Products and processes with microalgae

  

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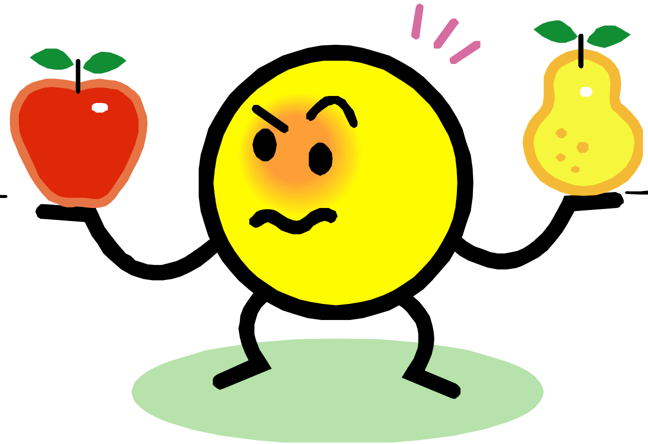
APPLICATIONS OF MICROALGAE

Pure chemicals:
- Carotenoids
- Fatty acids
- Phycobiliproteins
- Toxins

Biomass
- Functional foods
- Aquaculture
- Animal feeding



Biofuels/biofertilizers
- Biofertilizers
- Biodiesel
- Biogas
- Bioethanol

Bioremediation
- Flue gases
- Wastewater
- Soils

ONLY SOME OF THEM ARE PERFORMED AT REAL SCALE

STILL TECHNICAL AND ECONOMIC BOTTLENECKS EXIST

MARKETS

High value products

Tab. 1. Market Estimations for Microalgal Products

	Product	US$ kg^{-1}	Market Size US$ · 10^6
Biomass	health food	15–28	180–200
	functional food	25–52	growing
	feed additive	10–130	fast growing
	aquaculture	50–150	fast growing
	soil conditioners	>10	promising
Coloring substances	astaxanthin	>3,000	>50
	phycocyanin	>500	>10
	phycoerythrin	>10,000	> 2
Antioxidants	β-carotene	>750	>25
	superoxide dismutase	>1,000	promising
	tocopherol	30–40	stagnant
	AO-extracts	20–35	12–20
PUFA	ARA		20
	EPA		>500
	DHA		30
	PUFA extracts	30–80	10
Special products	toxins		1–3
	isotopes		<5

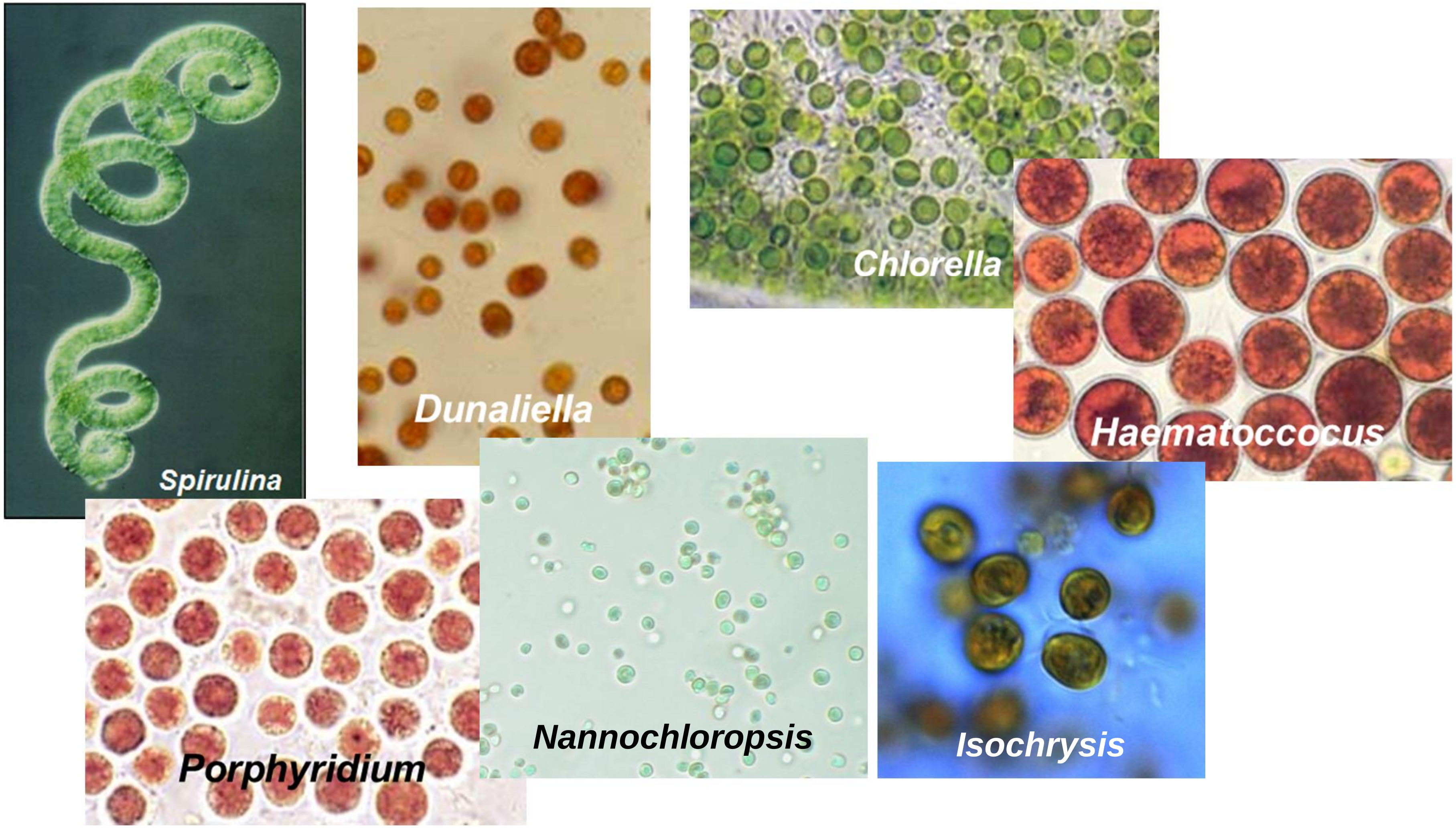
Low value products

Biofuels, biofertilizers, wastewater treatment, etcé (Market size?)

INDEX

1. PRODUCED STRAINS

Although thousands species are know, only a few are used commercially



Utilization of consortiums is usually disregarded

1. PRODUCED STRAINS

PRODUCTION OF Spirulina

Uses: Foods and functional foods, ɔ-linolenic acid, phycocianin, cosmetic, suplement for feeds

Companies: Cyanotech (www.cyanotech.com) (U.S.A); Earthrise Nutritionals (www.earthrise.com) (U.S.A); Panmol/Madaus (www.panmol.com) (Austria); Parry Nutraceuticals (www.murugappa.com) (India); Spirulina Mexicana (Sosa Texcoco) SA (México); Siam Alga Co., Ltd. (Tailandia), Nippon Spirulina Co., Ltd. (Japan), Koor Foods Co., Ltd (Israel), Nan Pao Resins Chemicals Co., Ltd. (Taiwan); Myanmar Spirulina Factory (Myanmar), Blue Continent Co., Ltd (South Africa)

DIC's Spirulina bulk powder

1. PRODUCED STRAINS

PRODUCTION OF Dunaliella

Uses: Foods and functional foods, ß- carotene, cosmetic, antioxidant, suplement for feeds

Companies: Nature Beta Technologies Cognis (www.cognis.com) (Australia); Cyanotech (www.cyanotech.com) (U.S.A.); Nikken Sohonsha Corp. (www.chlostanin.co.jp) (Japan); Earthrise Nutritionals (www.earthrise.com) (U.S.A.), Betatene (www.betatene.com.au) (Australia); Inner Mongolia Biological Eng. (China); Nature Beta Technologies (Israel); Parry agro Industries (www.murugappa.com) (India); ABC Biotech Ltd. (India); Tianjin Lantai Biotechnologyd, (China); Western Biotechnology Ltd.(Australia); Aqua Carotene Ltd.(Australia)

Nature Beta Technologies, Eilat, Israel
Raceway ponds

▲N.B.T.日健総本社ドナリエラ純粋管理培養工場（イスラエル・エイラット）

Cognis, Australia
Open ponds

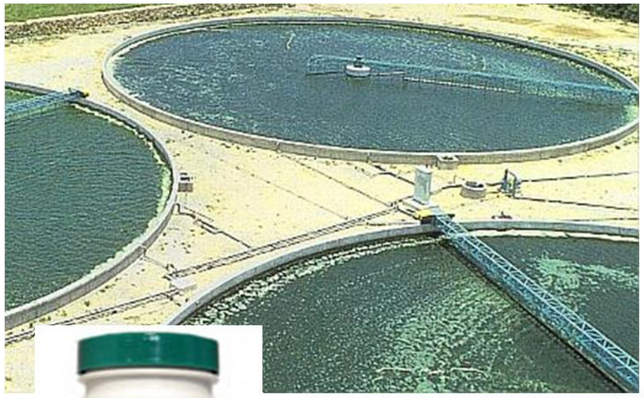
1. PRODUCED STRAINS

PRODUCTION OF Chlorella

Uses: Foods and functional foods, cosmetic, suplement for feeds, aquaculture

Companies: Nikken Sohonsha Corp. (www.chlostanin.co.jp) (Japan), Earthrise Nutritionals (www.earthrise.com) (USA), Ocean Nutrition (www.oceannutrition.com) (Canada), Iâge vert[d] (www.agevert.com) (France), Chlorella manufacturing and Co. (Taiwan), Roquette Klötze[d] (Germany)

Yaeyama *Chlorella, Japan*



1. PRODUCED STRAINS

PRODUCTION OF Haematococcus

Uses: Astaxanthin, antioxidant, funtional foods, cosmetic, aquaculture

Companies: Mera Pharmaceuticals (www.aquasearch.com) (U.S.A.); Cyanotech (www.cyanotech.com)[a,e] (U.S.A.); BioReal (www.bioreal.se) (U.S.A.); Algatech Algaltechnologies (www.algatech.com)(Israel); Fuji Health Science (www.fujichemical.co.jp); Dutch State Mines (http://www.dsm.com), Changsha Organic Herb Inc. (http://www.organic-herb.com), Health Sources Industry Co., Ltd (http://www.health-sources.com) (China); Parry agro Industries (www.murugappa.com)(India)

Pigmentos Naturales, Pica, Chile
Closed+Open raceway reactors

1. PRODUCED STRAINS

PRODUCTION OF Chrypthecodinium, Schizochytrium

Uses: DHA source, funtional foods, infant formula, pharmacy

Companies: Martek (USA), DSM (Netherland), Csiro (Australia)

DSM
BRIGHT SCIENCE. BRIGHTER LIVING.

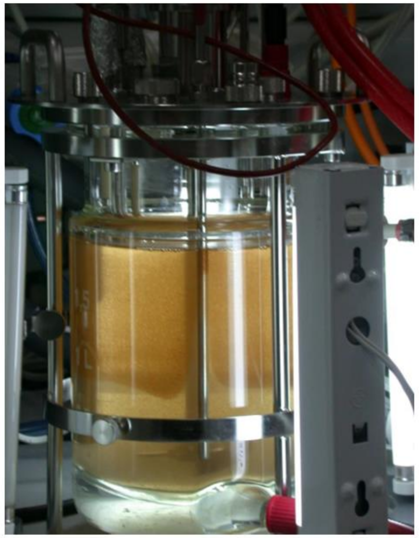
life's DHA™
HEALTHY BRAIN, EYES, HEART

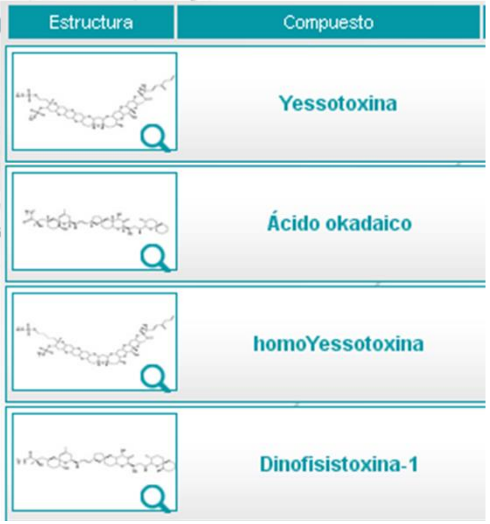
1. PRODUCED STRAINS

PRODUCTION OF Dinoflagellates

Uses: Toxins, pharmacy, standards

Companies: Cifga (Spain)



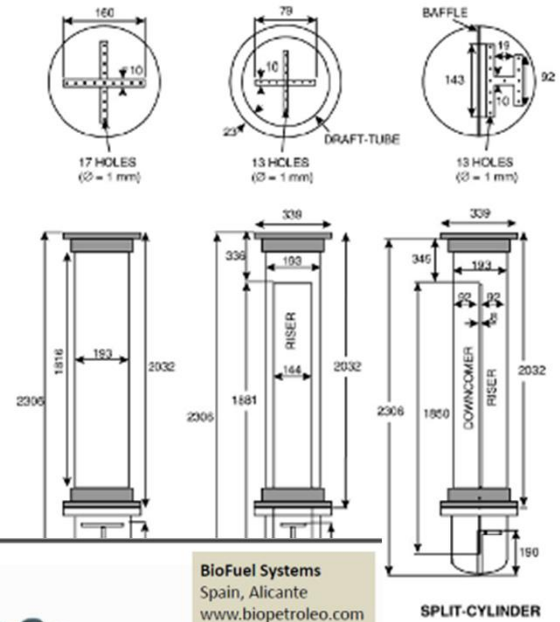


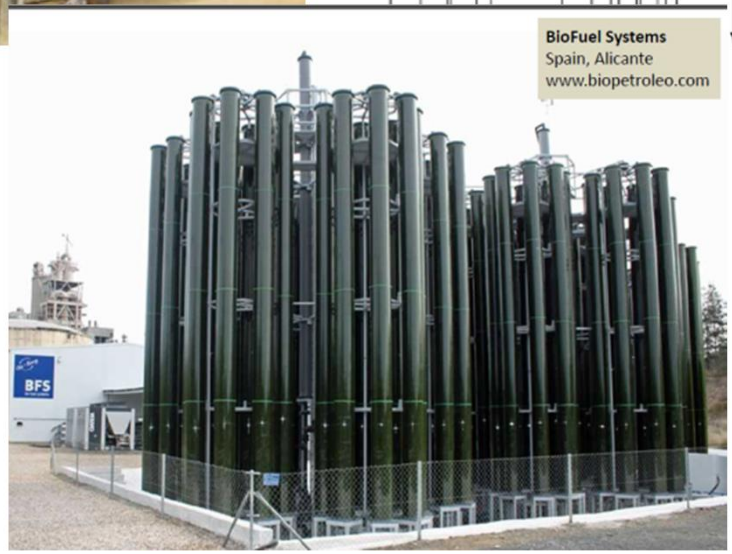
2. MICROALGAE BASED PROCESSES

Specific processes according to the final product

2. MICROALGAE BASED PROCESSES

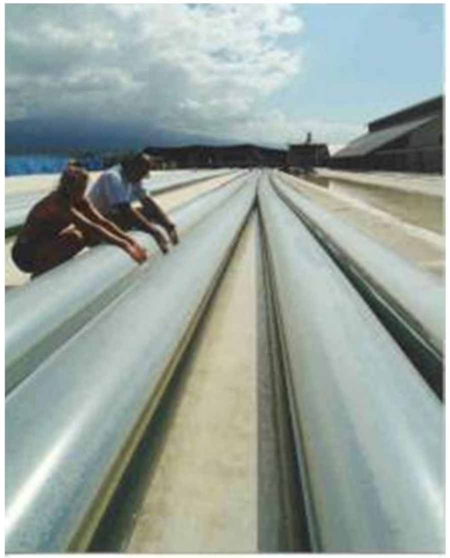
Closed photobioreactors: Bubble columns





2. MICROALGAE BASED PROCESSES

Closed photobioreactors: Tubular photobioreactors



Typical biomass productivity

0.050 kg m^{-2} day^{-1} (~100 tons ha^{-1} $year^{-1}$)

Maximum biomass concentration

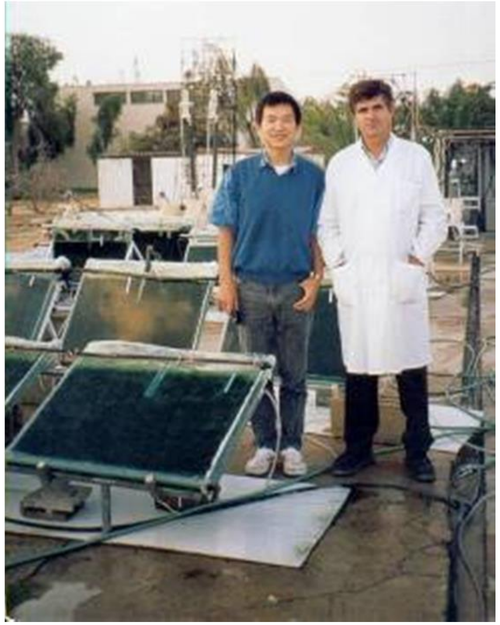
3.0 kg m^{-3} (1.5 kg m^{-3} typical)

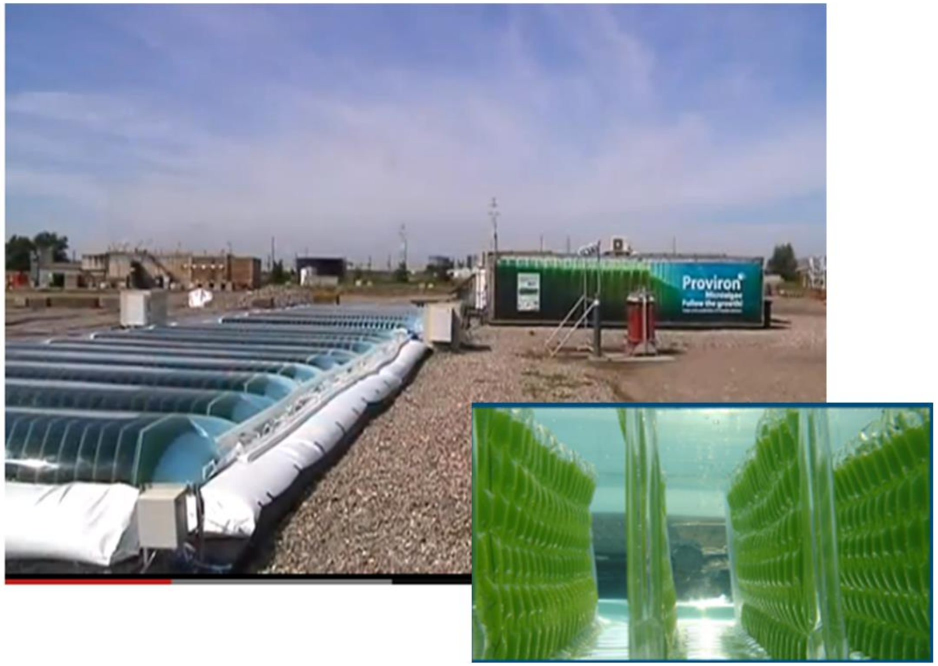
Volume to surface ratio

0.04-0.08 m^3 m^{-2}

2. MICROALGAE BASED PROCESSES

Closed photobioreactors: Flat panel photobioreactors





Typical biomass productivity

0.035 kg m^{-2} day^{-1} (~80 tons ha^{-1} $year^{-1}$)

Maximum biomass concentration

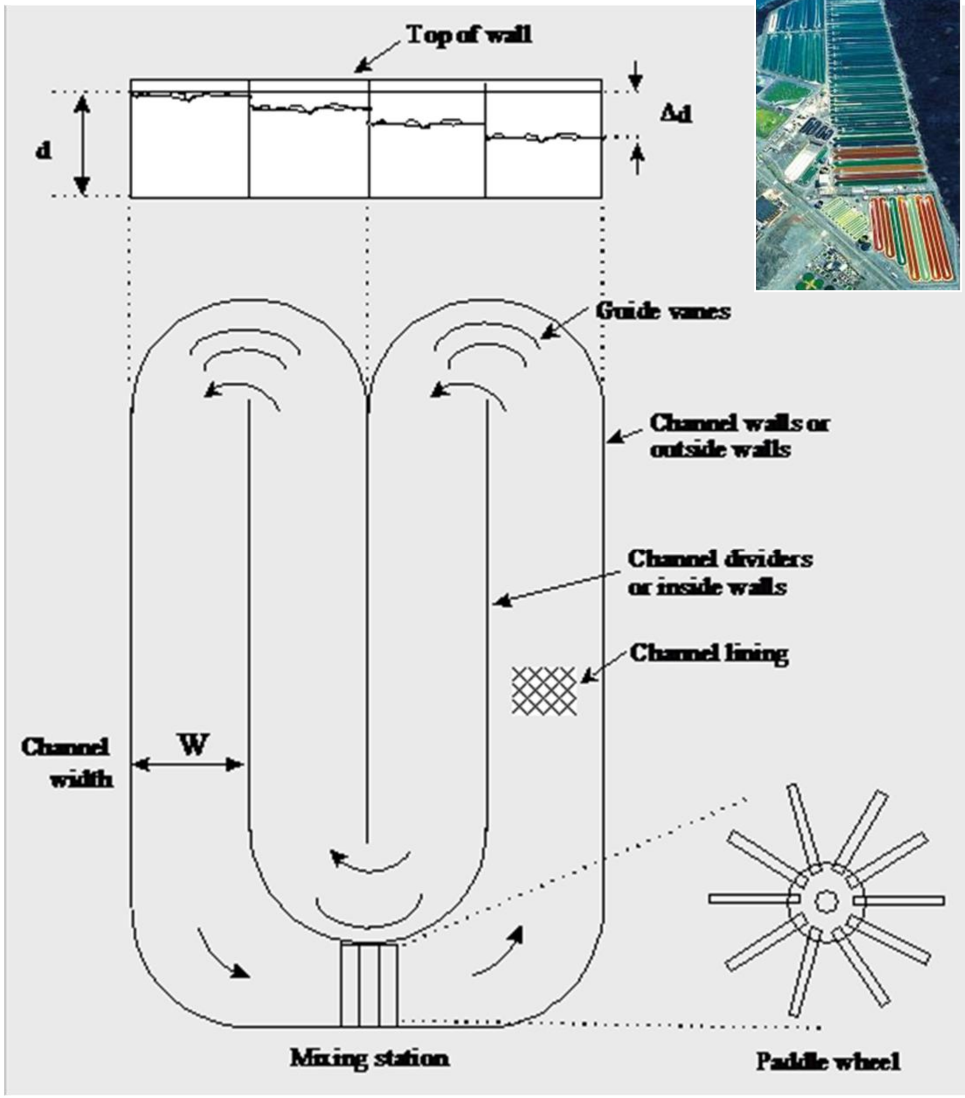
2.0 kg m^{-3} (1.0 kg m^{-3} typical)

Volume to surface ratio

0.07-0.1 m^3 m^{-2}

2. MICROALGAE BASED PROCESSES

Open photobioreactors: Raceways



Typical biomass productivity

0.015 kg m^{-2} day^{-1} (~45 tons ha^{-1} year^{-1})

Maximum biomass concentration

0.5 kg m^{-3} (0.25 kg m^{-3} typical)

Volume to surface ratio

0.2-0.4 m^{3} m^{-2}

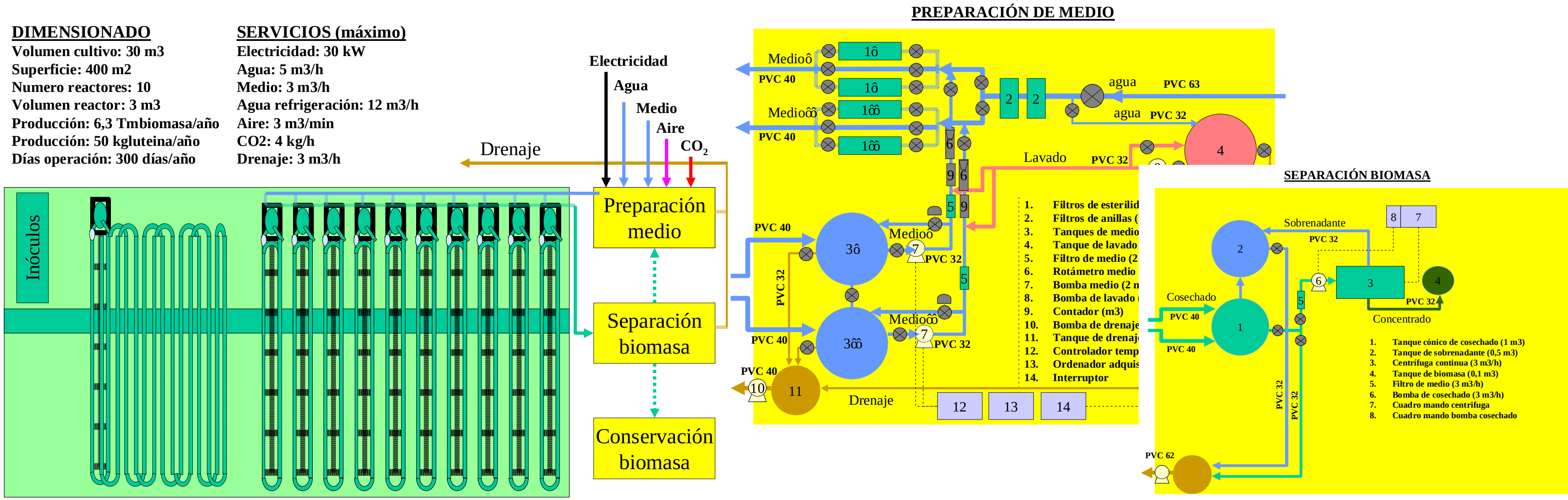
2. MICROALGAE BASED PROCESSES

Tubular industrial facility

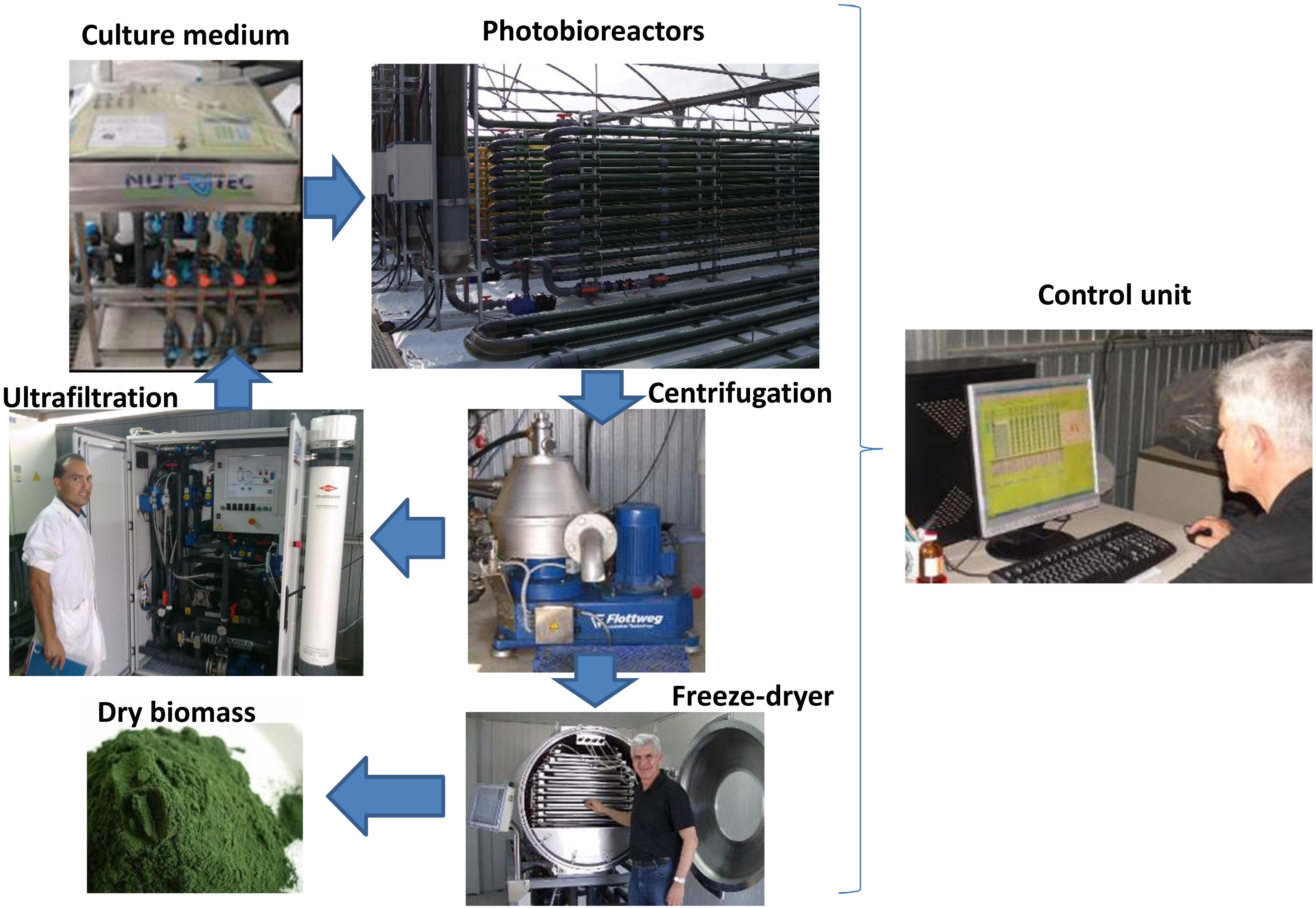
DIAGRAMA GENERAL

DIMENSIONADO
- Volumen cultivo: 30 m3
- Superficie: 400 m2
- Numero reactores: 10
- Volumen reactor: 3 m3
- Producción: 6,3 Tmbiomasa/año
- Producción: 50 kgluteina/año
- Días operación: 300 días/año

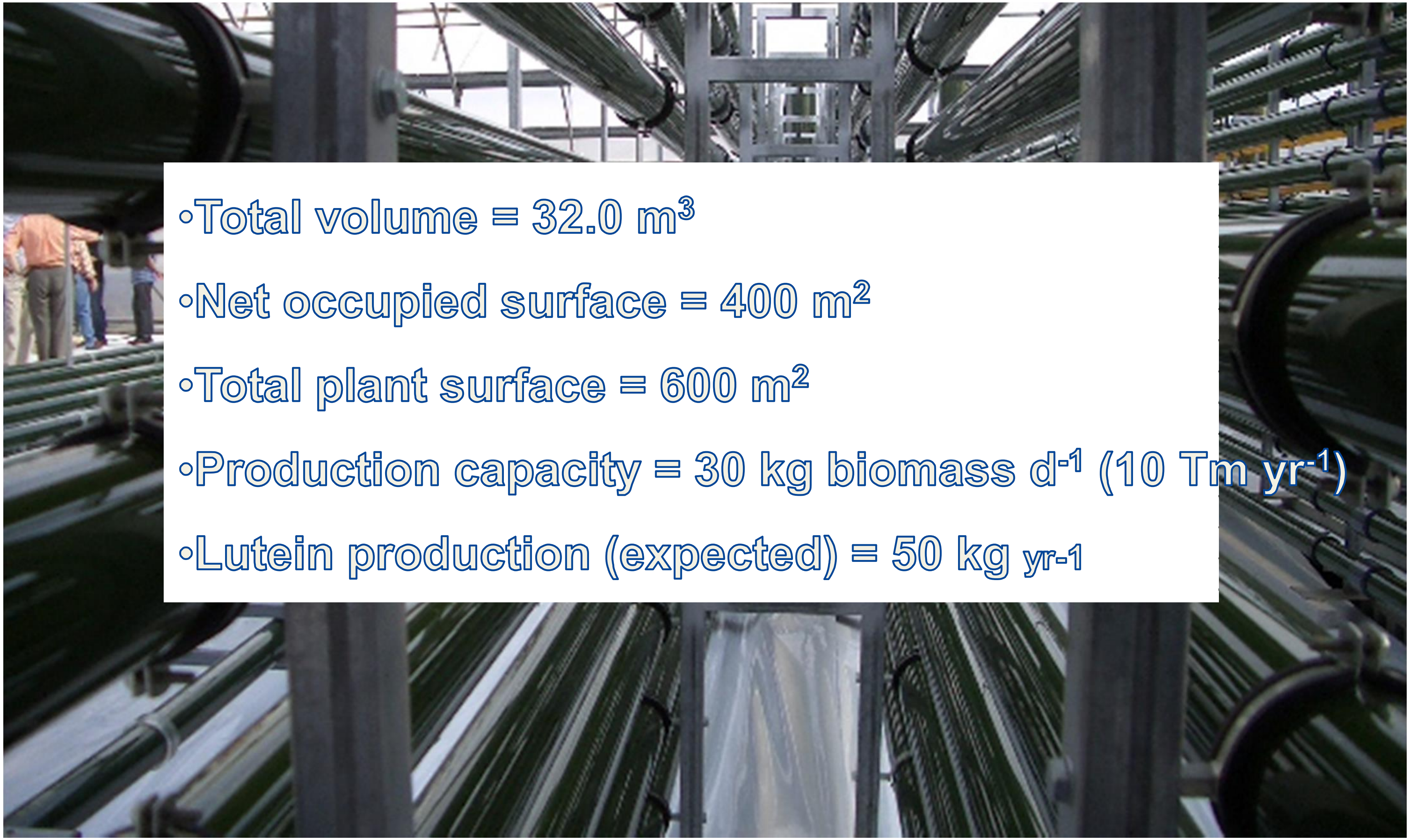
SERVICIOS (máximo)
- Electricidad: 30 kW
- Agua: 5 m3/h
- Medio: 3 m3/h
- Agua refrigeración: 12 m3/h
- Aire: 3 m3/min
- CO2: 4 kg/h
- Drenaje: 3 m3/h



2. MICROALGAE BASED PROCESSES



2. MICROALGAE BASED PROCESSES



- Total volume = 32.0 m^3
- Net occupied surface = 400 m^2
- Total plant surface = 600 m^2
- Production capacity = 30 kg biomass d^{-1} (10 Tm yr^{-1})
- Lutein production (expected) = 50 kg $_{yr-1}$

2. MICROALGAE BASED PROCESSES

Characteristics of raw material

Complex biomass
Many different compounds in small quantities
Homogeneous: no mechanical separation
High water content
Protein rich
Variable lipid content
Variable carbohydrate content
Some high value products
Minerals, nucleotides, etc...

Table V. (A) Chemical composition of some food source microalgae compared with other human food sources (% of dry matter) (adapted from Miao and Wu [15]), (B) Some of microalgae products with applications in cosmetics (adapted from Derner *et al.* [38]) and (C) Chemical composition of biofuel source microalgae.

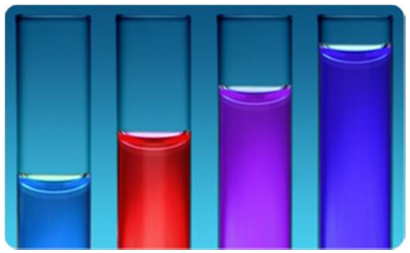
Source	Carbohydrates (%)	Proteins (%)	Lipids (%)
(A)			
Anabaena cylindrica	25–30	43–56	4–7
Chalmydomonas rheinhardii	17	48	21
Chlorella vulgaris	12–17	51–58	14–22
Dunaliella salina	32	57	6
Porphyidium Cruentum	40–57	28–39	9–14
Spirulina maxima	13–16	60–71	6–7

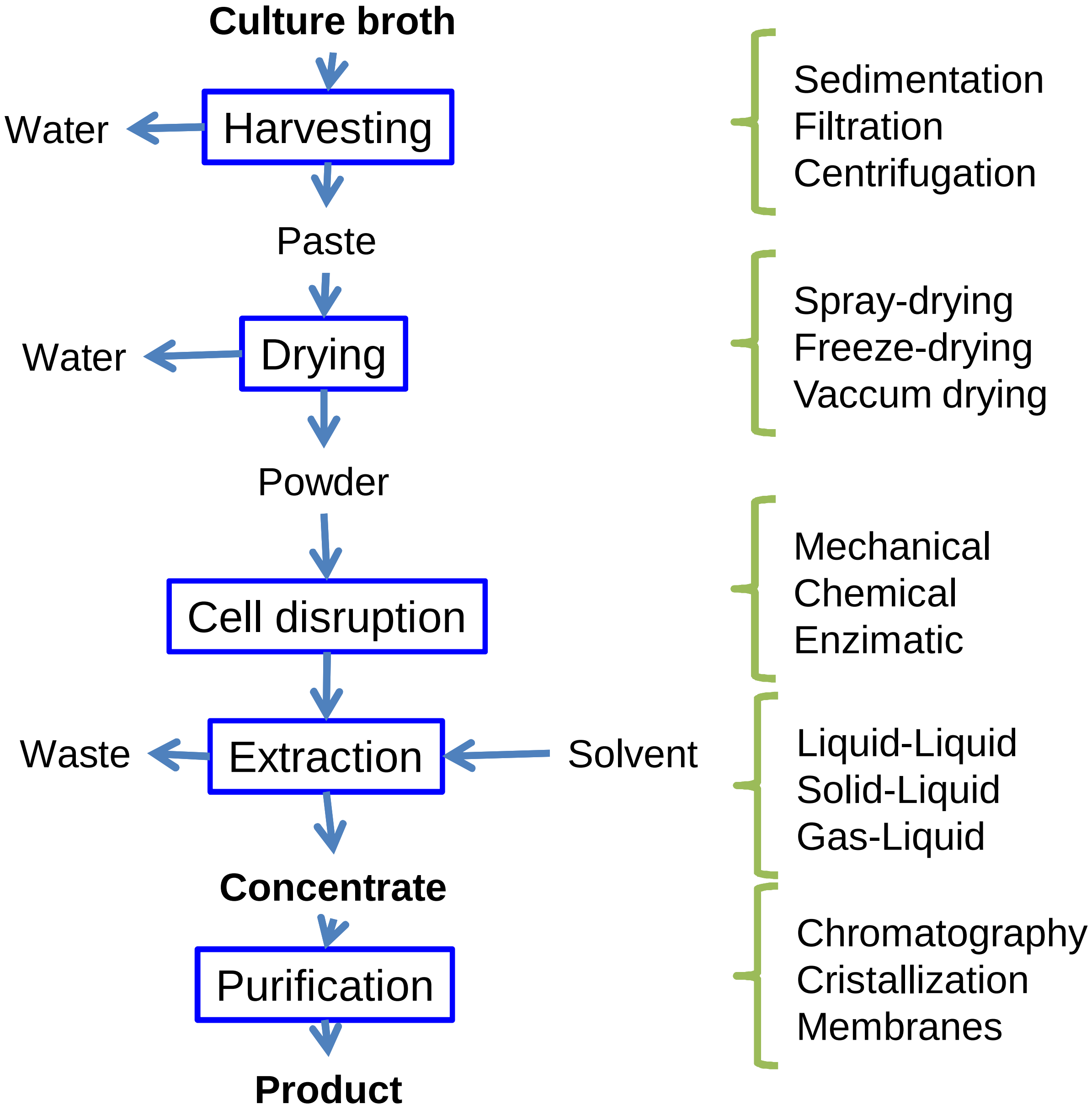
Basic component classes:

Proteins
Carbohydrates
Lipids
Ashes

2. MICROALGAE BASED PROCESSES

Overall scheme





2. MICROALGAE BASED PROCESSES

Product-specific vs integrated processes

Product-specific	
	Strain selected for its high content/purity/productivity in the desired product
	Extraction/recovery steps designed for maximum product yield/purity
	By-products and waste disregarded

Integrated	
	The main product is defined and a variety of strains are considered
	By-products and waste recycling is considered for each.
	Extraction/recovery step are designed to preserve by-products.
	Main product yield is sacrificed for the overall performance including recycling.

For microalgal biofuel, integrated processing is a must, not an option.

2. MICROALGAE BASED PROCESSES

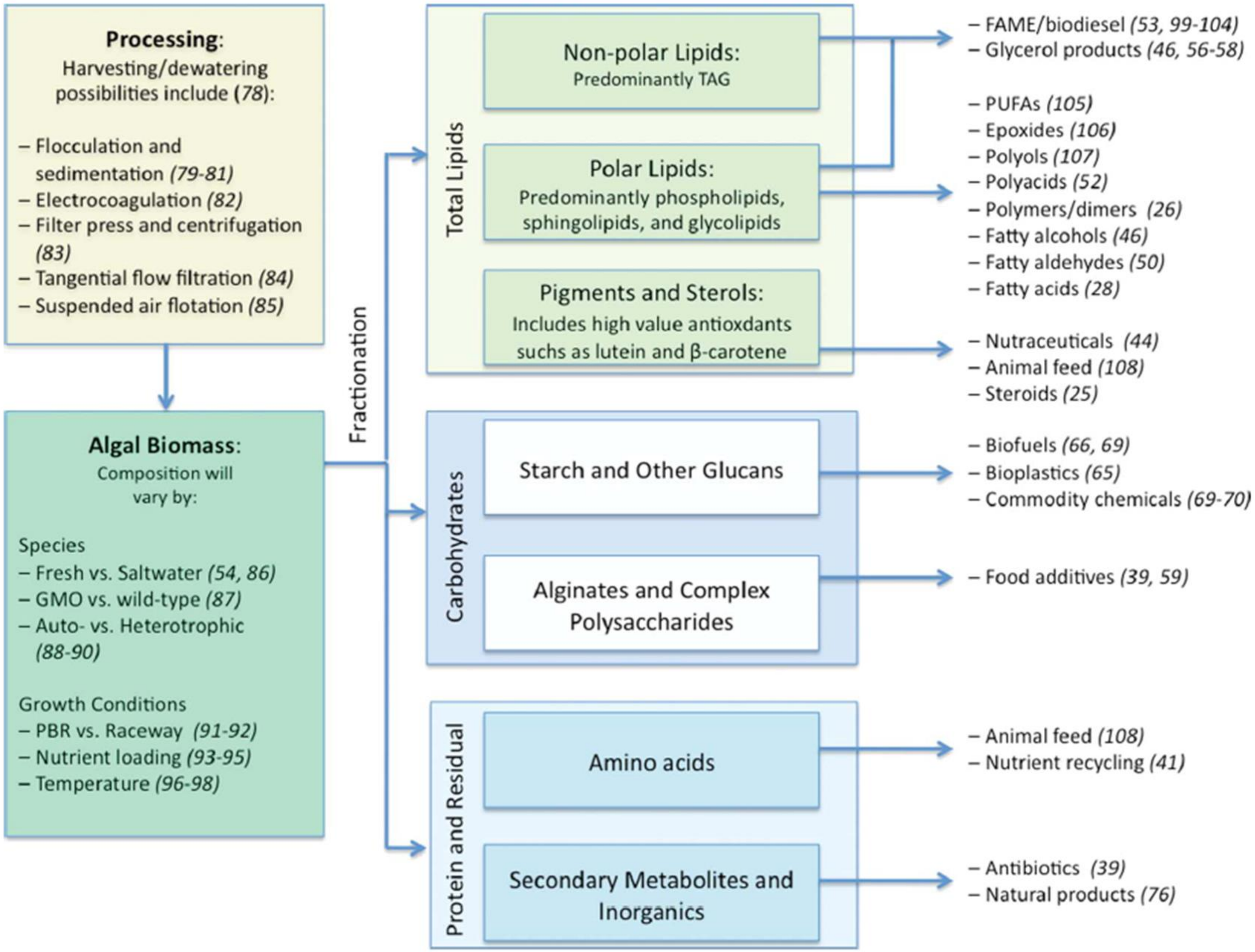


Fig. 2 General schematic for algal biomass fractionation and co-product generation. References are provided in italics.

Sharma et al. 2011. Green Chem. 13,2993

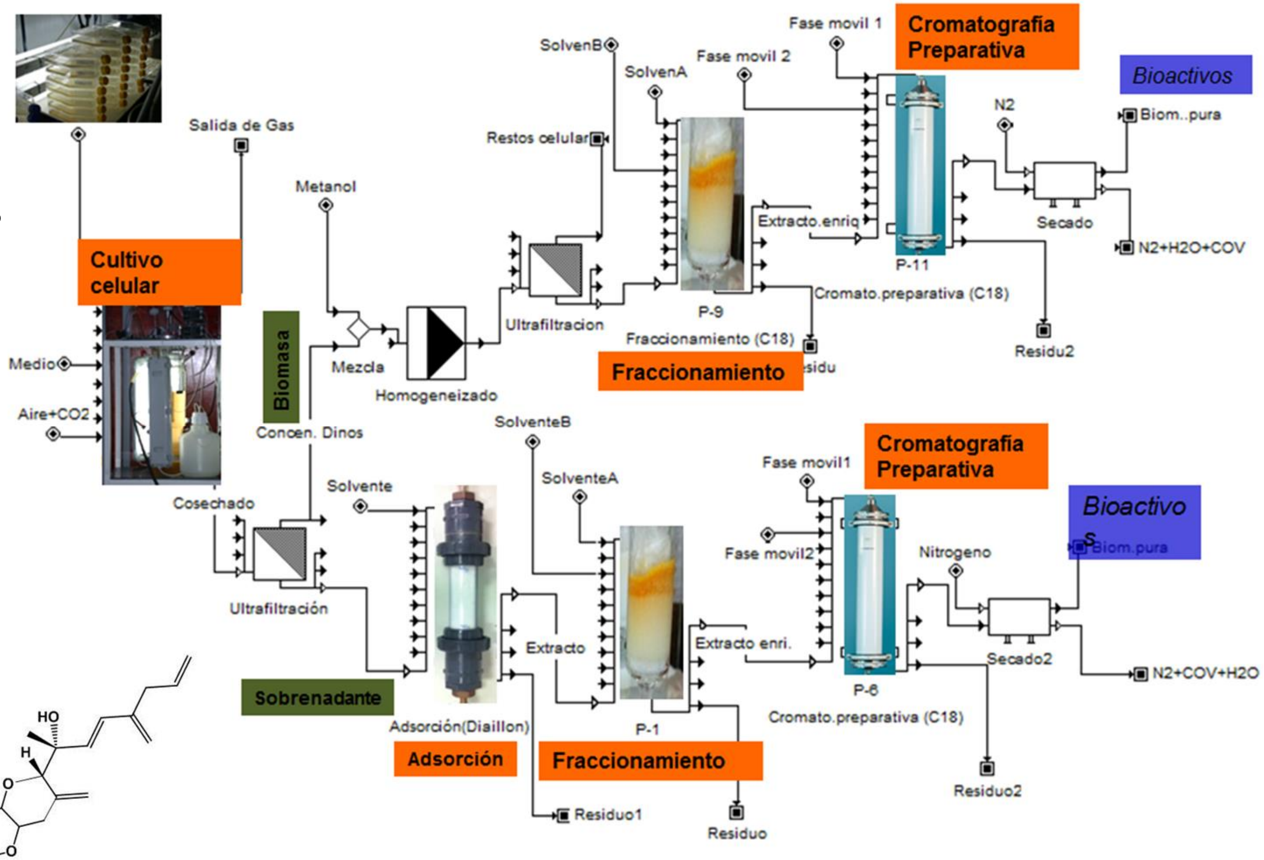
2. MICROALGAE BASED PROCESSES

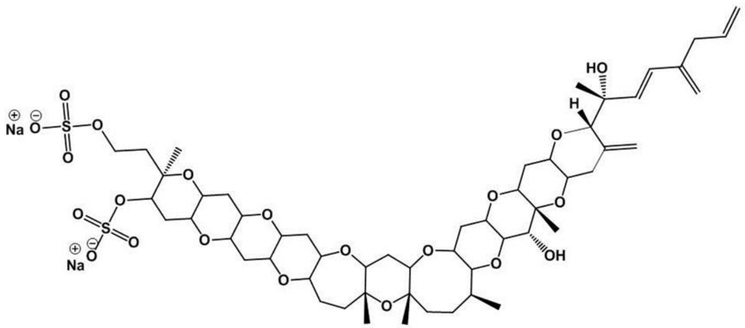
Example: Yesotoxins from *Dinoflagellates*

Comercial

Highlights:

- **Sensible microorganisms**
- **Low shear stress conditions**
- **Simple cell disruption**
- **Complex product recovery**
- **Chromatography necessary**





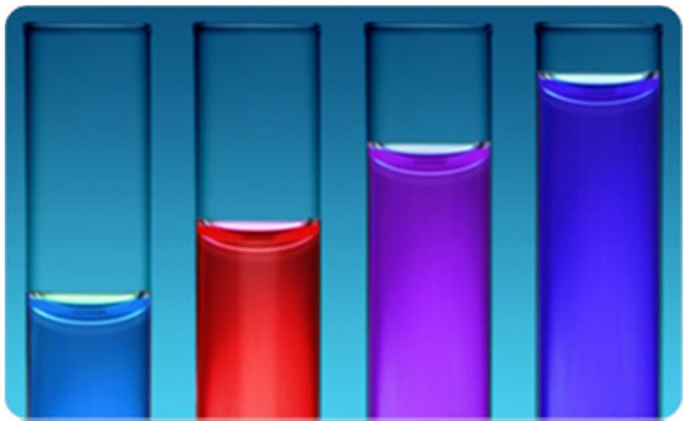
2. MICROALGAE BASED PROCESSES

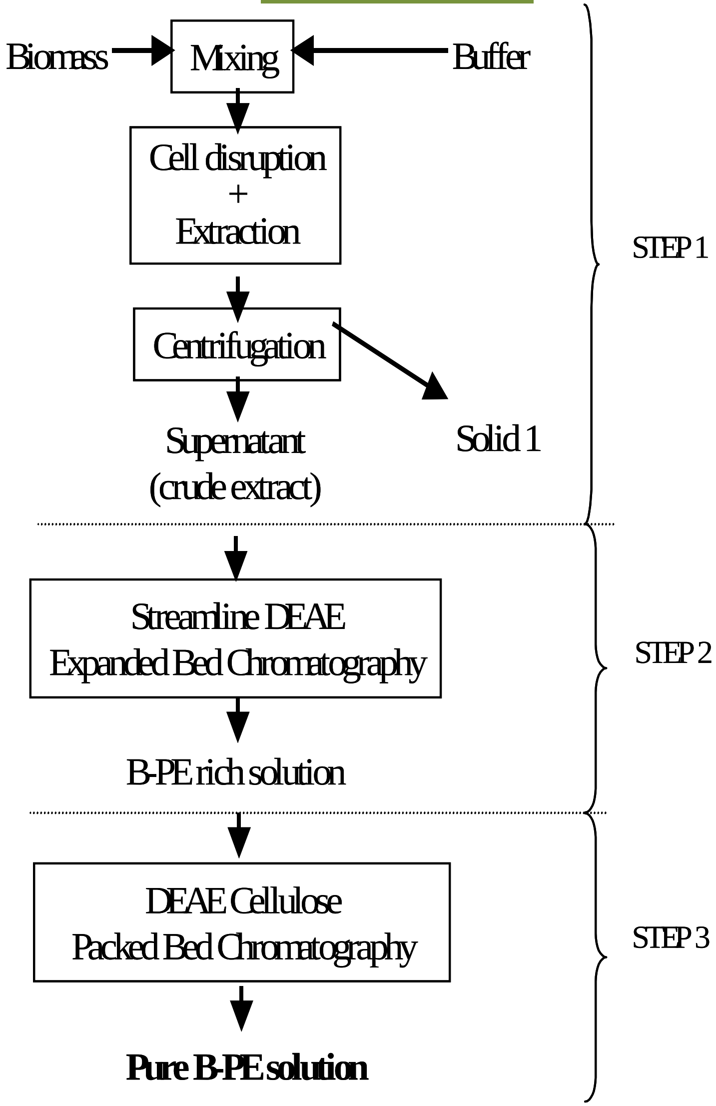
Example: Phycocyanin recovery from *Spirulina* *(real process)*

Comercial

Highlights:

- **Colorant and biomedical uses**
- **Protein nature**
- **Sensible to extreme pH and temperatures**
- **Utilization of expanded bed chromatography**
- **Purification is performed by chromatography**





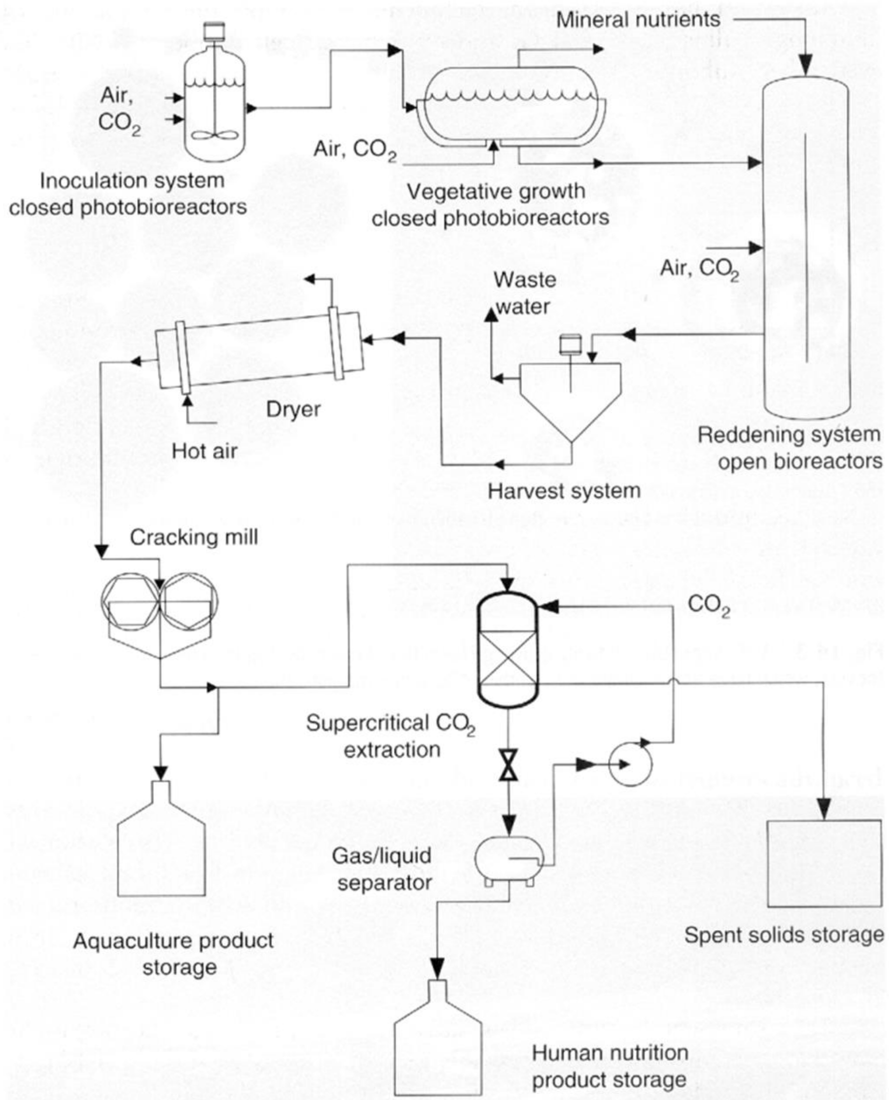
2. MICROALGAE BASED PROCESSES

Example: Astaxanthin recovery from *H. pluvialis* (real process)

Comercial

Highlights:

- **Hot drying: temperature sensitive?**
- **Cell-breakage step: strong cell wall?**
- **Separation: SCF CO_2 extraction.**
- **Over 95% d.wt. waste.**
- **Absence of other carotenoids allows obtaining pure astaxanthin**



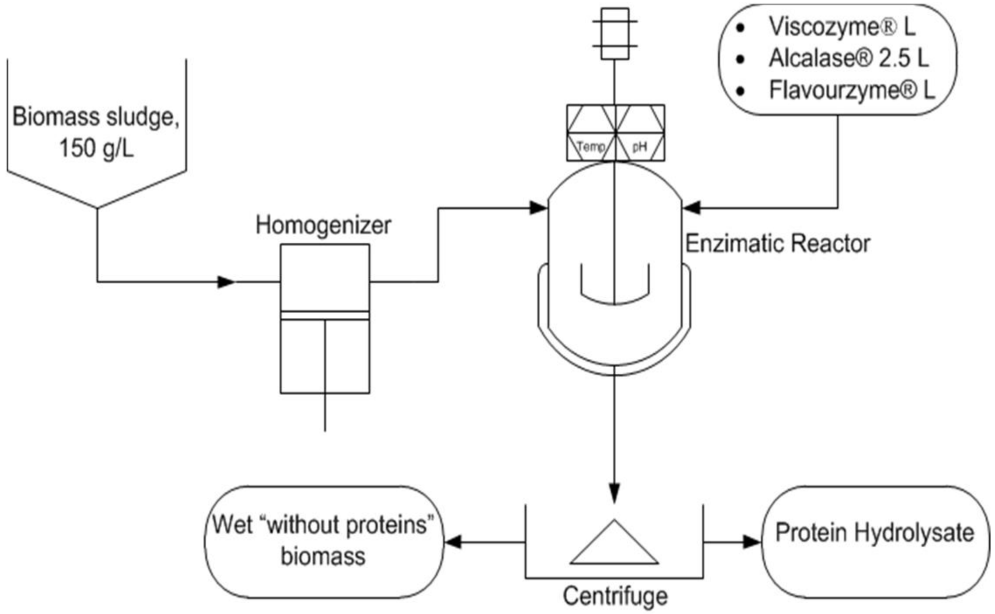
2. MICROALGAE BASED PROCESSES

Example: Aminoacids concentrates from *Spirulina*

Comercial
Real production with local company

Highlights:

- **No dry biomass is required**
- **Process at soft conditions**
- **No purification required**
- **Simply and easy to carry out**
- **Low quality biomass accepted**



Enzymatic process with commercial enzymes

Centrifugation/filtration

Hydrolysis degree=60-70%

Free amino-acids concentration=40 g/L

2. MICROALGAE BASED PROCESSES

Example: Biodiesel from *Nannochloropsis*

Non comercial

Highlights:

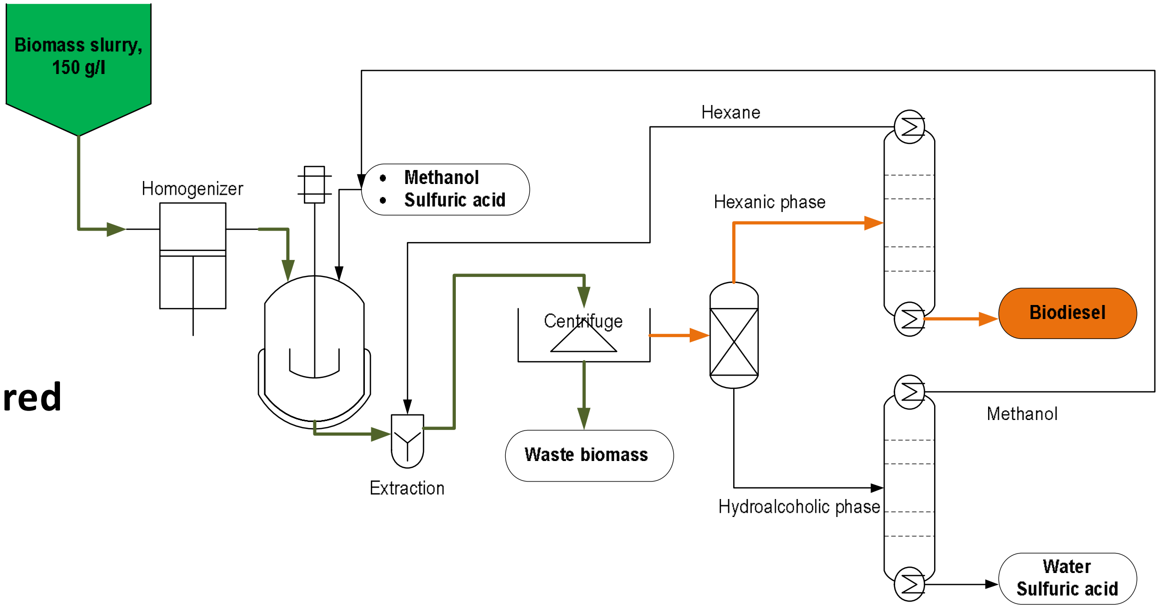
Å **No dry biomass is required**

Å **Process at hard conditions**

Å **Utilization of solvents**

Å **Only fatty acids are used**

Å **High fatty acids content required**



Direct transesterification + extraction:

Overall 50% of lipids are saponificable

Sulfuric acid 5%d.wt., Methanol 3 v/v, 80ºC, 1 h

Hexane 3 v/v

Transesterification yield =85%

Fatty acid recovery=80%

3. ENERGY FROM MICROALGAE

Biodiesel production

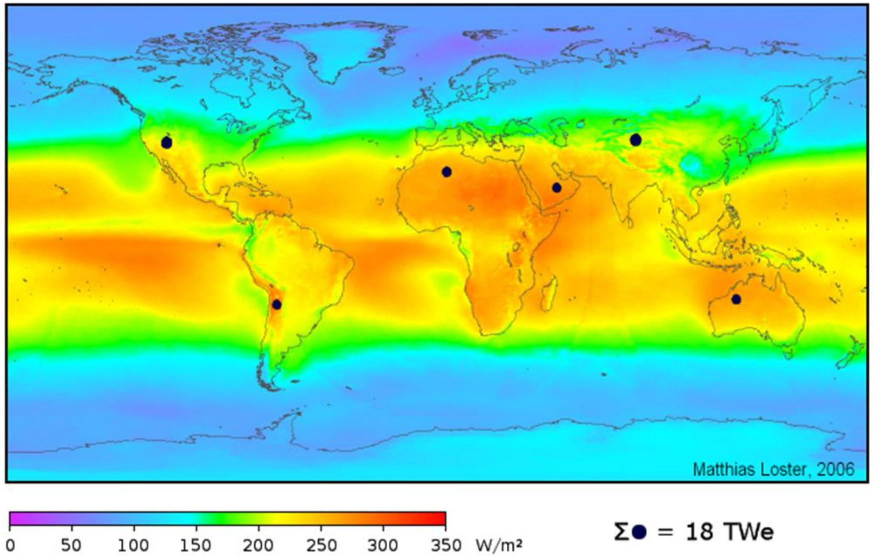
United States biodiesel needs = 0.53 billion m^3 (to replace all transport fuel)

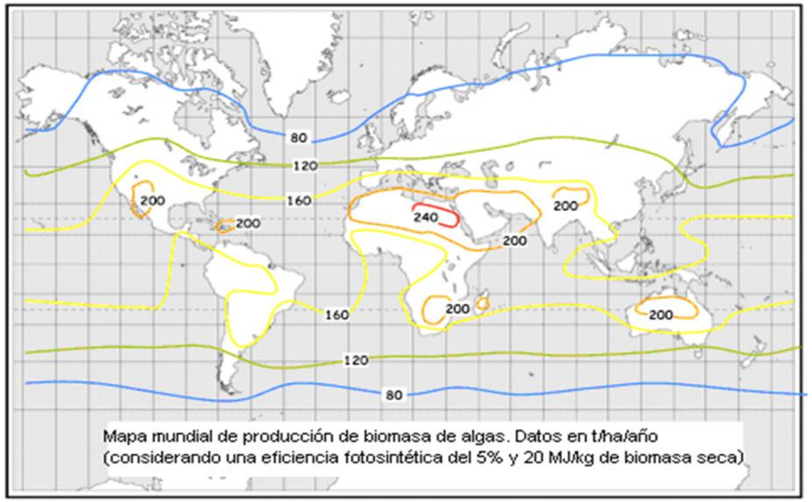
Crop (Y. Chisty, 2007. Biotechnol. Adv.)	Oil yield (L/ha)	Land area needed (M ha)	Percent of existing US cropping area	
Corn	172	3,080	1,692	Not feasible
Soybean	446	1,188	652	
Canola	1,190	446	244	
Jatropha	1,892	280	154	
Coconut	2,689	198	108	
Oil palm	5,950	90	48	
Microalgae[a]	35,202	15.2	8	Optimistic values
Microalgae[b]	70,405	7.6	4	
Microalgae[c]	18,750	28.2	15.0	Proved values
Microalgae[d]	17,330	30.6	16.3	
Microalgae[e]	23,500	20.9	11	Proved
Microalgae[f]	35,300	15.2	8	Estimated

a, 20% w/w oil in biomass (Y. Chisty, 2007. Biotechnol. Adv.)
b, 40% w/w oil in biomass (Y. Chisty, 2007. Biotechnol. Adv.)
c, *Phaeodactylum tricornutum* 20% oil in biomass, 5g_{lipids}/m^2·day. Acién Fernández et al., (1998)
d, *Scenedesmus almeriensis*, 16% oil in biomass. Fernández Sevilla et al., (2008)
e, *Nannochloropsis* sp. Two-step process 200 mg_{oil}/L·day, 9.5 $g_{biomass}$/m^2·day, Rodolfi et al., (2009)
f, *Nannochloropsis* sp. Two-step process tropical area, Rodolfi et al (2009)

3. ENERGY FROM MICROALGAE

Maximum energy conversion achievable





Direct PAR	⟷	Biomass	⟷	Oil
30,511 GJ ha^{-1}		180-200 Tn ha^{-1}		30 tn ha^{-1}

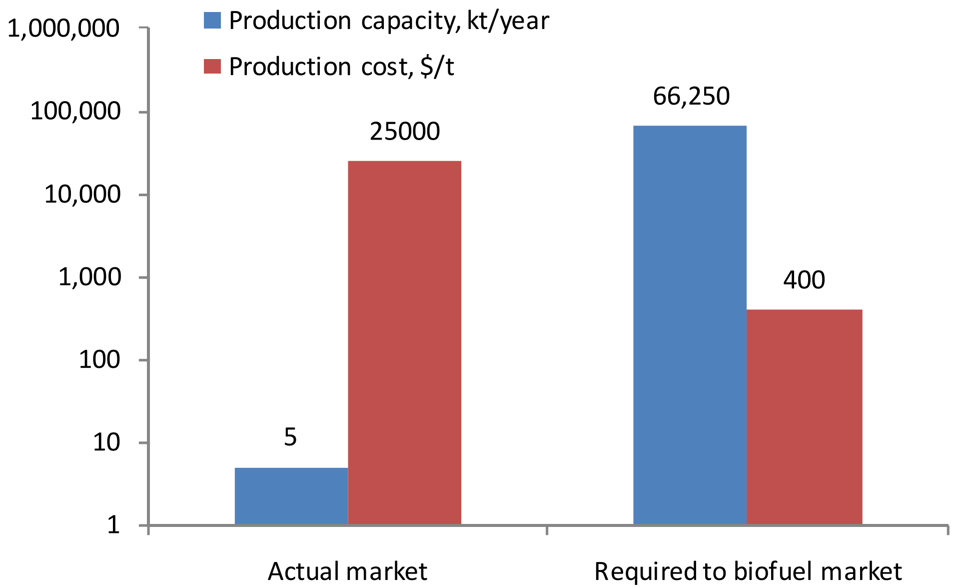
CHALLENGE

ENERGY ⟷ COST

3. ENERGY FROM MICROALGAE

Actual and biofuel markets

- The microalgal biomass market produces about 5 kt of dry matter/year at production costs of 25000 $/t (Pulz and Gross, 2004)
- To meet the biofuel market requirements it is necessary to increase the production capacity by four orders of magnitude and to reduce the production cost by two orders of magnitude.



International initiatives for microalgae production

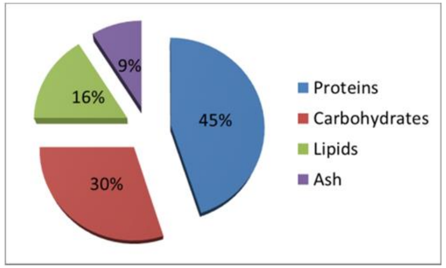
1. Europe: **MBD** (PBR), **Algae.Tec** (PBR) - at power plants, **Ecoduna** (PBR, also had project with Vattenfall), **Proviron** (PBR, at landfill) **, Vattenfall, RWE, E.ON** (PBRs, all inactive now), **Eni** (ponds, at their Gela oil refinery, Sicily), **A4F** (PBR, at a cement plant), **BioFuel Systems**; **Abengoa**; **Endesa** (PBRs), **EnAlgae** Plymouth Univ. (PBRs at power plant), **Seambiotics** (ponds, coal-fired plant)
2. Asia: **ENN** (PBRs) and **Hearol** (ponds) at power plants
3. North America: **Pond Biofuels** (PBR, at Cement Plant), **Touchstone** (ponds), **Bioprocess Algae** (PBRs), k**uehnle Agro systems** (PBRs), **Joule** (PBRs), **Solix** (PBR), **GreenFuels** (PBRs, broke in 2009)
4. SouthAmerica: **DesertBioenergy** (flat panels).
5. Australia: **Muradeel Pty Lt**d. (PBR), **Crucibe** (PBR)

3. ENERGY FROM MICROALGAE

Different technologies for microalgae production

3. ENERGY FROM MICROALGAE

Production of biofuels from microalgae



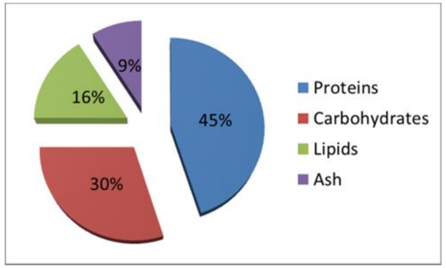
MICROALGAE BIOMASS

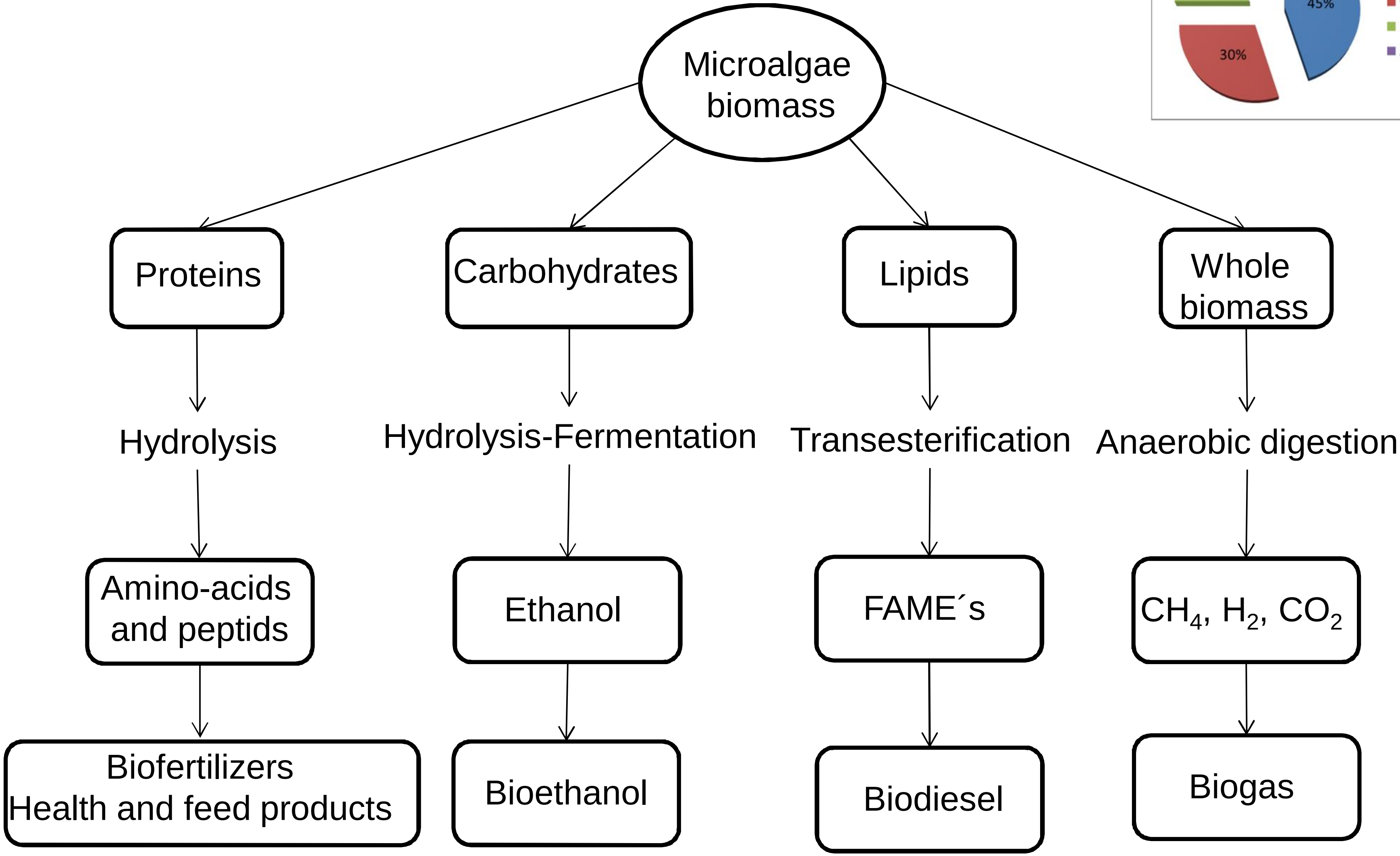
- COMBUSTION
  - Electricity
  - Heat
- DRY CHEMICAL CONVERSION
  - Pirolysis → Oils, Gas, Carbon
  - Gasification → Poor-medium gas
  - Hydrogasification → Methane, Ethane, Carbon
  - → Methanol, Methane, Ammonia, Electricity
- WET PROCESSES
  - Chemical reduction → Oils
  - Alcoholic fermentation → Ethanol
  - Anaerobic digestion → Methane

On this way only the CARBON fraction is used, nitrogen fraction is disregarded

3. ENERGY FROM MICROALGAE

Valorization routes for microalgae WET biomass

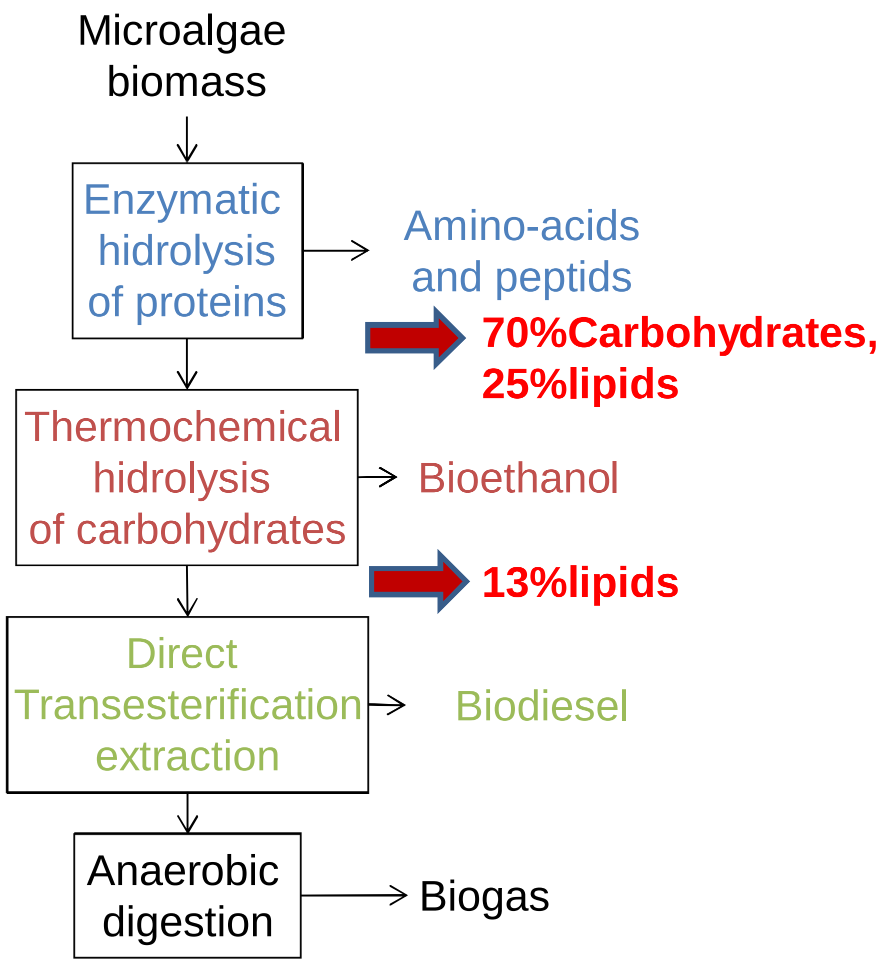




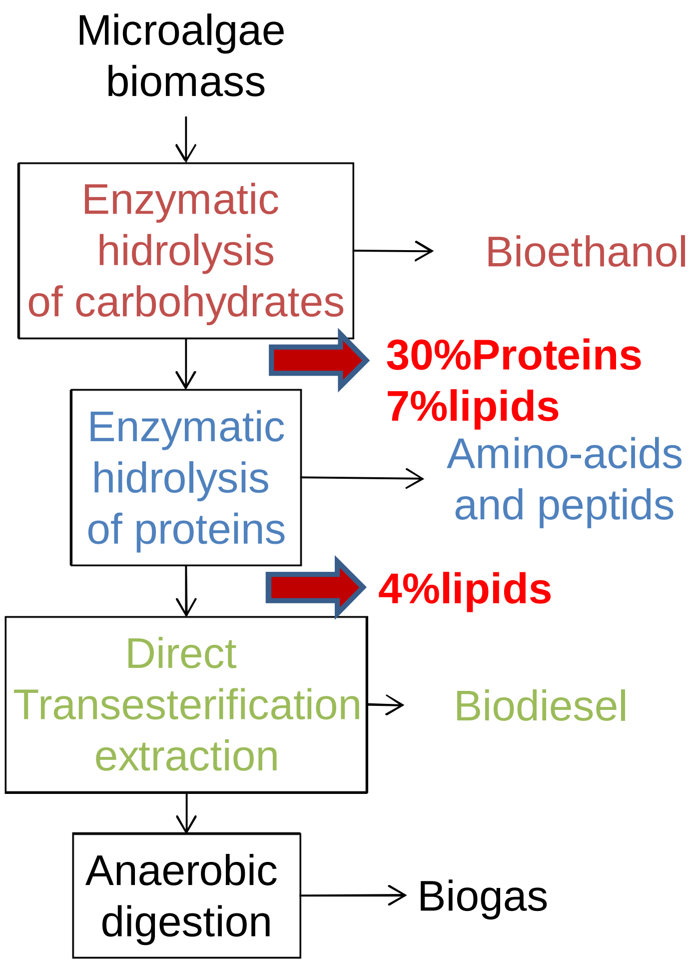
3. ENERGY FROM MICROALGAE

Integrated valorization of microalgae biomass

Strategy 1



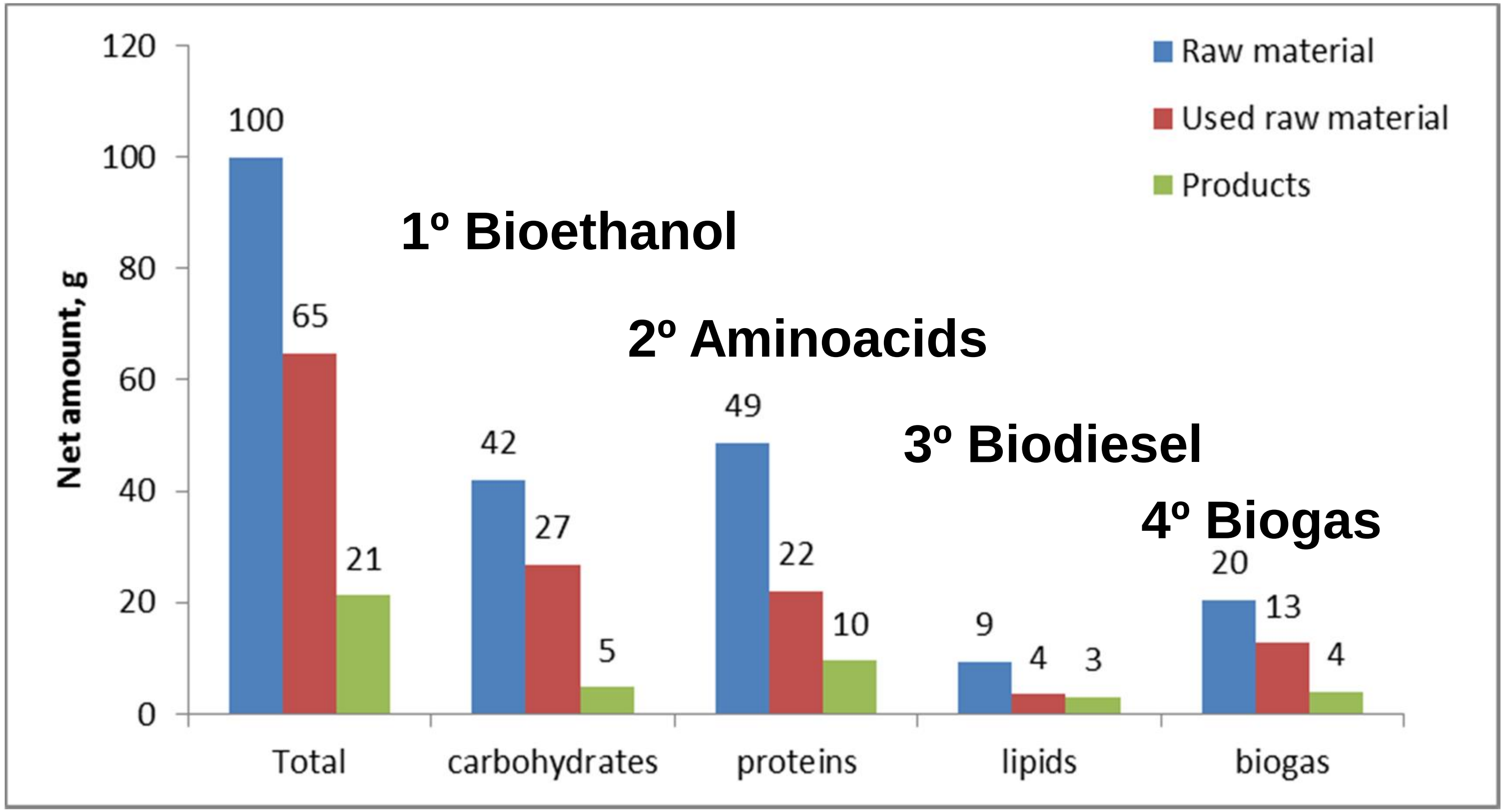
Strategy 2 (Patented)



3. ENERGY FROM MICROALGAE

Results by integrated valorization of microalgae biomass

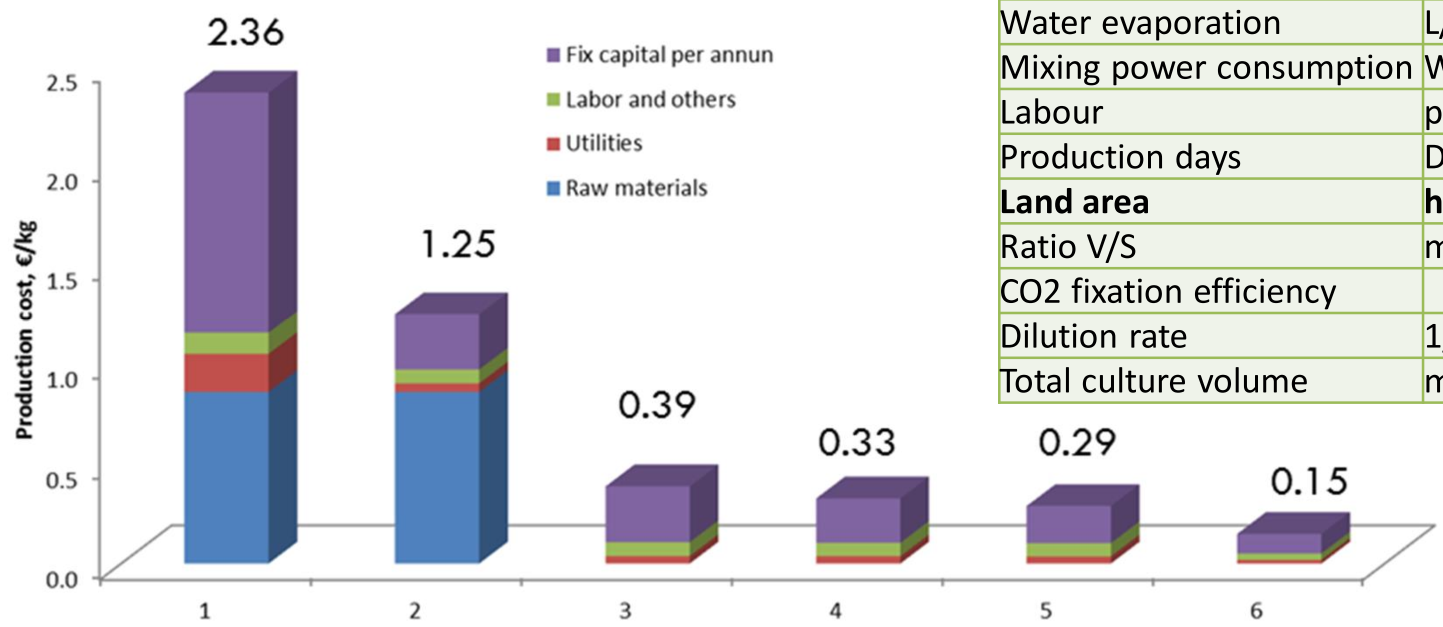
Ash-free biomass basis



Using the proposed integrated process a maximum amount of 65% of raw material is used, although due to the conversion yield to final products a 21% of end-product is obtained

3. ENERGY FROM MICROALGAE

Technological alternatives to produce biomass



Biomass productivity	g/m2/day	20
CO2 usage	kg/kgbiomass	4
Water evaporation	L/m2/day	10
Mixing power consumption	W/m3	2
Labour	people/ha	0.1
Production days	Days	365
Land area	**ha**	**100**
Ratio V/S	m3/m2	0.15
CO2 fixation efficiency		0.45
Dilution rate	1/day	0.2
Total culture volume	m3	150000

Scenario	Inputs	Reactor	Productivity	Harvesting
1	Water, CO2 and fertilizers	Raceway	Real	Centrifugation
2	Water, CO2 and fertilizers	Raceway	Real	Flocculation-Sedimentation+Centrifugation
3	Free flue gases and wastewater	Raceway	Real	Flocculation-Sedimentation+Centrifugation
4	Free flue gases and wastewater	Raceway	Real	Flocculation-LamellarSedimentation+Centrifugation
5	Free flue gases and wastewater	Raceway	Real	Flocculation-LamellarSedimentation+Filtration
6	Free flue gases and wastewater	Raceway	Theoretical	Flocculation-LamellarSedimentation+Filtration

Utilization of wastewater is the best option to reduce the microalgae production cost

3. ENERGY FROM MICROALGAE

To produce biofuels from microalga it is necessary to achieve biomass <u>production cost</u> lower than 0.5 ú/kg

Å **At 1 ha scale 10 ú/kg**
Å **At 100 ha scale 4 ú/kg**
Å **What will be possible 0.40 ú/kg**

Norsker et al., (2011) Microalgal production-a close look at economics, Biotechnology Advances 29:24-27

Å **Using CO_2 and fertilizers 1.25 ú/kg**
Å **Using flue gases and wastewater 0.39ú/kg**
Å **Maximal theoretical (ideal conditions) 0.15 ú/kg**

Acién et al., (2013) Economics of microalgae biomass production, *Biofuels from Algae*, Elsevier

Although it is possible to achieve this production cost, it is only feasible using effluents from other industries

3. ENERGY FROM MICROALGAE

Necessity of coupling with wastewater to produce biofuels

Biofuels market requires large productions, and thus large amounts of resources.
To replace petrodiesel consumed in Spain not enough resources are available

				Equivalent to:
	Diesel consumption, Spain 2009	**31.10**	**Million tonnes**	
	To replace 10% consumption	**3.1**	**Million tonnes**	
Biodiesel yield 90%	Microalgae oil required	3.4	Million tonnes	
Oil content 20%	Microalgae biomass required	17.3	Million tonnes	0.8 Million Ha (100 Tn/Ha)
1.8 $kgCO_2/kg$	Carbon dioxide required	35.2	Million tonnes	5.5 GWe (6300 Tn/GW)
0.3 $kgNO_3/kg$	Nitrate required	5.6	Million tonnes	>4 times produced
0.03 $kgPO_4/kg$	Phosphate required	0.6	Million tonnes	>10 times produced

Large amounts of water, carbon dioxide, nitrate and phosphate are available in wastewater treatment field

Population	**150,000.00**	**people**
Water flow	50,000.00	m^3/day
Nitrate/amonia content	21.00	mgN/L
Phosphate content	4.00	mgP/L
nitrate/amonia amount	4.65	Tn/day
Phosphate amount	0.61	Tn/day

Biomass by nitrate/amonia	15.82	Tn/day
Biomass by phosphate	20.00	Tn/day
Land required	57.73	Ha
Microalgae biomass	5,772.96	Tn/year
Microalgae oil	1,154.59	Tn/year
Biodiesel	1,039.13	Tn/year

3. ENERGY FROM MICROALGAE

Wastewater treatment by activated sludge imposes a high cost and energy consumption, nutrients being lost

Aqualia (250 Wastewater treatment plants=500 Mm3/yr)

- **Water treatment cost=0.2 ú/m3**

- **Energy consumption= 0.5 kWh/m3**
- **Nitrogen removal/losses=25.000 t/yr**
- **Phosphorous removal/losses =5.000 t/yr**

} **“Microalgae=0.5 Mt/yrò**

Wastewater treatment is designed to remove nutrients and not to produce biomass, employing a large amount of energy to do it

4. WASTEWATER TREATMENT

Depuration of wastewater by recicling nutrients and producing biomass to biofuels

I. Rawat et al. / Applied Energy 88 (2011) 3411–3424

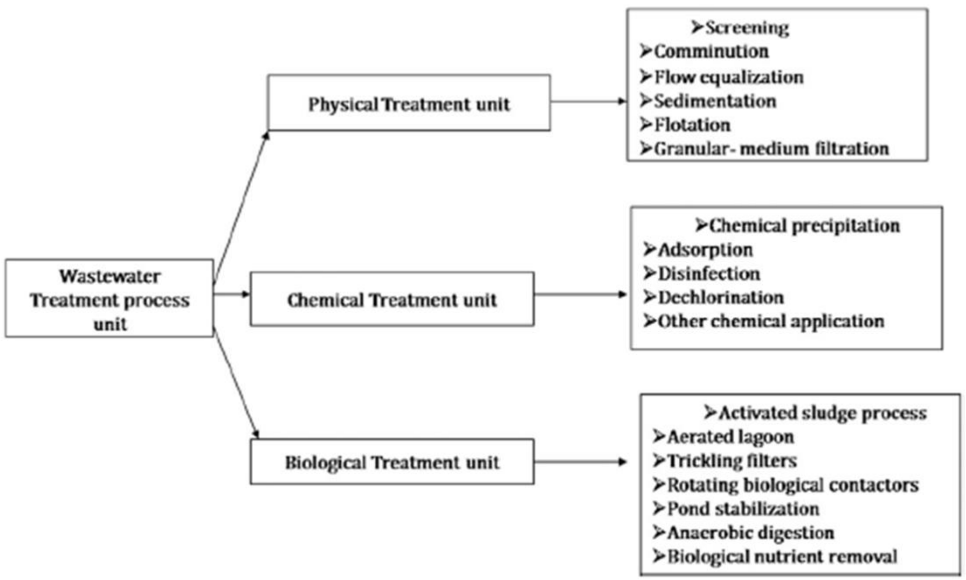


Fig. 1. Common wastewater treatment processes.

WATER RESEARCH 40 (2006) 2799–2815
ELSEVIER
Available at www.sciencedirect.com
SCIENCE DIRECT
journal homepage: www.elsevier.com/locate/watres

Review

Algal–bacterial processes for the treatment of hazardous contaminants: A review

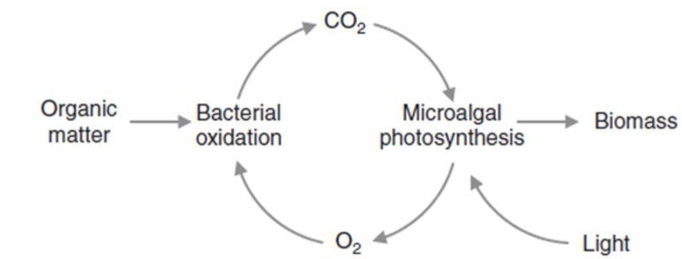


Fig. 1 – Principle of photosynthetic oxygenation in BOD removal processes.

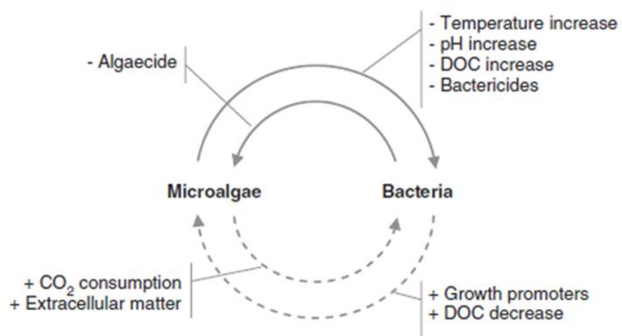


Fig. 2 – Positive (dashed line) and negative (plain line) interactions between microalgae and bacteria.

<u>Advantages</u>:

- Lower power consumption
- Nutrients recovery
- Water recovery

<u>Disavantages?</u>

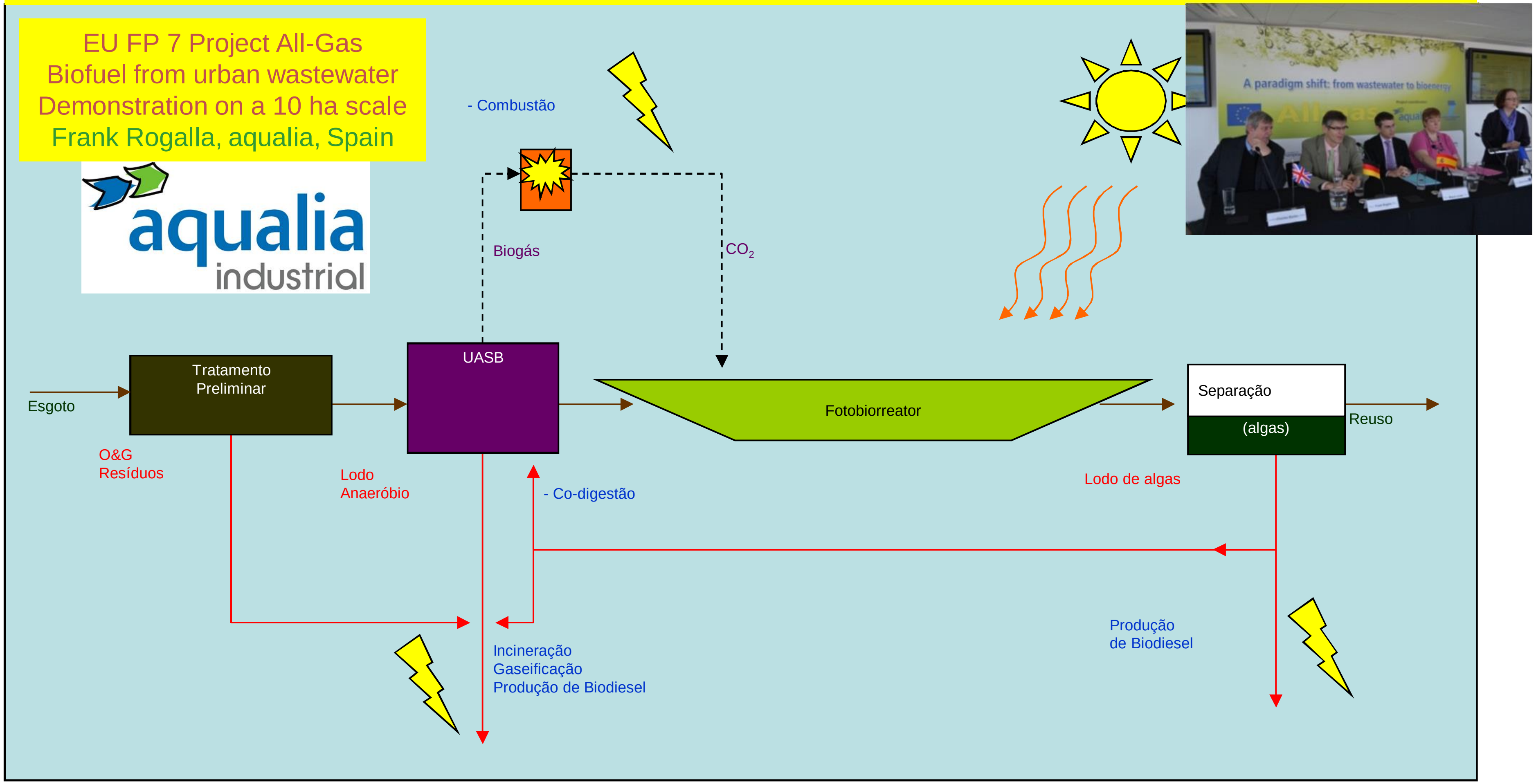
- Large areas required
- High light and moderate temperature required

4. WASTEWATER TREATMENT

Nutrients: recovery of nutrients from efluents

New Wastewater Treatment Flowsheet ?

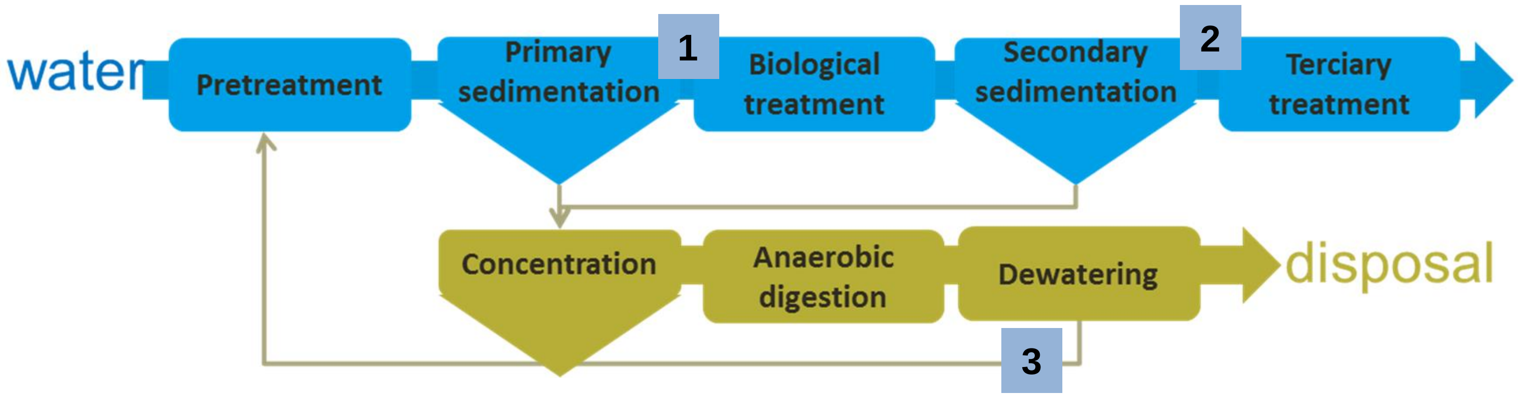
Value Creation instead of Waste Production …



4. WASTEWATER TREATMENT

Types of wastewater

Different wastewaters are available at industrial plants



Conc., mg/L	Arnon	1 Primary treatment	2 Secondary treatment	3 Anaerobic digestion
COD	-	500.0	110.0	300.0
N-NO3	114.0	2.4	0.0	5.3
N-NH4	0.0	62.6	20.8	506.5
P-PO4	41.0	11.3	10.0	12.0

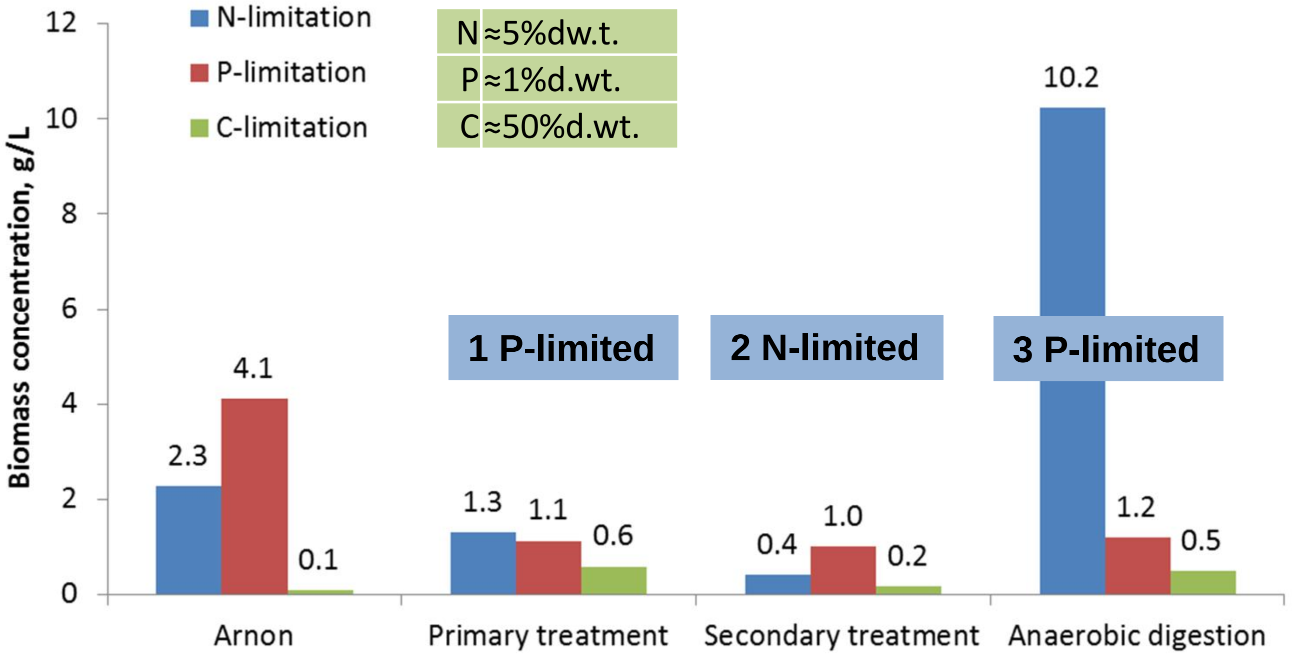
Conc., mg/L	Arnon	1 Primary treatment	2 Secondary treatment	3 Anaerobic digestion
TKN	114	65	20	511
TP	41	11	10	12
TC	47	296	82	247

Composition of each wastewater is largely different, thus them must be managed differently

4. WASTEWATER TREATMENT

Limiting factors

Wastewater composition limits the biomass productivity

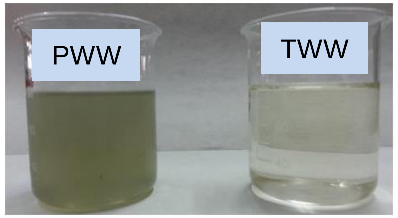


Using wastewater the cultures are ever carbon limited , but also N and P limitation exist versus the use of standard culture mediums

4. WASTEWATER TREATMENT

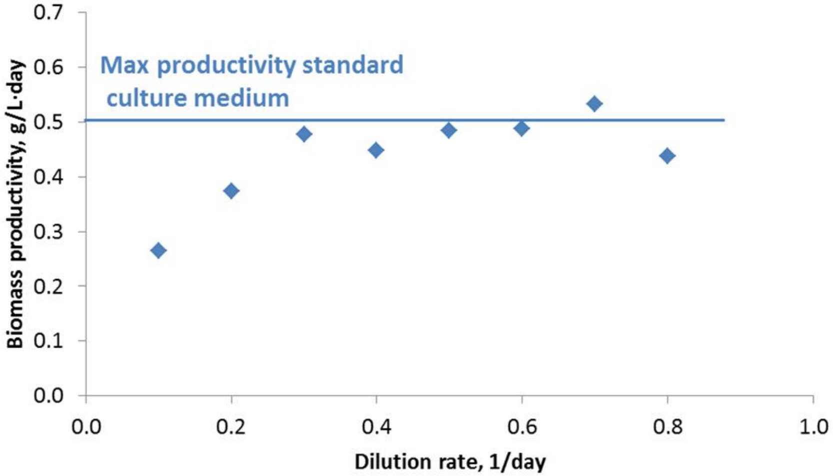
Wastewater from primary treatment

Characteristic: Dirty water, with high COD, N and P content

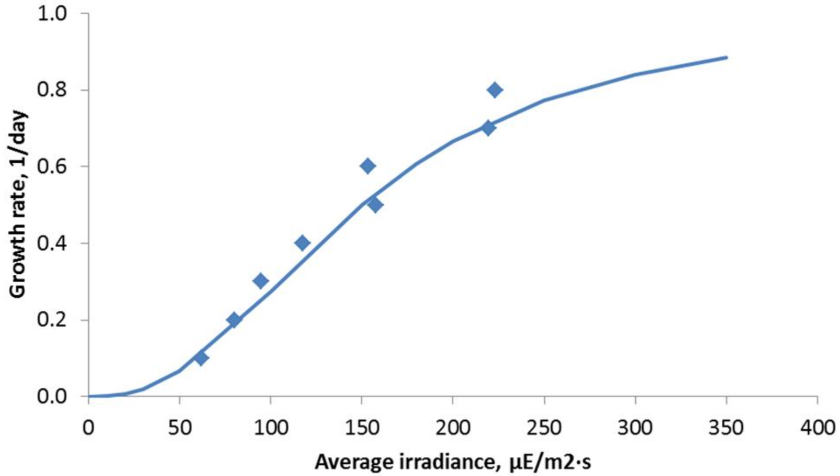


PWW=Primary WW
TWW=Treated WW

Biomass productivity



Growth rate



Data from laboratory under optimal culture conditions

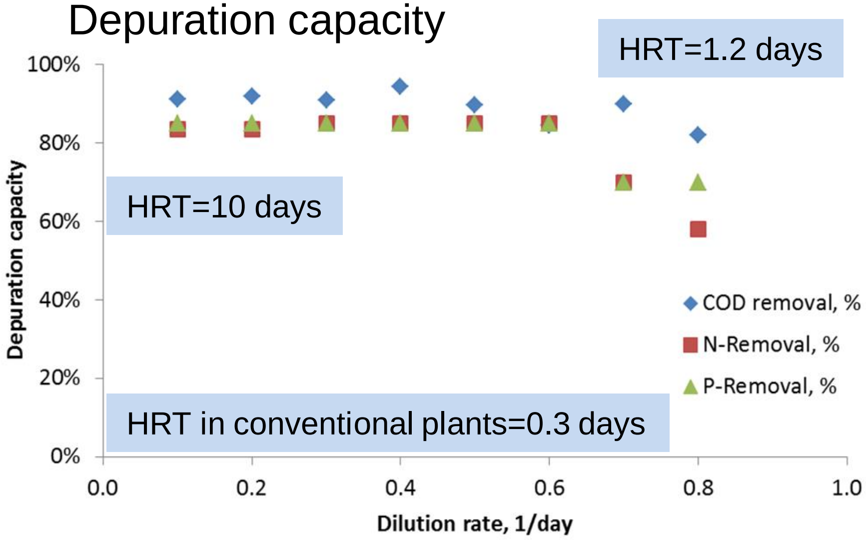
Using wastewater as culture medium the cultures performed as light-limited cultures, no other limitation being observed indoor

4. WASTEWATER TREATMENT

Wastewater from primary treatment

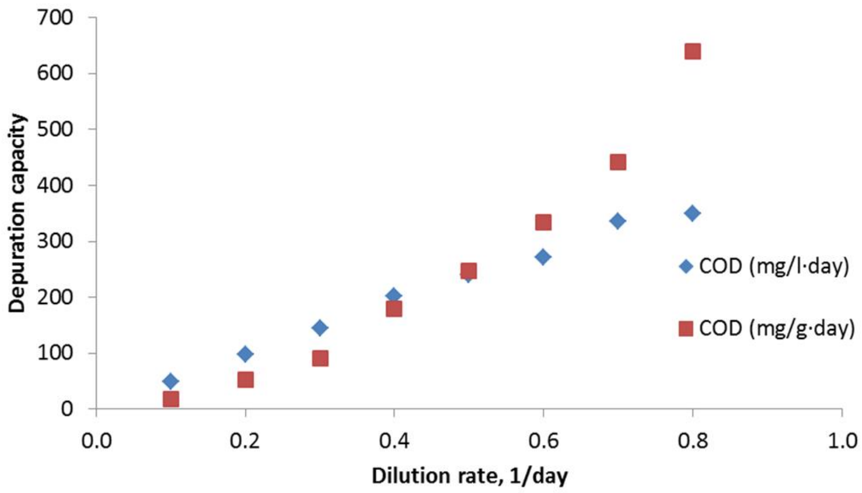
Removal capacity per reactor volume basis must be maximized increasing the water flow rate

Depuration capacity



HRT=Hydraulic retention time

Data from laboratory under optimal culture conditions



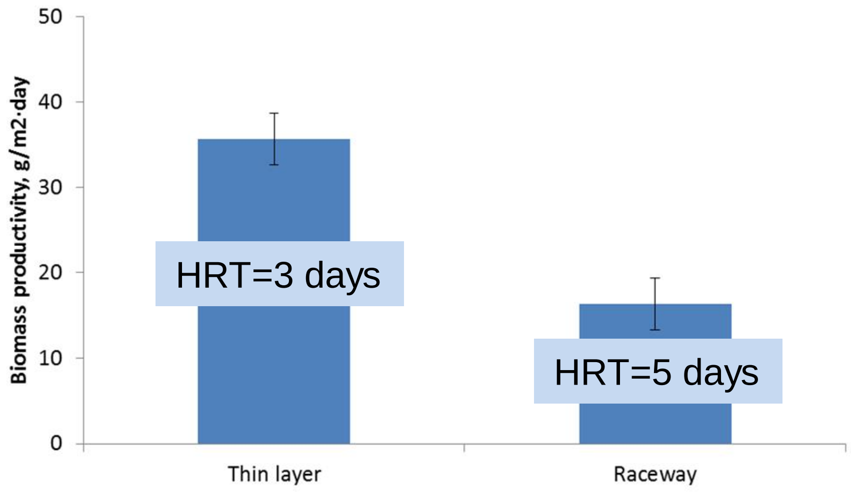
N and P are efficiently removed till 0.7 1/day, but the COD depuration capacity is not saturated, then COD removal is much higher than N-P

4. WASTEWATER TREATMENT

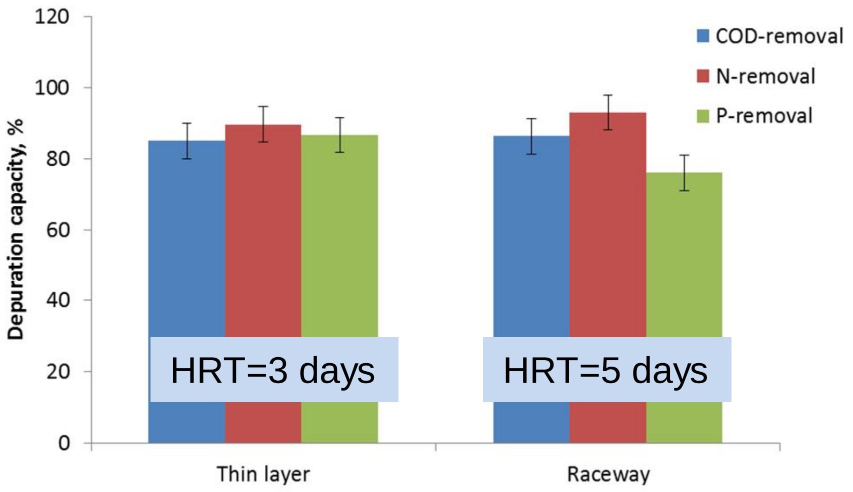
Nutrients: recovery of nutrients from efluents

Outdoor the performance of the system has been verified in continuous mode

Biomass productivity



Depuration capacity



Data from outdoor photobioreactors under real conditions

Biomass productivity is much higher in the thin layer reactor than in raceway reactor although the depuration capacity is high in both systems

ACKNOWLEDGEMENTS

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THANKS

QUESTIONS?

Products and processes with microalgae



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Madrid, May 6th, 2014