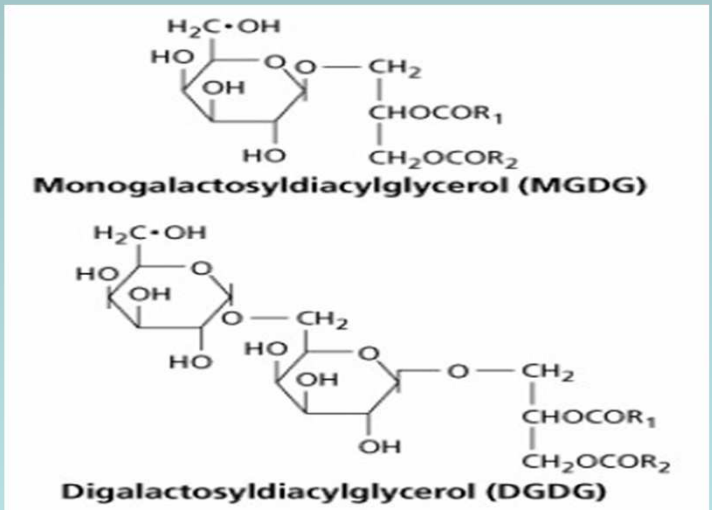


Hydrocarbones



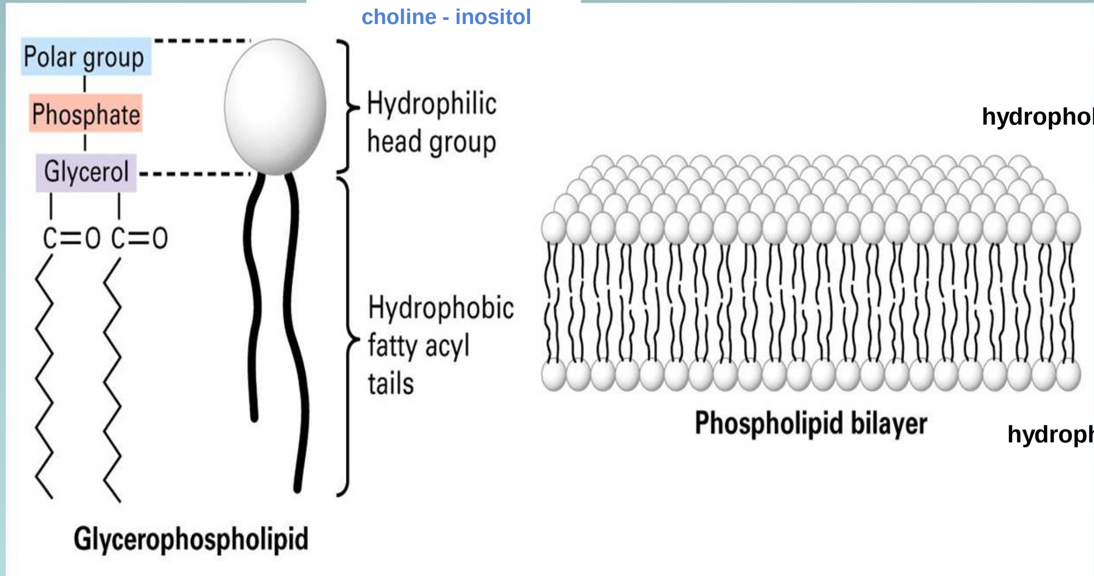


Lipides (principalement dans le chloroplaste)



Phospholipides

Éthanol amine – serine choline - inositol



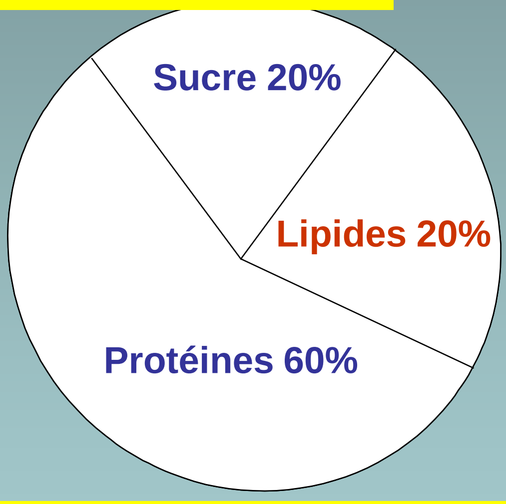
hydrophobe

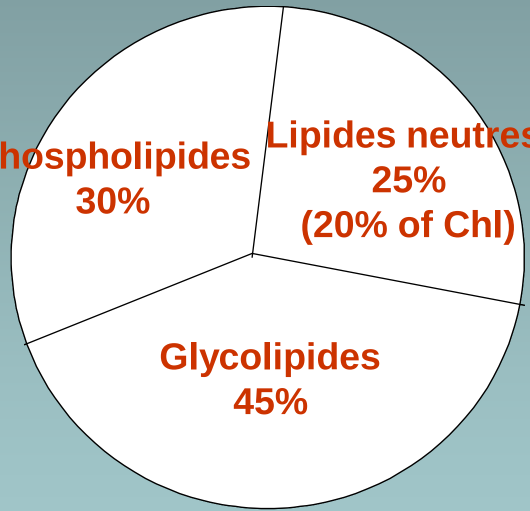
hydrophile

Modification des profils de lipides

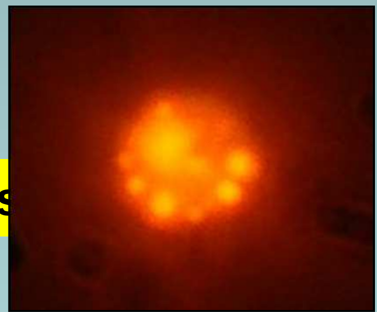
Neochloris oleoabundans

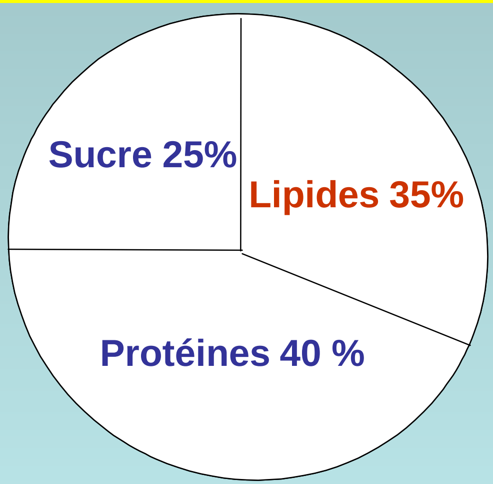
Conditions standard





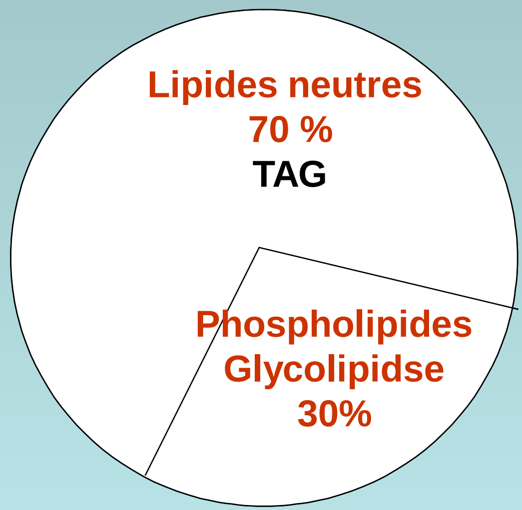
Conditions de carence en nitrates





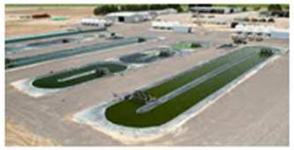
Accumulation des lipides

Principalement en TAGs



CAN WE PRODUCE BIODIESEL FROM MICROALGAE?

Cultivation of robust species in open systems	Harvesting (30%DW)	Biomass thermal drying (95%DW)	Solvant extraction and TAG conversion in biodiesel



5-8 g/m²/day (1-1.5g_{TAG}/m²/day)
10 to 30 g/m3/day (3-6g_{TAG}/m3/day)

Centrifugation

2-10 kWh/m3
3.5 kWh/kg DW

Thermal drying

800-2500 kWh/m³

Lipids extraction on dry biomass

TAG transesterification and biodiesel (FAME) purification

Current process for biodiesel production from microalgae ("the dry route")

Shamash-PE project (2009-2013)

Production of 100 kg of DW biomass in raceway (AlphaBiotech, AlgoSource group)

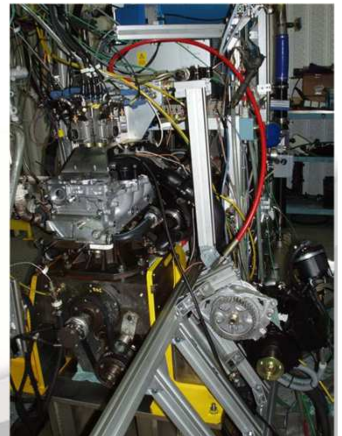
Extraction of 5-8 l of lipids from microalgae (CO2sc, M2P2)

Production of microalgal biodiesel (CIRAD)

Engine test (PSA)

Flask 20 l

Columns 60ls

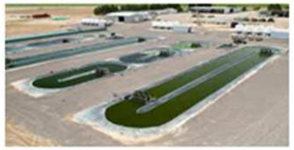


Biodiesel from microalgae was produced and tested in HDi engines (*see Perrier et al., Fuel, 2015*)

ALGOSOLIS
MICROALGAE R&D FACILITY

CAN ALGO-FUELS BE SUSTAINABLE?

Cultivation of robust species in open systems	Harvesting (30%DW)	Biomass thermal drying (95%DW)	Solvant extraction and TAG conversion in biodiesel



5-8 $g/m^2/day$ (1-1.5$g_{TAG}/m^2/day$)
10 to 30 g/m3/day (3-6g_{TAG}/m3/day)

Centrifugation

2-10 kWh/m3
3.5 kWh/kg DW

Thermal drying

800-2500 kWh/m^3

Lipids extraction on dry biomass

TAG transesterification and biodiesel (FAME) purification

Current process for biodiesel production from microalgae ("the dry route")

What could be the impact of technological innovations?

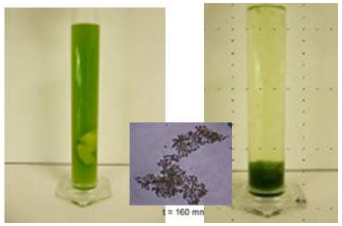
45° inclined PBR

13 $g/m^2/day$
260g/m3/day
Mixing 0.35 kWh/m3
Thermal regulation 1.1 kWh/m3

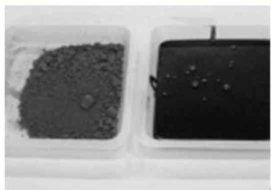
AlgoFilm© PBR
(ultrathin system)

13 $g/m^2/day$
6000g/m3/day
Mixing 0.35 kWh/m3
Thermal regulation 1.1 kWh/m3
(0 if passive regulation)

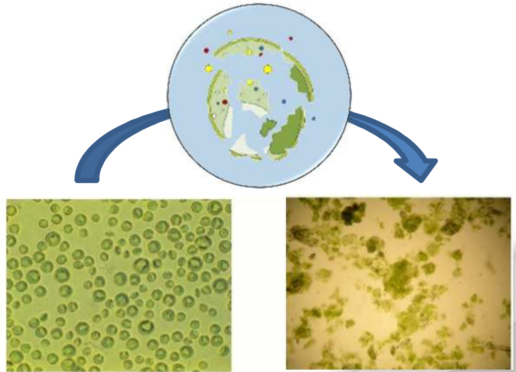
ANR Biosolis (2007-2011)



Floculation



Hydroliquefaction



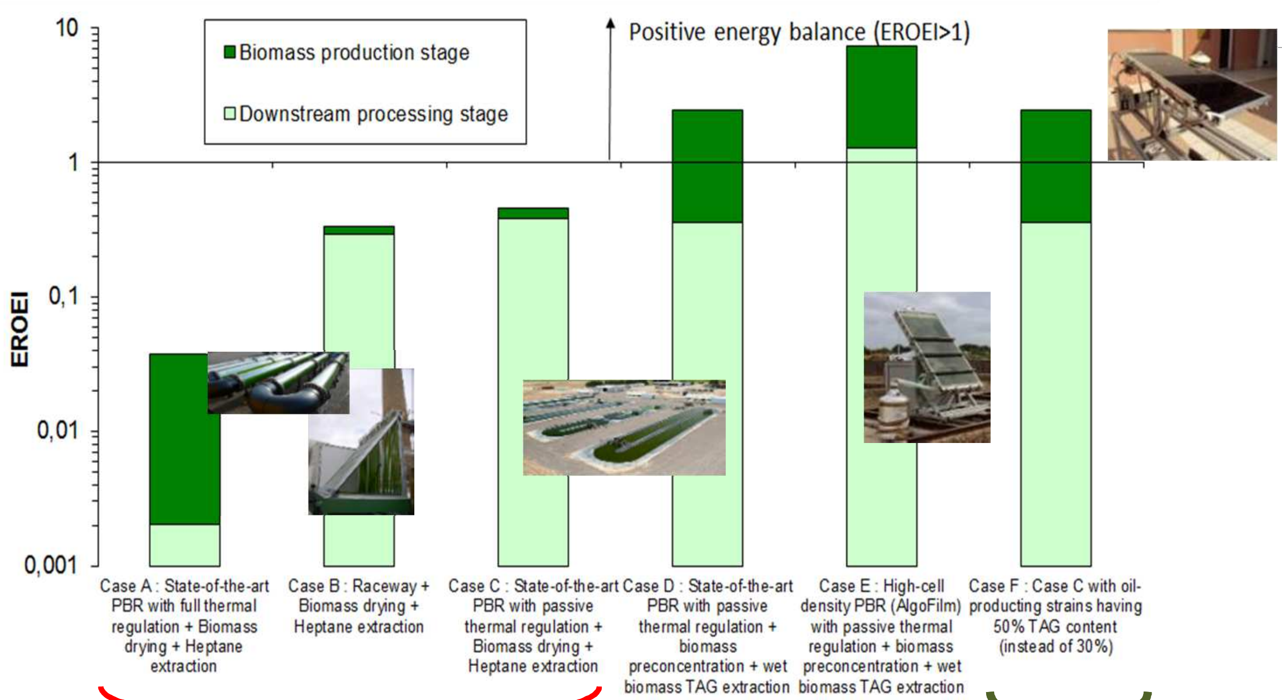
Wet-biomass extraction

ALGOSOLIS
MICROALGAE R&D FACILITY

TOWARDS INDUSTRIAL SUSTAINABLE PRODUCTION

Study case: Production of 100 kT of oil/year

	Surface (ha)	Volume (Mm^3)
Lagoon	50 000	200
Raceway	16 700	50
PBR (5 cm)	5 000	2.5
AlgoFilm	5 000	0.25



Production in raceway or in PBRs with full thermal regulation, following by biomass drying and $scCO_2$ extraction, leads to a negative energy balance

Improving/finding strains with high TAG production

Developing new technologies for sustainability

Intensified photobioreactors have a significant effect on the overall energy balance:

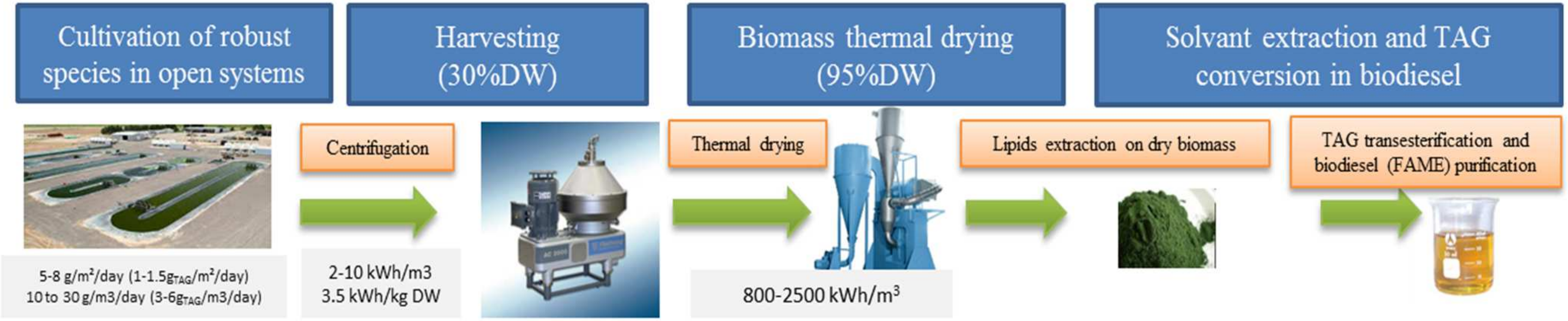
→ The volumes decrease allows reducing the global energy consumption due to thermal control, agitation, pumping

The work on wet biomass has also brought a significant improvement by decreasing by one order of magnitude the consumed energy compared to the classical method

Possibility of a positive overall energy balance (maximal EROEI of about 7)

This was retained as guidelines of the GEPEA R&D effort

THE DIESALG PROJECT (ANR)



Current process for biodiesel production from microalgae ("the dry route")

Current process lines present negative energy balance: technological breakthroughs and systematic optimization are needed for a sustainable and effective biofuel production.

Key-aspects

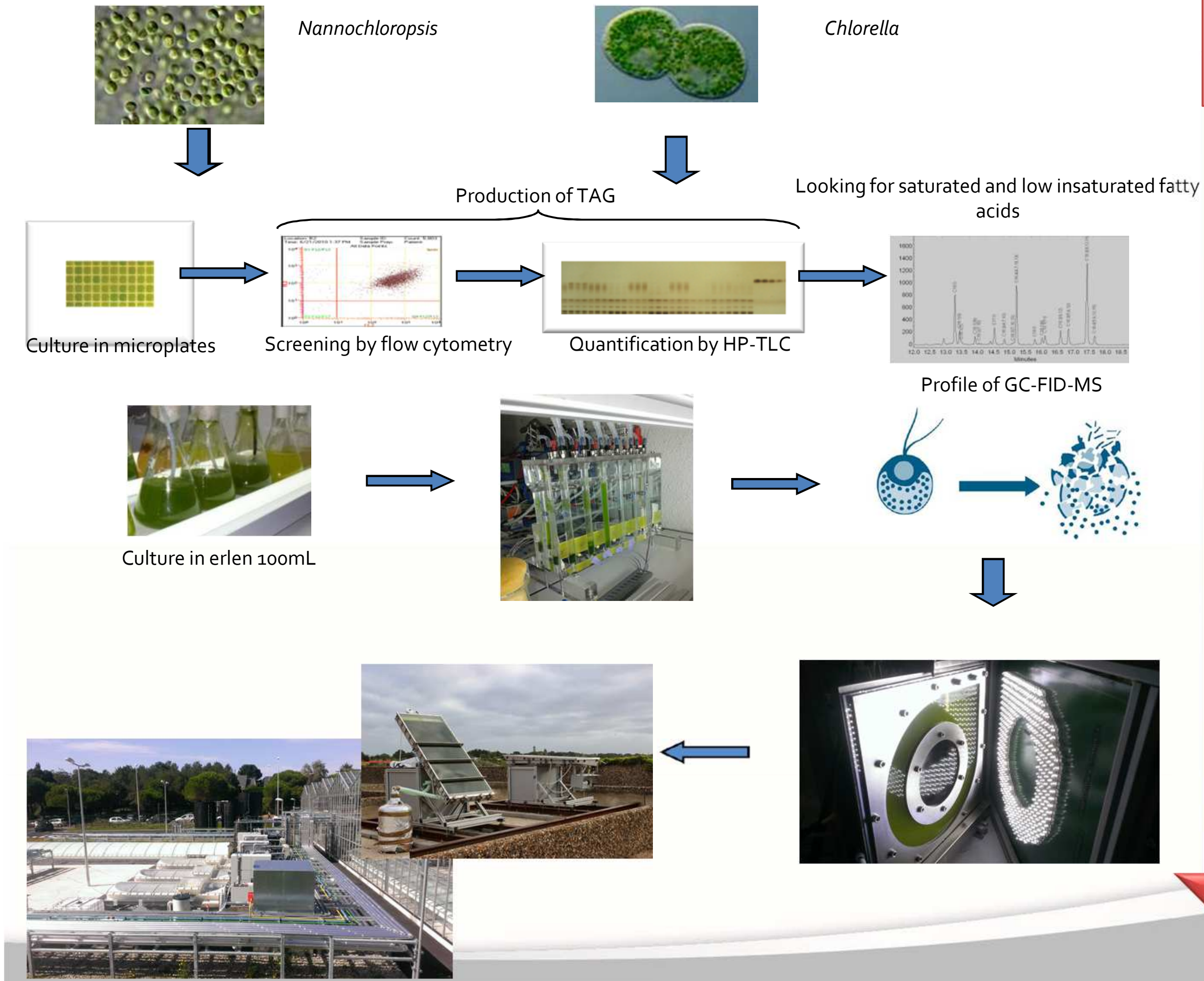
- **Strain screening** : the strain has a global impact on the process (culture, extraction, scalability, robustness). Selection have to consider this impact and not only TAG content has usually done…
- **New process development and intensification**: optimized and intensified cultivation systems, extraction methods able to work on wet-biomass
- **Overall optimisation and industrial integration**

ANR DiesAlg (2012-2015)

ALGOSOLIS
MICROALGAE R&D FACILITY

THE DIESALG PROJET: STRAINS SCREENING

Combining high-throughput and process-scale screening approaches for selection of industrially efficient oil-producing strains



An integrated approach combining both HelioBiotec and GEPEA-AlgoSolis facilities

HélioBiotec

(high-throughput techniques)

GEPEA

(characterization at process scale)

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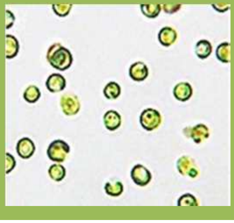
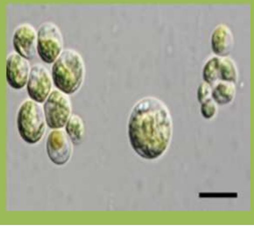
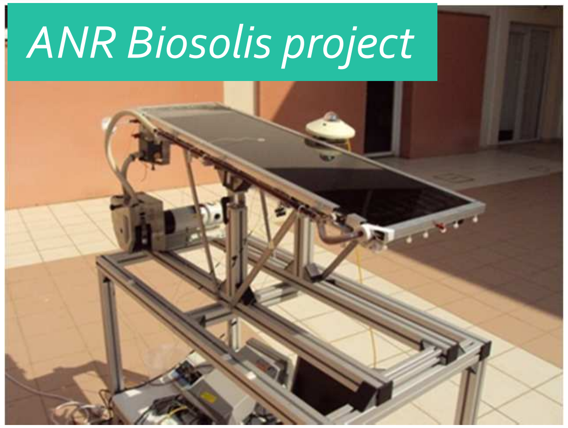
MICROALGAE R&D FACILITY

THE DIESALG PROJET: STRAINS SCREENING

	Nannochoropsis gaditana (sea water strain) 	Parachlorella kessleri (fresh water) 
Biomass productivity (+N)	27g/m²/day (100t/ha/year)	27g/m²/day (100t/ha/year)
Lipid productivity	2,3-2,5g_{TAG}/m²/day (8-10t_{TAG}/ha/year)	2,7-4,4g_{TAG}/m²/day (10-16t_{TAG}/ha/year)
Oil productivity	9-12m^3_{TAG}/ha/year	12-20m^3_{TAG}/ha/year
Lipid content	62% Total lipids 56% TAG	41-65% Total lipids 38-46% TAG
Cells disruption (TAG wet-extraction)	>70%	>90%

Selection of two oil-producing strains (1 fresh and 1 seawater)
(1) with high TAG accumulation, (2) with high growth rate in N deprivation, (3) with high culture robustness and (4) easy to process in wet-extraction

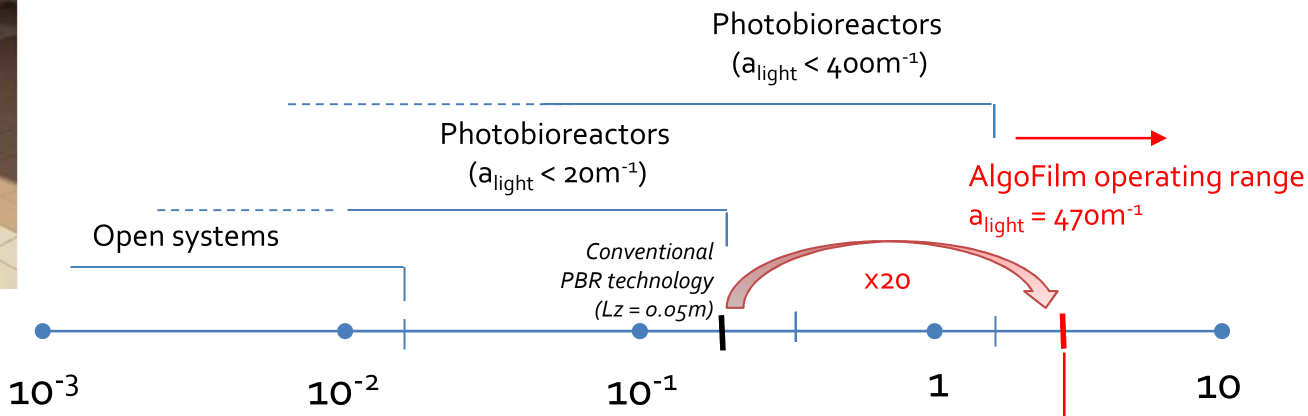
SOLAR PHOTOBIOREACTORS INTENSIFICATION

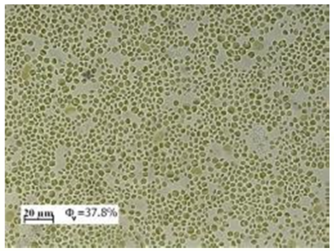


2 Patents (CNRS-Univ.Nantes)

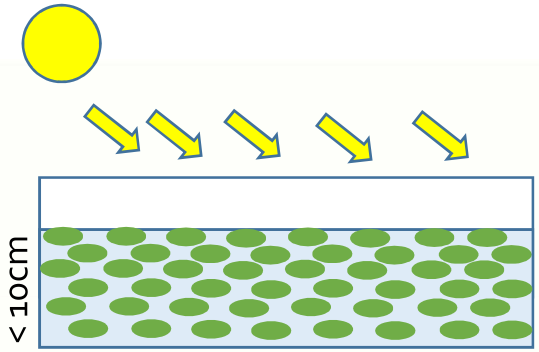
2.1liter/m² of culture
(150liter/m² for a raceway)

AlgoFilm PBR: PBR technology for solar production with High Cell Density culture (>10g/l in continuous culture)

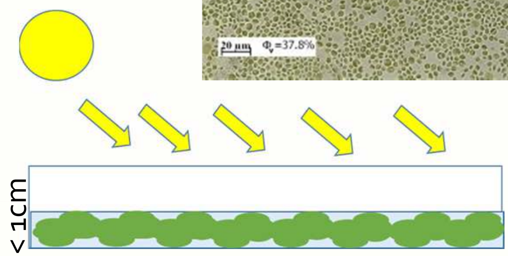




Maximal productivity achieved:
6.0 kg.m^{-3}d^{-1}
(Cx > 15kg.m^{-3})
(C.vulgaris - chemostat - 3 weeks stable production – Average PFD 270µmole/m²/s)



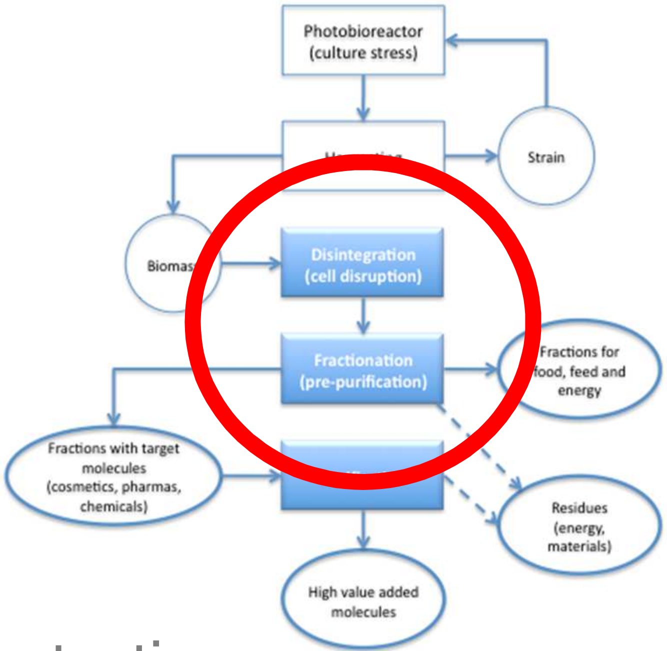
Standard PBR
Cx_{max} ≈ 1-10 (g/L)



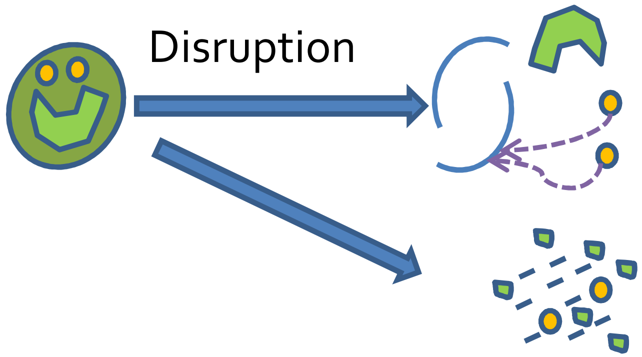
High-Cell density culture
(High Volumetric Productivity PBR)
Cx_{max} > 10 (g/L)

WET EXTRACTION OF LIPIDS FROM MICROALGAE

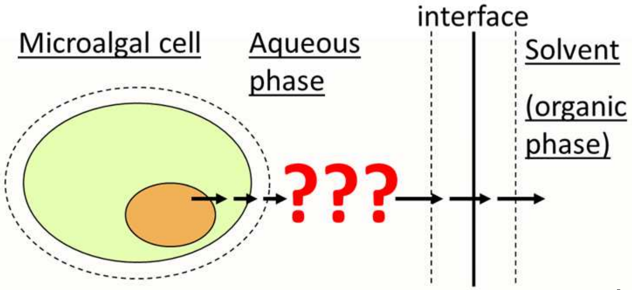
ANR Diesalg project



High pressure disrupter or bead milling



Wet-extraction



Oil bodies extractability combines :

- ➔ *Release from the microalgal cells : integrity effect*
- ➔ *Liquid-liquid mass transfer and water effect*
- ➔ *Dissolution in the organic phase : solvent effect*

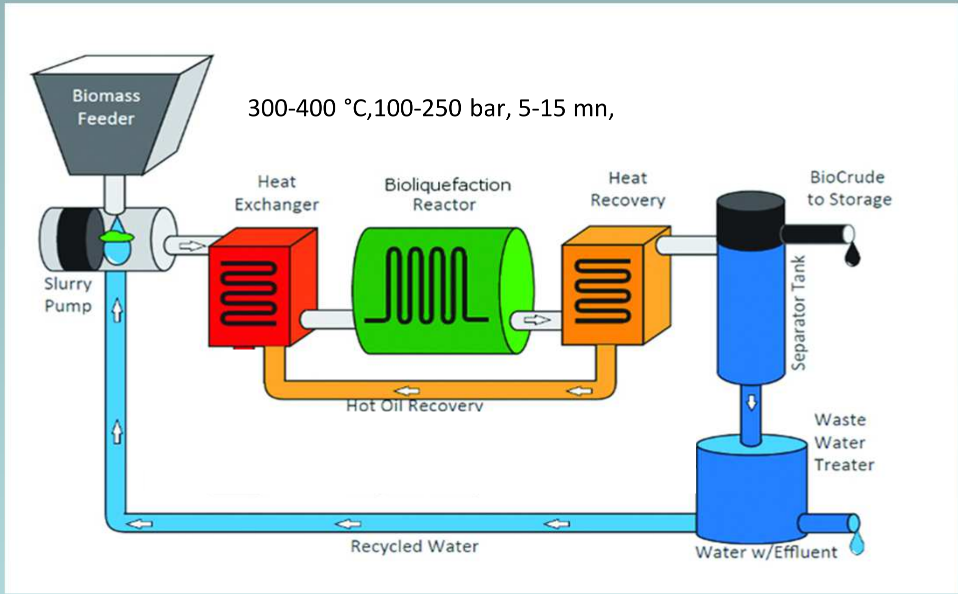
ALGOSOLIS MICROALGAE R&D FACILITY

Principe liquéfaction hydrothermale

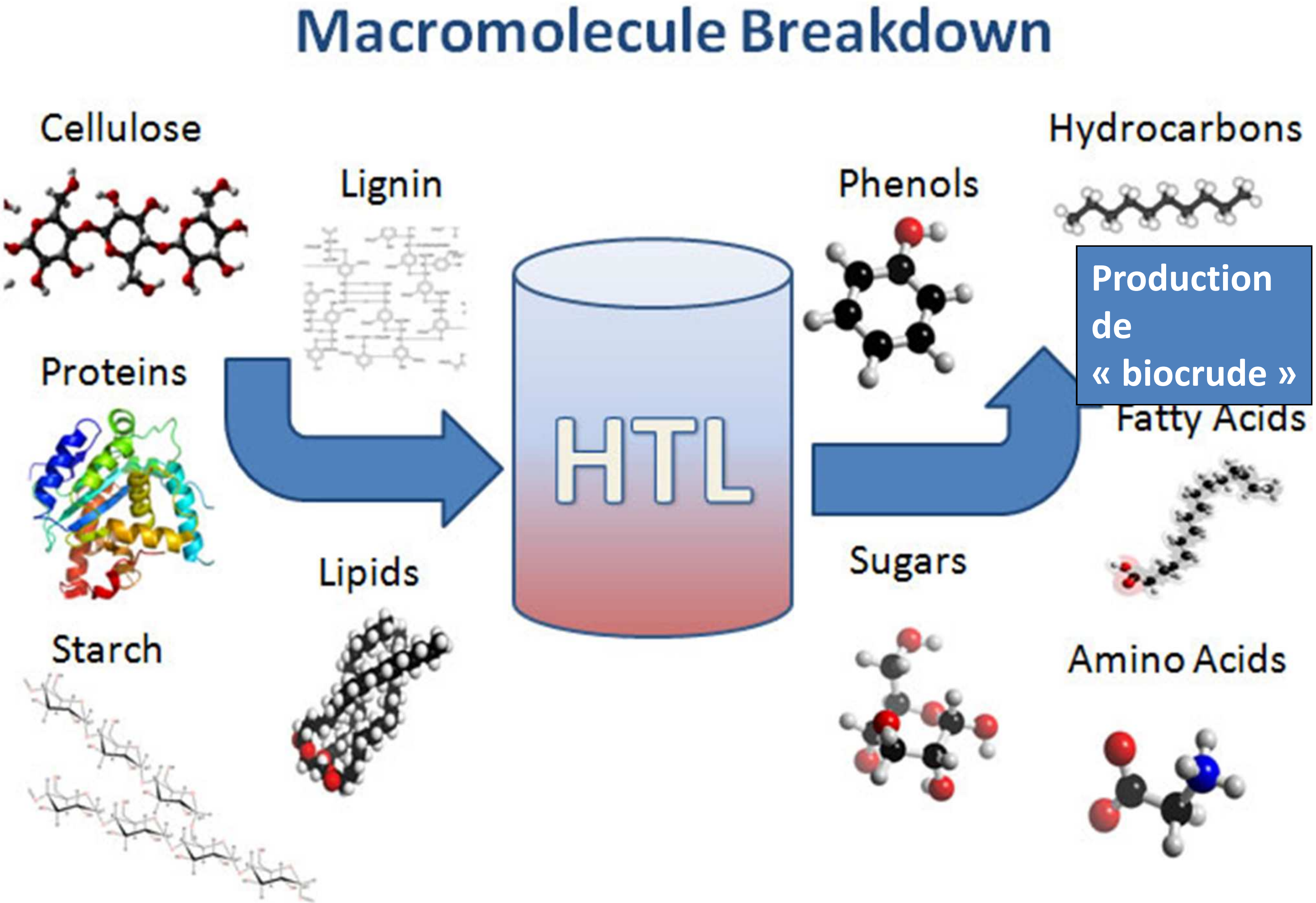
- Liquéfaction hydrothermale (HTL) : conversion en eau sous pression
- Permet de transformer de la biomasse humide en biocrude à température modérée (300-400°C) et à haute pression (100-250 bar) durant 5-15 minutes.
- Ces procédés de liquéfaction permettent l'utilisation de biomasses humides et très humides évitant les procédés de séchage très coûteux
- L'utilisation de catalyseurs alcalins et/ou de métaux permet d'augmenter l'efficacité et la qualité.

Matières premières

- **résidus de l'industrie agro alimentaire**
- **bio déchets**
- **micro algues**
- **Boues de station d'épuration**
- **…**

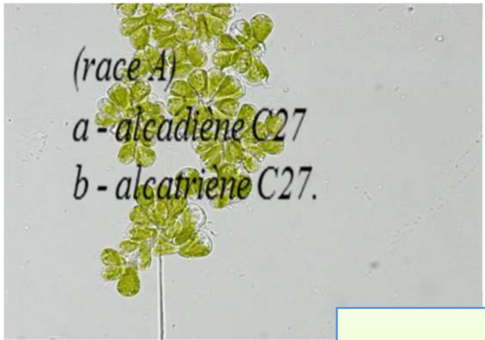


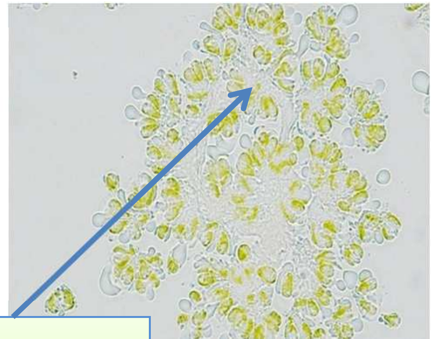
La séparation s'effectue par décantation/filtration ou séparation avec un solvant


Macromolecule Breakdown
Cellulose
Lignin
Proteins
Lipids
Starch
HTL
Phenols
Hydrocarbons
Production
de
« biocrude »
Fatty Acids
Sugars
Amino Acids

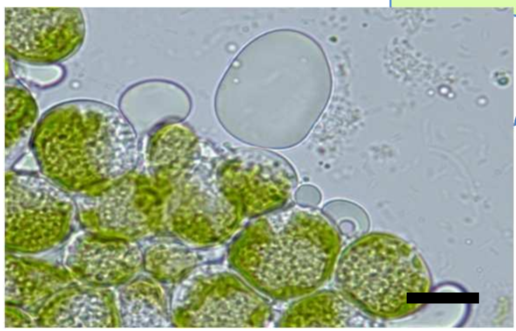
Production of hydrocarbons by *Botryococcus braunii*

Special strain: able to synthetise long chains hydrocarbons (C > 25)





HC Exsudation



a

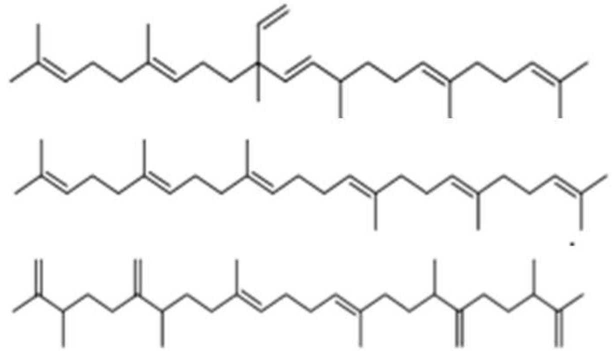
b

(race A)
a - alcadiène C27
b - alcatriène C27

c

d

e



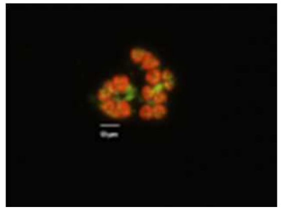
(race B)
c - botryococcène C30
d - squalène C30
e - tétraméthylsqualène

Formation of colonies

GEPEA
UMR CNRS 6144

BIOMASS PRODUCTION WITH HYDROCARBON

Stœchiometric equation of biomass production of *B. braunbi* cultivated in photoautotrophy



Species	Stoichiometric equations	$Y_{X/CO2}$ ($g\ g^{-1}$)	$Y_{X/NO3}$ ($g\ g^{-1}$)	Reference
Botryococcus braunii	$CO_2 + 0.03\ NO_3 + 0.88\ H_2O \rightarrow CH_{1,75}O_{0,15}N_{0,03} + 1.41\ O_2$	**0.38**	**8.91**	[25]
Chlorella sp.	$CO_2 + 0.12\ NO_3 + 0.95\ H_2O \rightarrow CH_{1.89}O_{0.42}N_{0.12} + 1.44\ O_2$	0.51	3.00	[54]
Spirulina sp.	$CO_2 + 0.17\ NO_3 + 0.84\ H_2O \rightarrow CH_{1.68}O_{0.36}N_{0.17} + 1.50\ O_2$	0.50	2.07	[56]

Stoechiometry → 2.6 kg of CO2 to produce 1 kg of biomass de *B. braunii*

30 % than other microalgae, as *Chlorella,* or cyanobacteria, as *Spirulina*

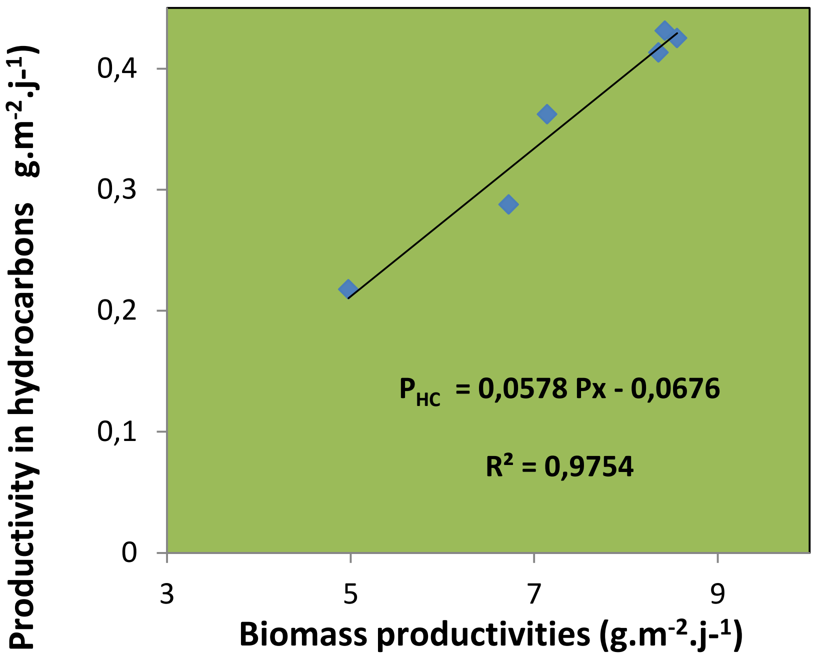
Hydrocarbon production

B. braunii **race A**

Continuous cultures

$$P_x = f(D)$$
$$P_{HC} = f(D)$$

$P_{HC} = f(P_x)$



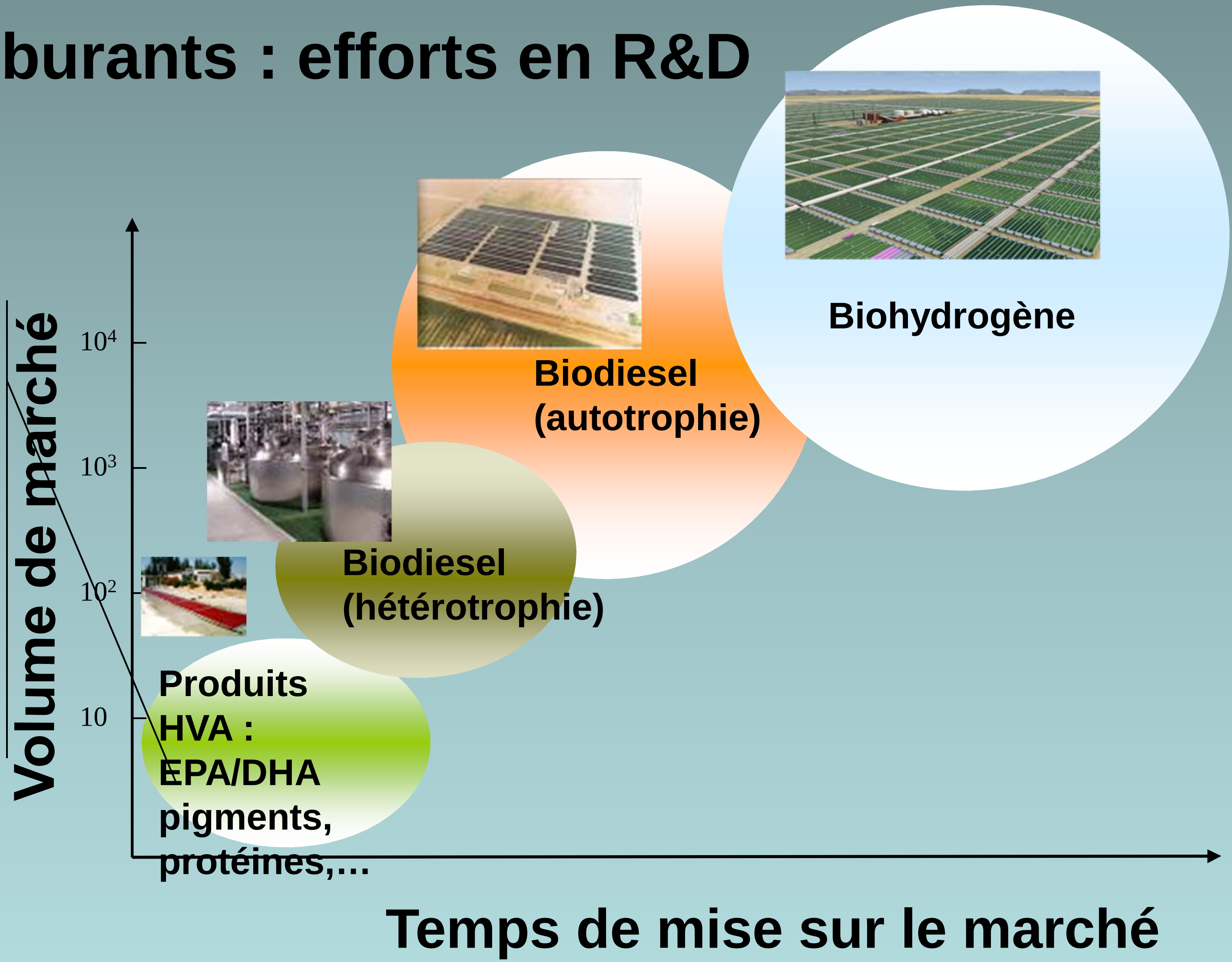
At pH constant ➔ hydrocarbon kinetic production is associated to biomass production

➔ Contrary to the TAG production (biodiesel)

nutritional limitations (nitrogen) non necessary

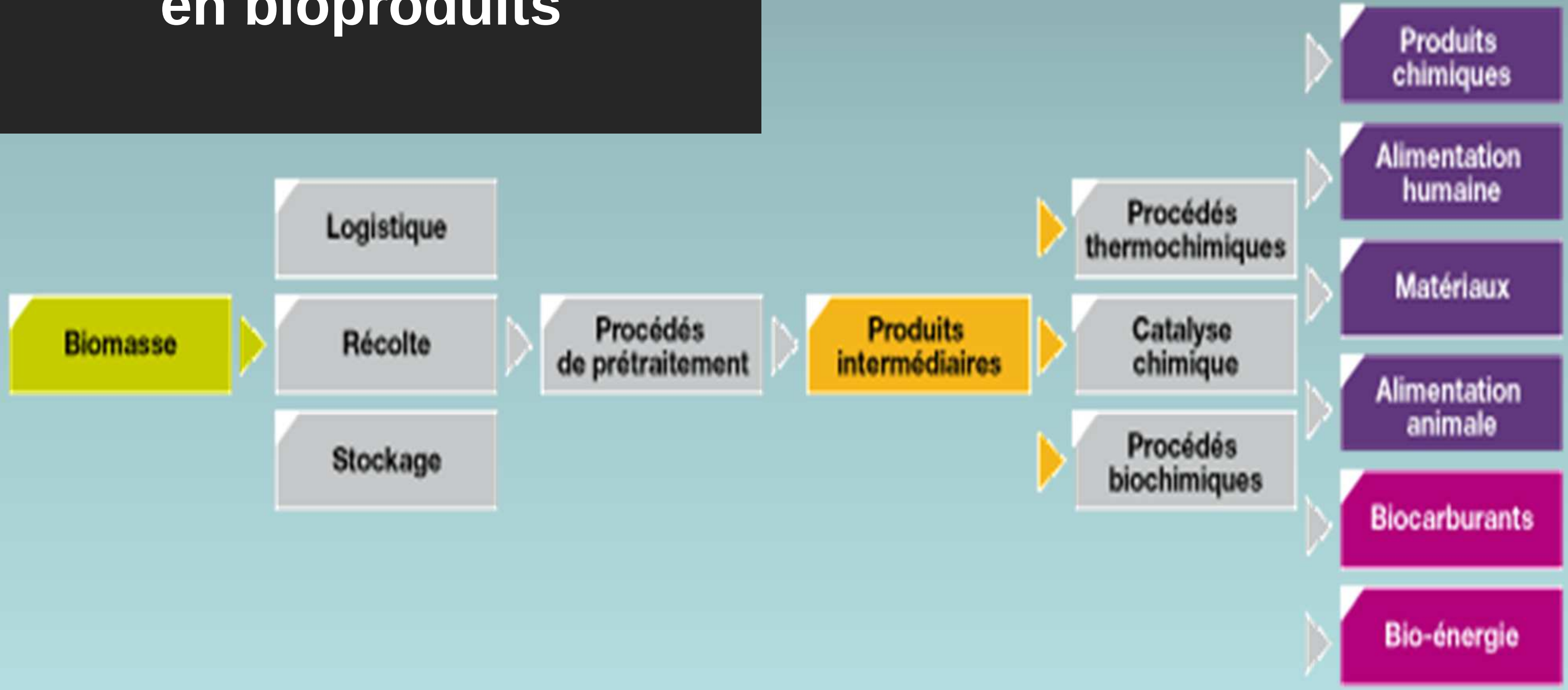
Les biocarburants : efforts en R&D

Sélection et performance des souches



Bioraffinerie

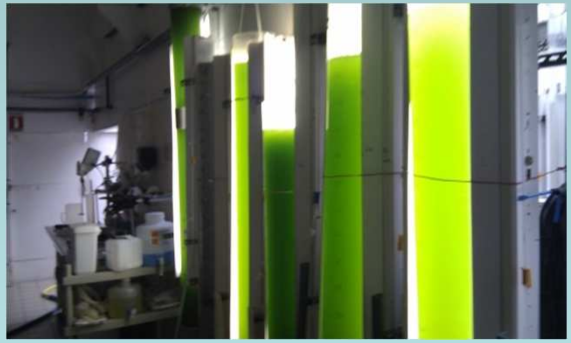
Installation industrielle pour la transformation de la biomasse en bioénergie et en bioproduits



Algoraffinerie : Projet Algoroute

- Fabrication de matériau visco-élastique thermo susceptible à partir de microalgues : biobitume
- Hydrothermale liquéfaction

Algeneans



ALGOSOLIS
MICOALGAE R&D PLATEFORM

Objectifs
•Etudes en conditions réelles et à une échelle représentative de la production industrielle.
•Développement et optimisation des briques du procédé d'exploitation (souches, technologies).
•Assemblage sur un même site des briques pour évaluer-optimiser un scénario d'exploitation.
•Mise en place et optimisation d'une production sur effluents industriels (gaz, liquides).

INFRASTRUCTURE
•Surface de production 1500m² (dont 350m² sous serre thermorégulée)
•Halle Process de bioraffinage des algues (240m²)
•Salles préculture et laboratoire d'analyse (100m²)

Procédés industriels de culture de 10 à 100m²
•Technologies low-cost type Raceways clos
•Photobioréacteurs intensifiés nouvelle génération

PROCEDES DE RECOLTE
•Systèmes de préconcentration/concentration innovants dédiés aux microalgues
•Procédés de filtration et séparations membranaires
•Centrifugeuses

PROCEDES DE BIORAFFINAGE
•Destructeur cellulaire
•Procédés d'extraction de fractions d'intéret
•Procédés de fractionnement de la biomasse microalgale

PROCEDES DE CONDITIONNEMENT DE LA BIOMASSE
•Sécheurs
•Lyophilisateur
•Congélateurs

Budget 3.5M€
Inauguration : Avril 2015