



“ENERGIA PER IL TERRITORIO - Il ruolo delle utilities nella transizione energetica”

Dalla CHIMICA VERDE al concetto di BIORAFFINERIA per un'ECONOMIA CIRCOLARE

Prof. Ing. Luigi Frunzo

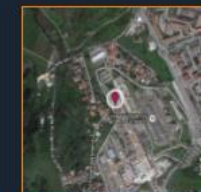
23 Giugno 2023

Contatti

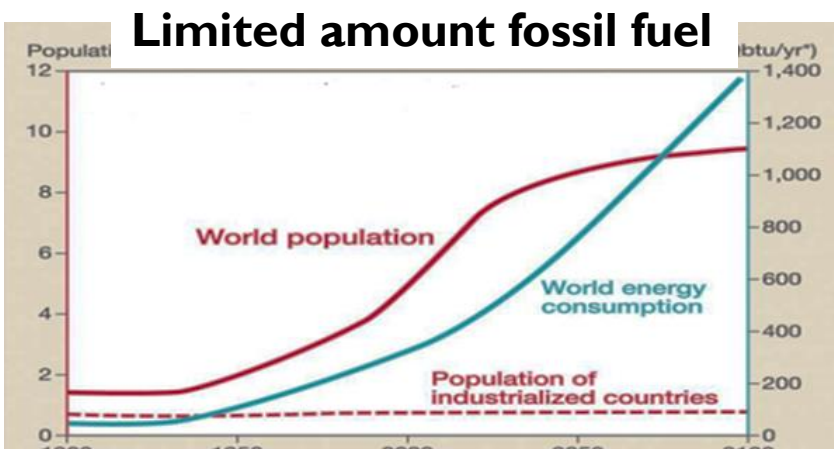
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The world is facing serious problems related to :



Intro...

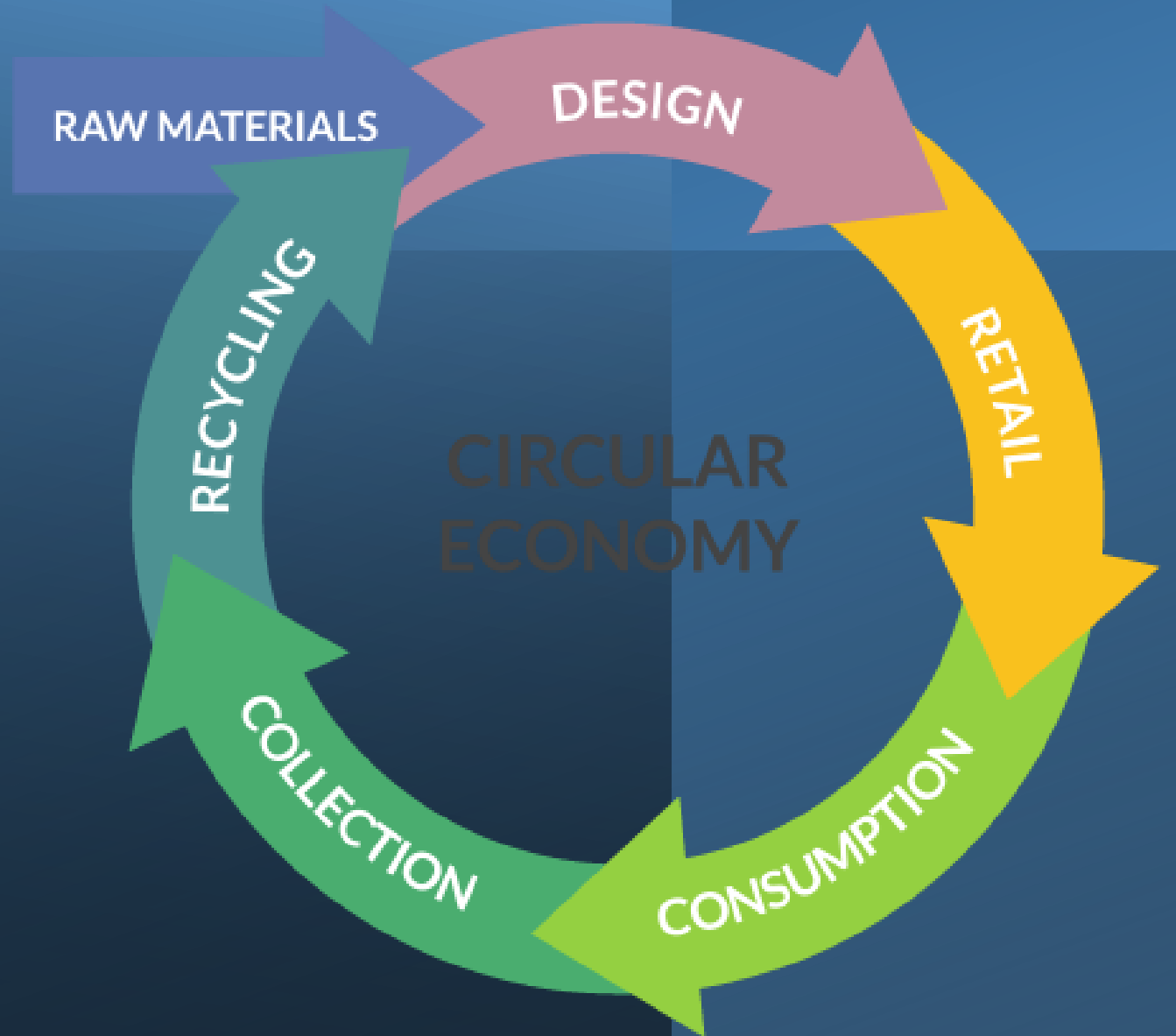
Renewable energy generation options

- ~~are potential solutions~~
- **MUST**





LINEAR ECONOMY



Nuove Biotecnologie
per la produzione di
BIOCOMBUSTIBILI:

Evoluzione nel processo di Digestione
Anaerobica

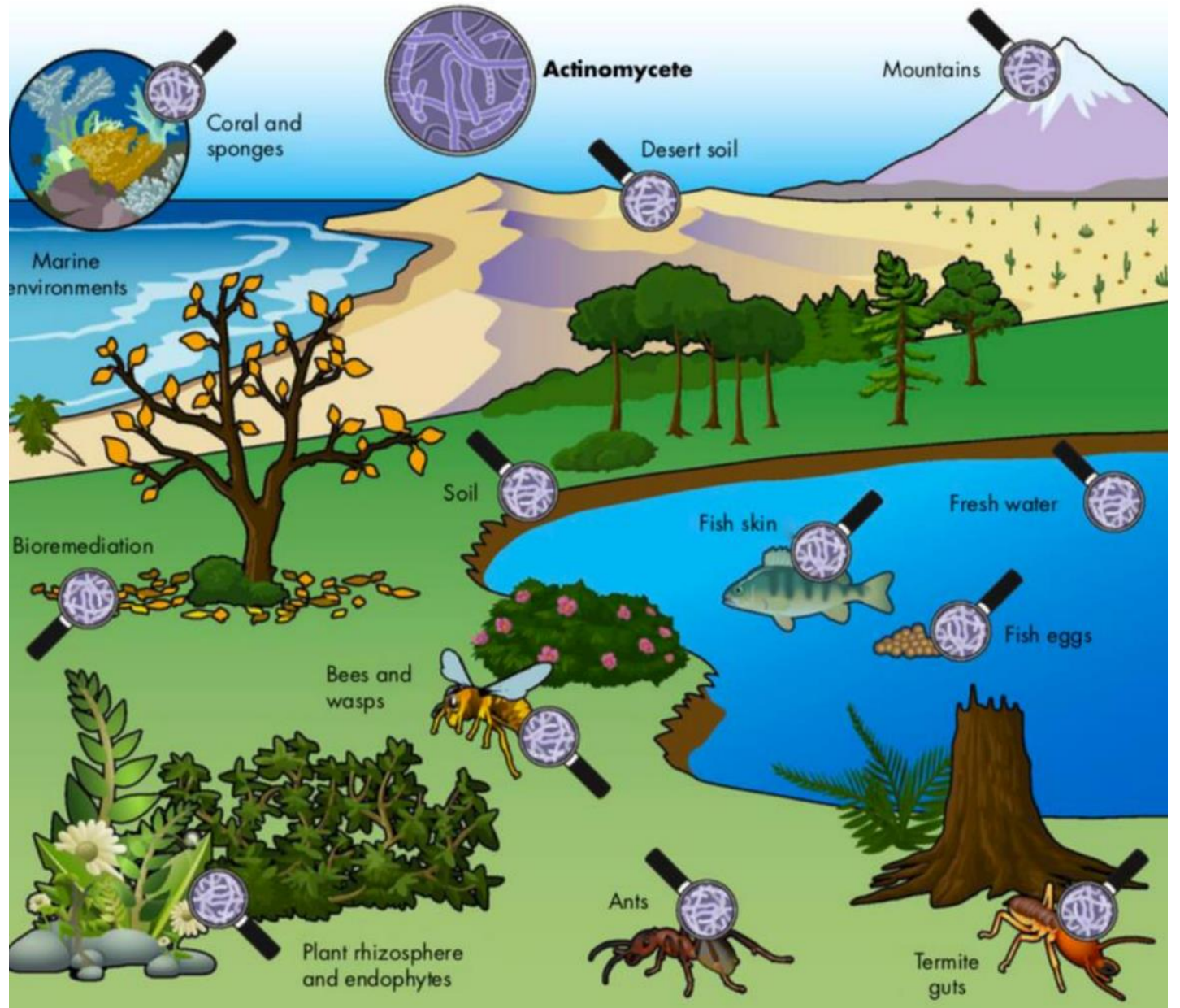
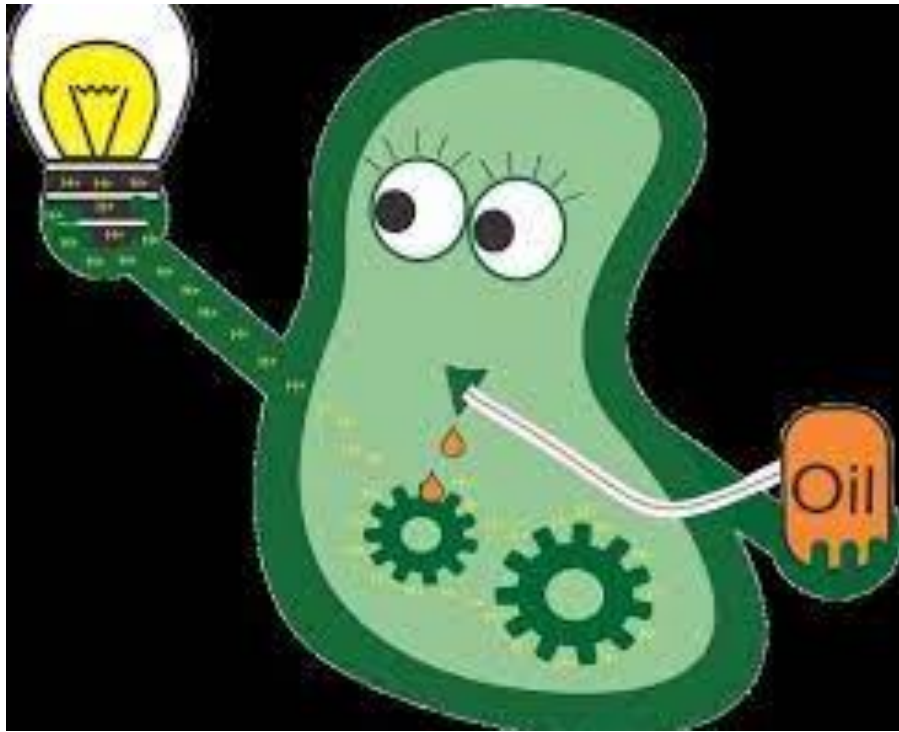
- PRETRATTAMENTI
- NUOVE CONFIGURAZIONI IMPIANTISTICHE

Produzione di Bioidrogeno

- DARK FERMENTATION
- PHOTOFERMENTATION

Microalghe

Concetto di BIORAFFINERIA



Nuove Biotecnologie:

Evoluzione nel processo di Digestione Anaerobica

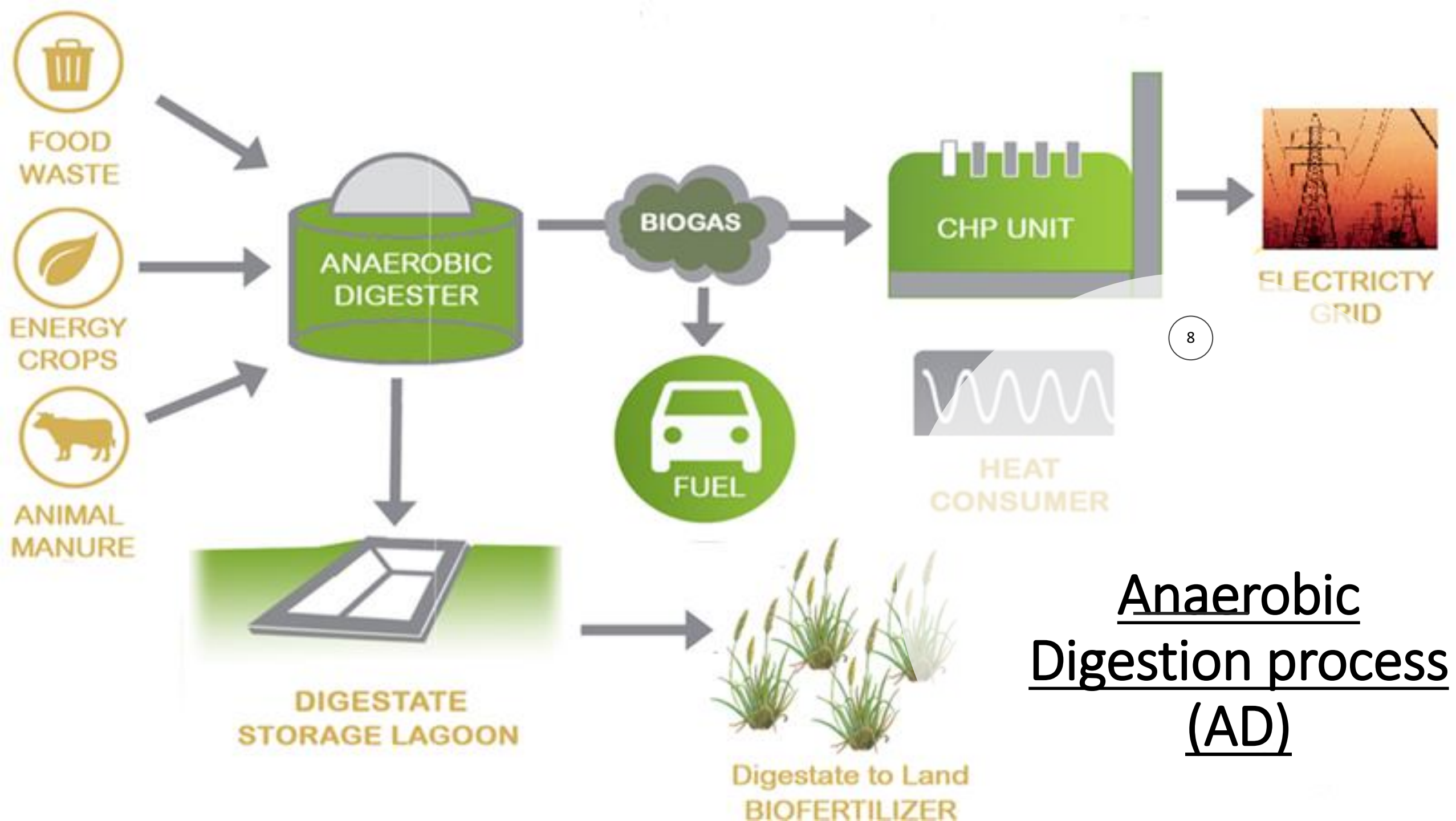
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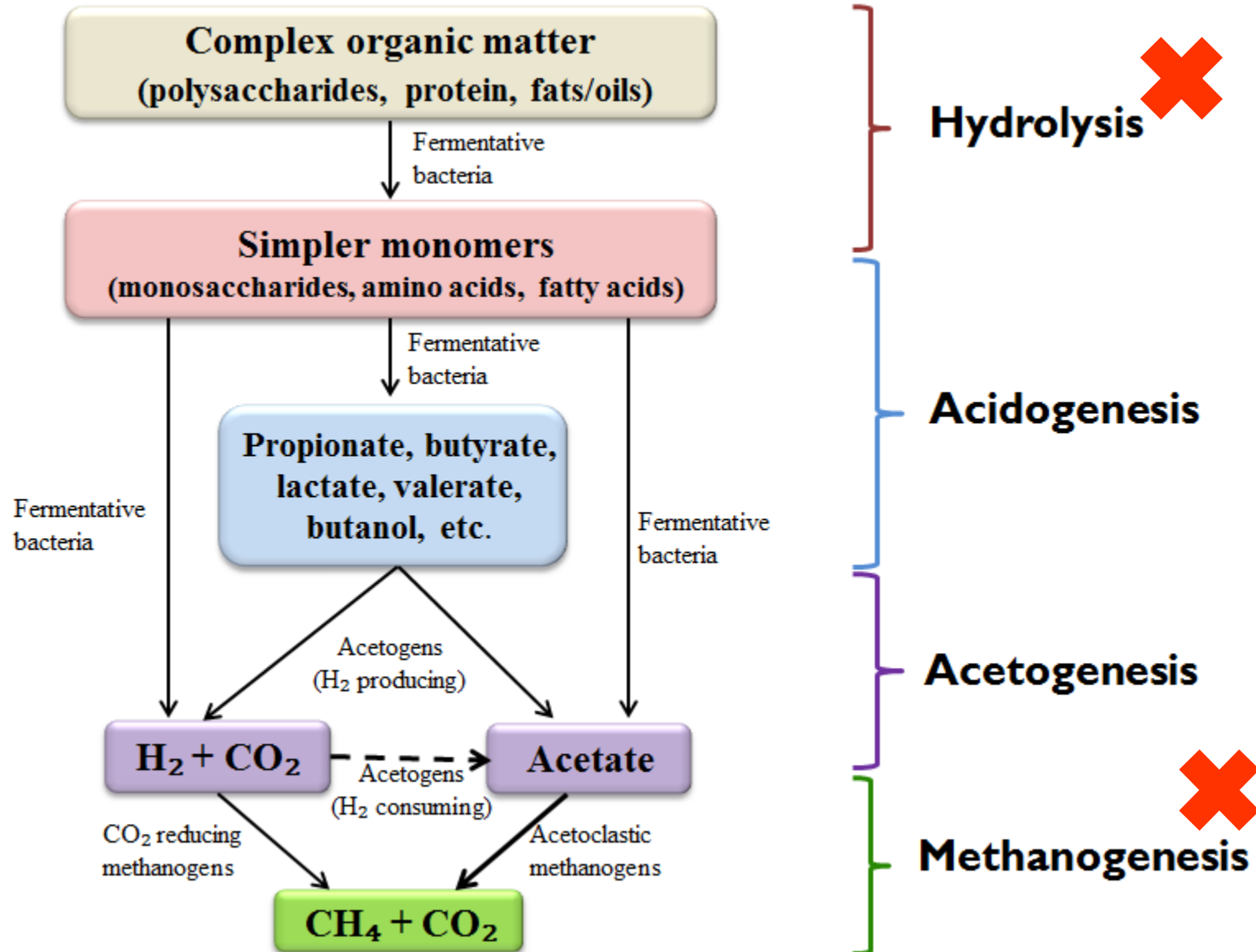
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AD process



Two strategies

Substrate pretreatment alternatives

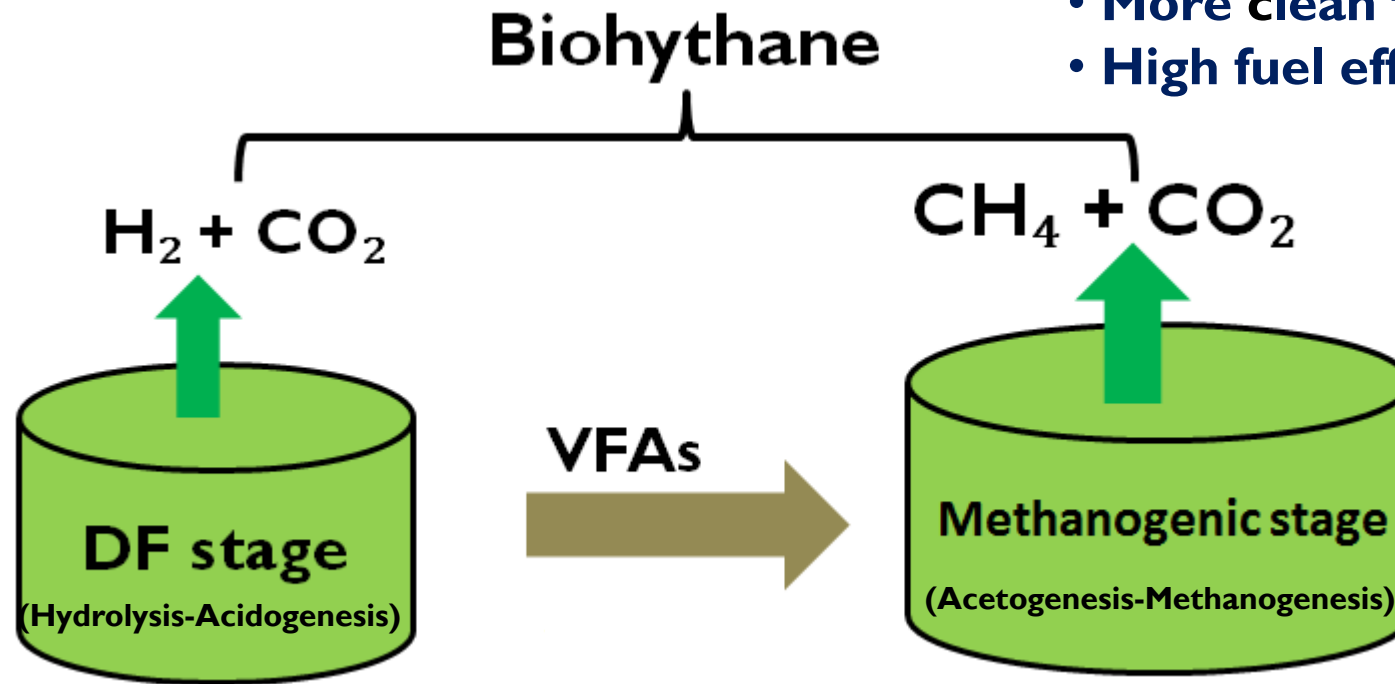
- Increase solubilization
- bio-accessibility of the substrate to next microbial action
- Several pretreatment methods
- Thermal pretreatment is considered as cost effective and environmental friendly

Reactor design

- Increase the biomass concentration
- Higher biological activity
- Several types of reactor design
- Biofilm based reactors has been attracting technology-
retention of biomass on solid carrier material
Increase efficiency of the process
Reduce the reactor size

Biohythane production from food waste using an integrated system of CSTR and AFBR

- High valued fuel
 - More clean than methane
 - High fuel efficiency

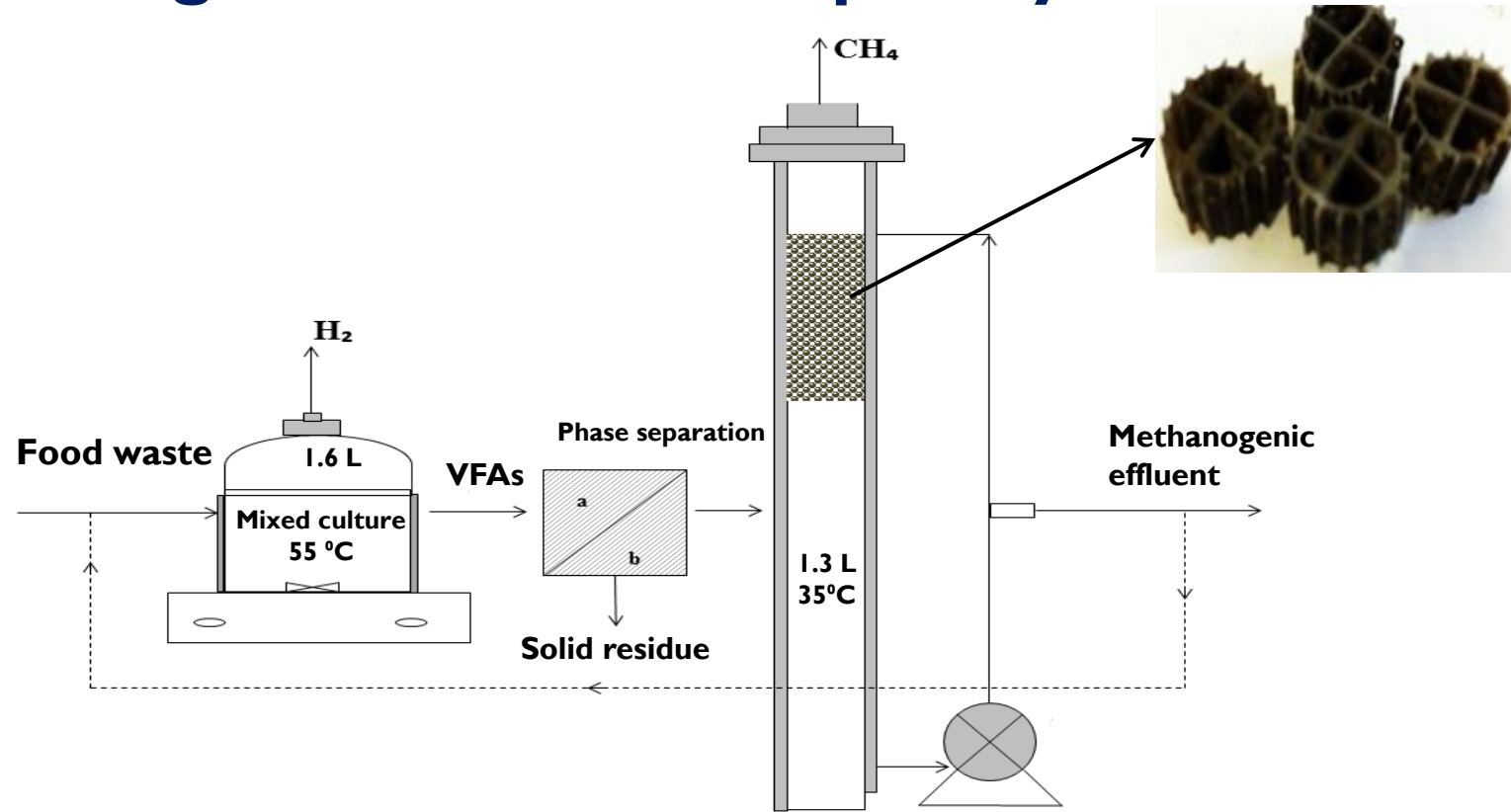


- Higher bacterial growth
- Less sensitive

CSTR

Biofilm based AD

Two stage AD - biofilm coupled system



The CSTR

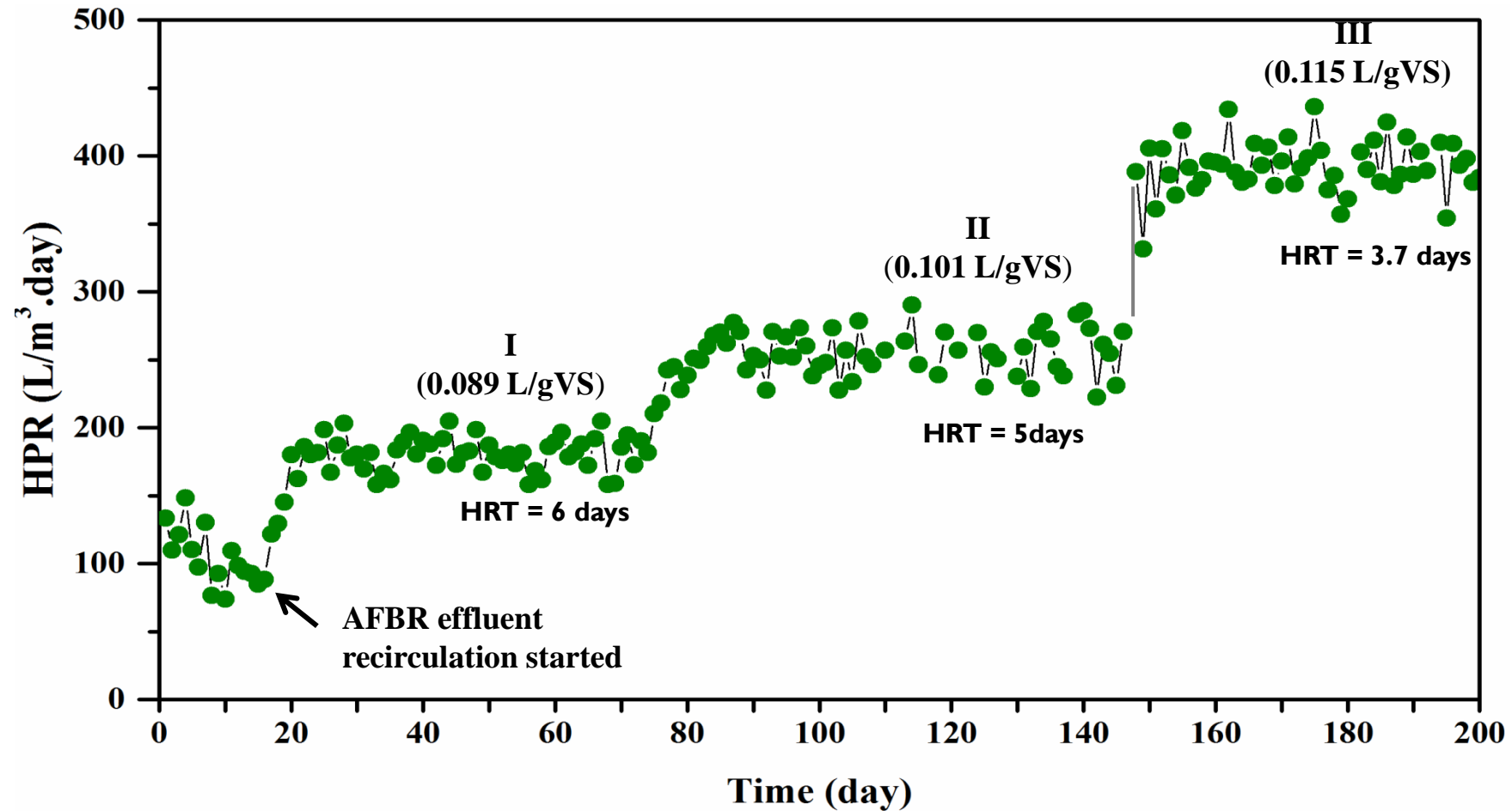
| Phase | I | II | III |
|-----------------|-----|-----|-----|
| HRT (day) | 6 | 5 | 3.7 |
| OLR (gVS/L.day) | 2.0 | 2.5 | 3.4 |

Methanogenic biofilm reactor

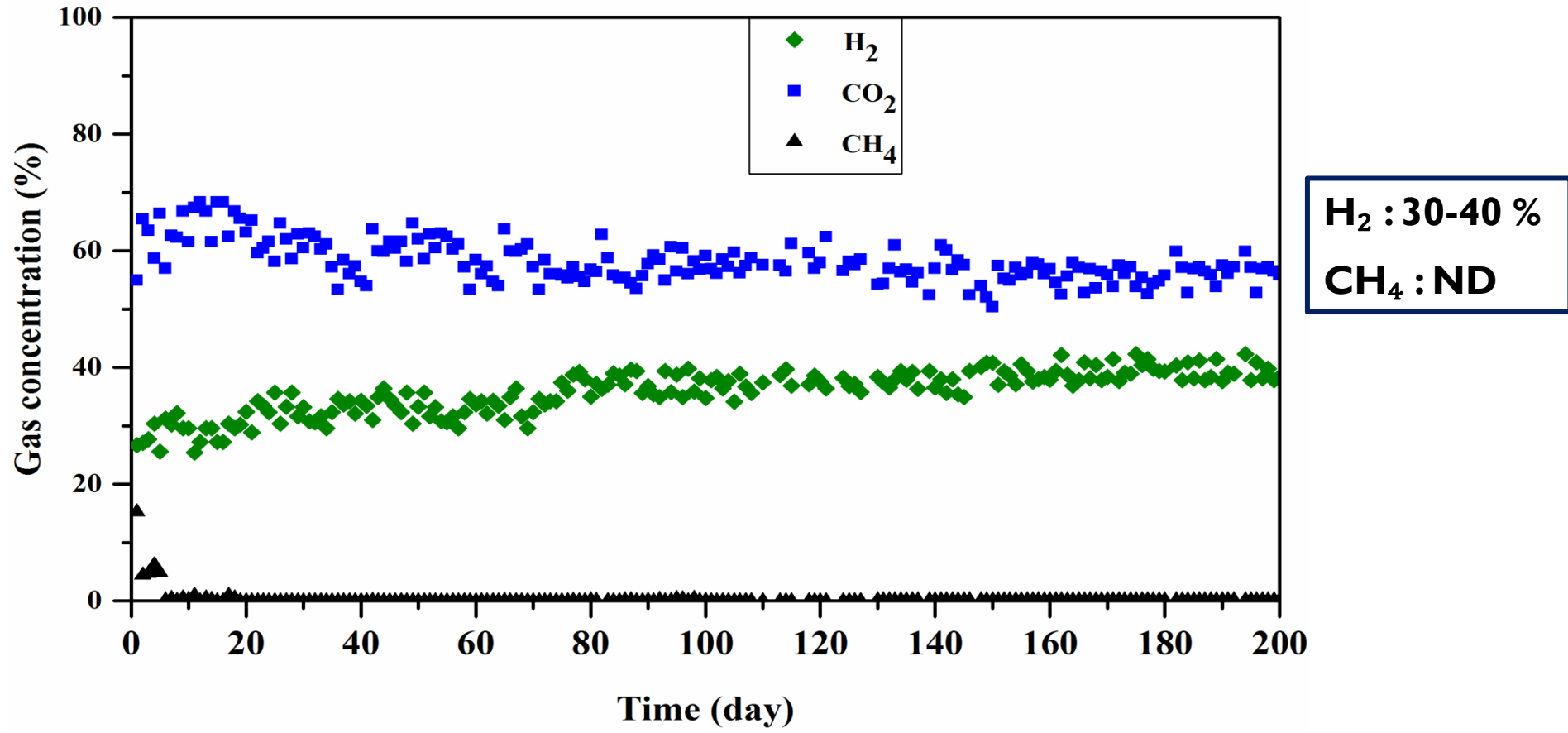
| Phase | I | II | III | IV | V | VI | VII |
|----------------|-----|-----|------|------|-----|-----|-----|
| HRT (day) | 20 | 15 | 10 | 8 | 5 | 3 | 1.5 |
| OLR gCOD/L.day | 0.1 | 0.4 | 1.01 | 1.26 | 1.8 | 3.6 | 6.0 |

Results

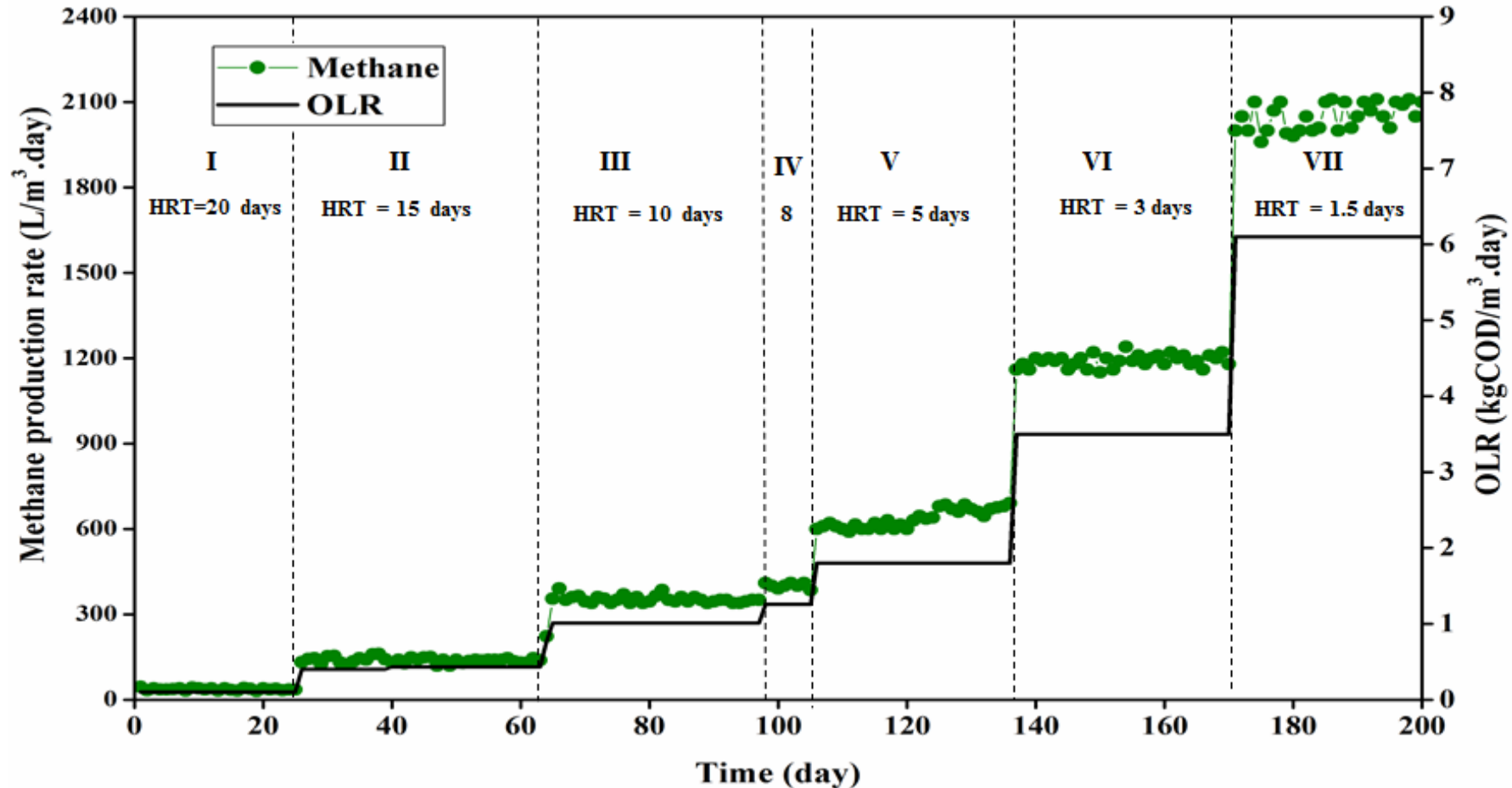
Biohydrogen production rate (CSTR)



Biogas composition (CSTR)

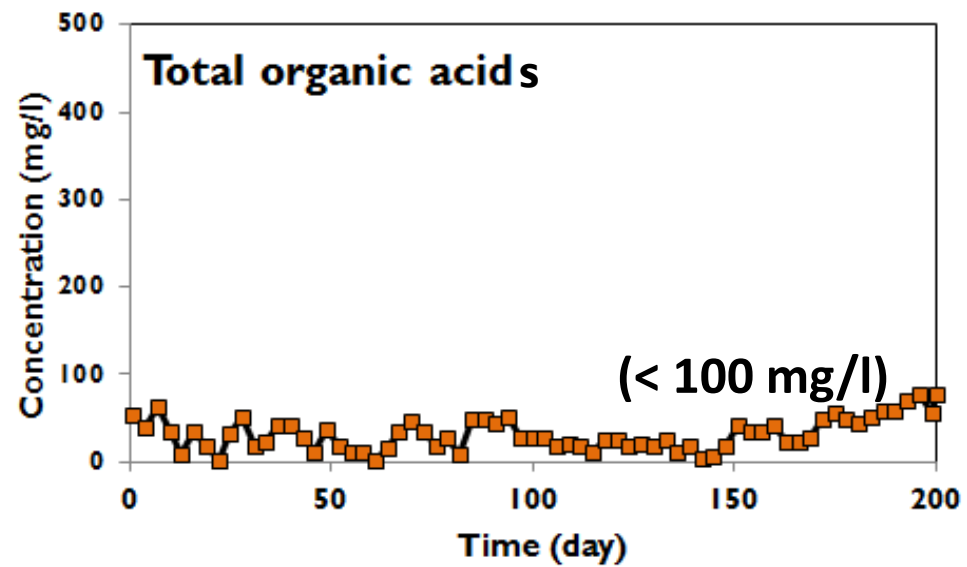
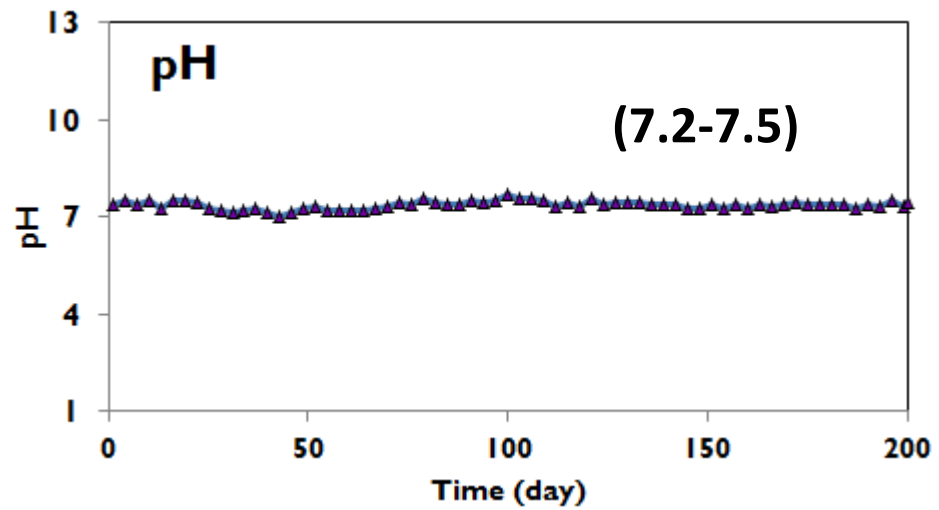


Methanogenic biofilm reactor (AFBR)



- Very stable process at each shortened HRT
- Near to theoretical methane yield
- Prolonged operation and HRT reached to 1.5 days

Effluent characteristics (AFBR)



Nuove Biotecnologie:

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I processi per la produzione di Idrogeno

PROCESSI TERMOCHIMICI

- Steam Reforming
- Pirolisi
- Gassificazione
- Ossidazione parziale non catalitica

PROCESSI ELETTROCHIMICI

- Elettrolisi
- Foto-elettrolisi
- Fotovoltaico

PROCESSI BIOLOGICI

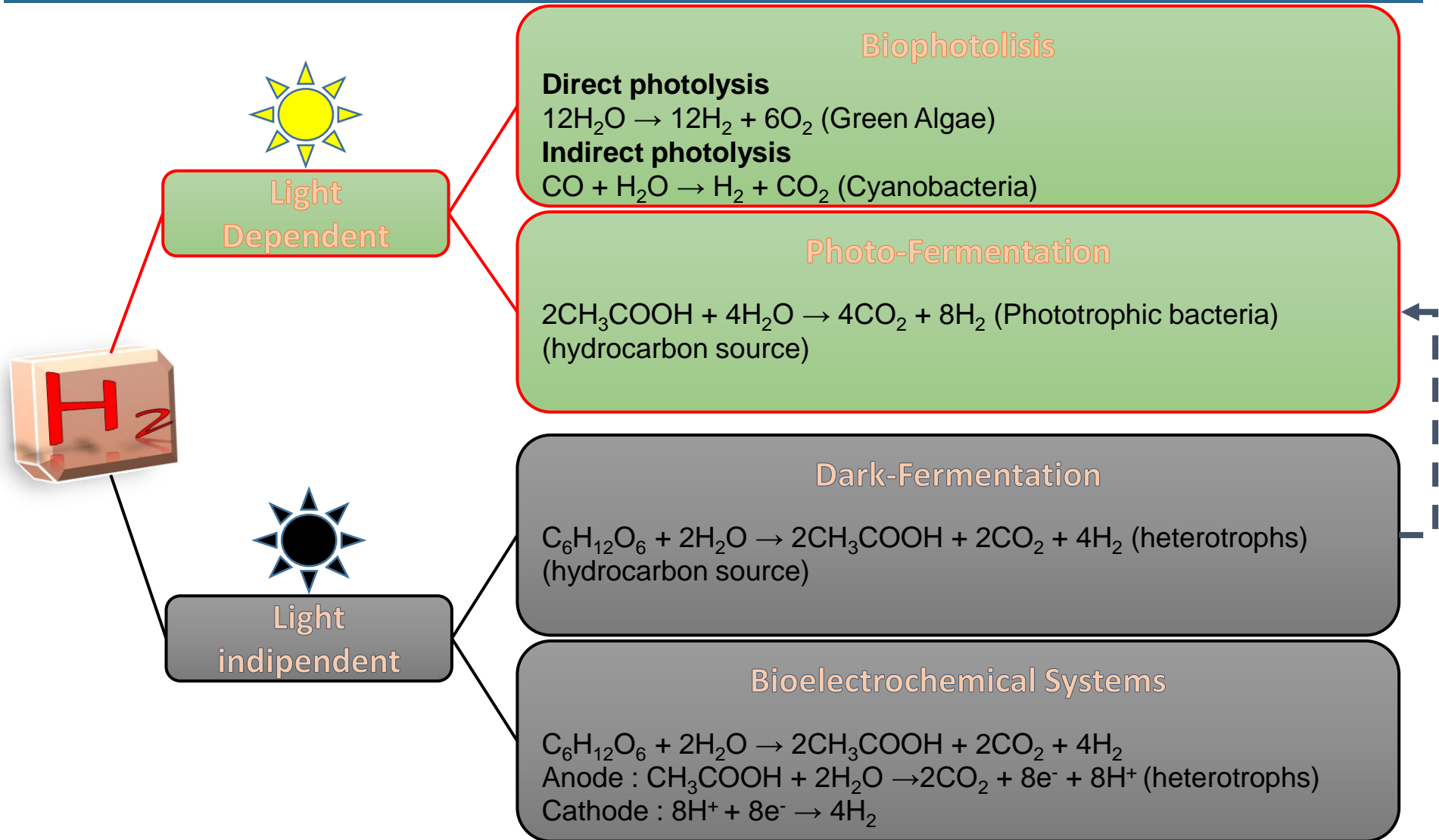
- Biofotolisi
- Dark Fermentation
- Photo Fermentation

■ Perché i Processi Biologici?

- Costi contenuti
- Valorizzazione energetica
- Mitigazione impatto ambientale
- Non richiesti combustibili fossili



I processi per la produzione biologica di Idrogeno



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Photo Fermentation



Photo-Fermentation

- Fermentazione operata da batteri Fototrofici

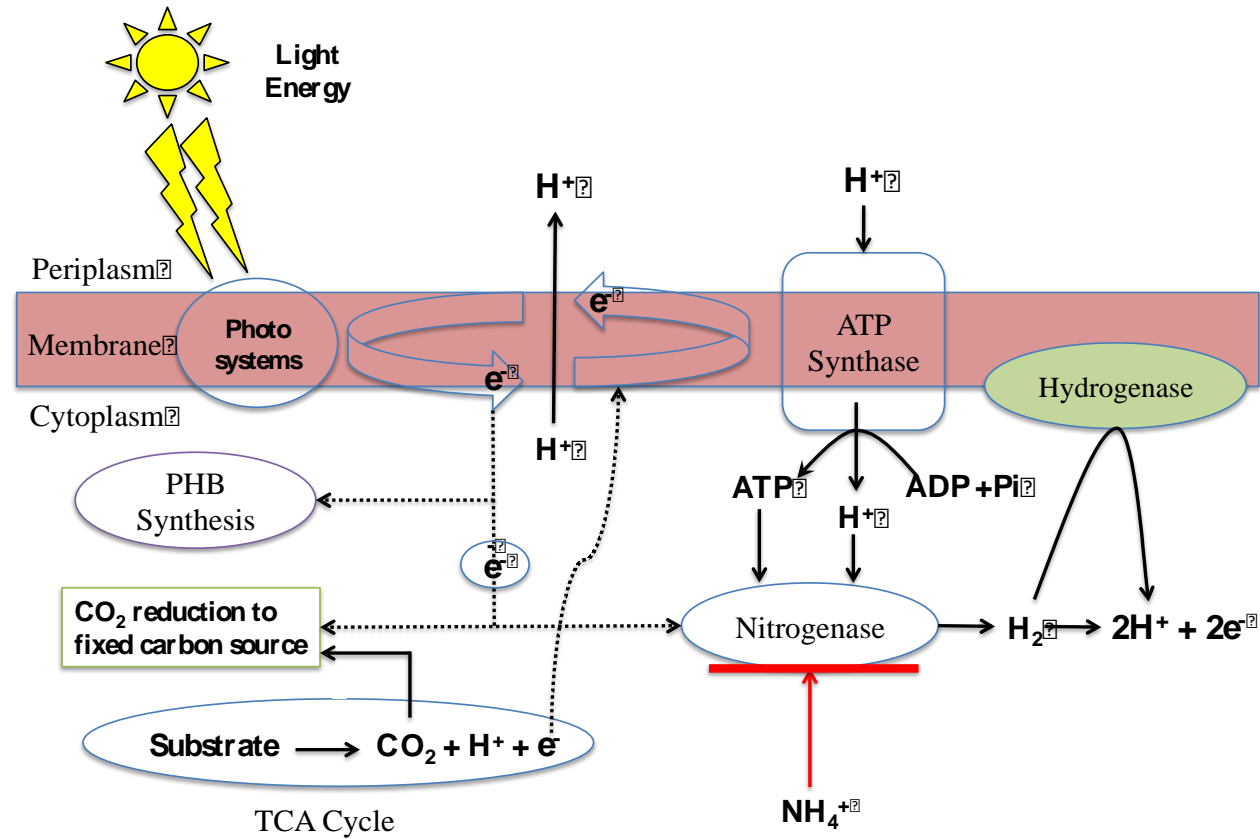


Consente:

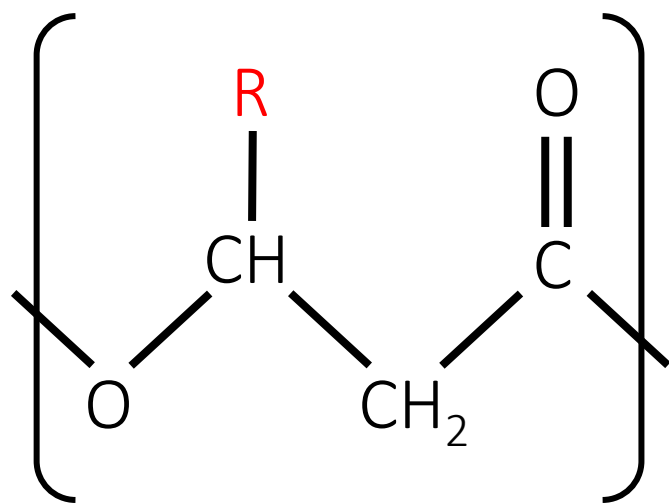
- *Produzione di H_2*
- ***Produzione di Biomassa di pregio (PHB)***
- ***Rimozione del COD***



Photofermentation Process



Poly- β -hydroxybutyrate

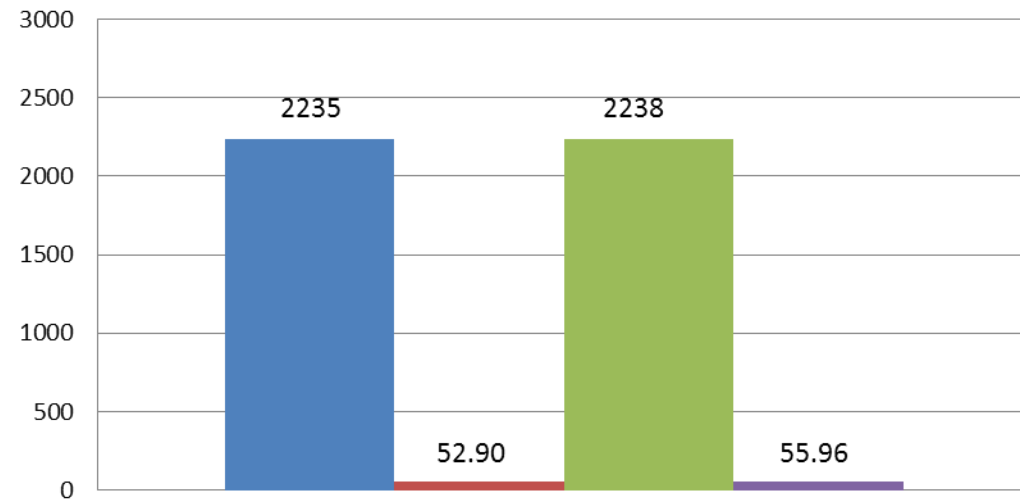
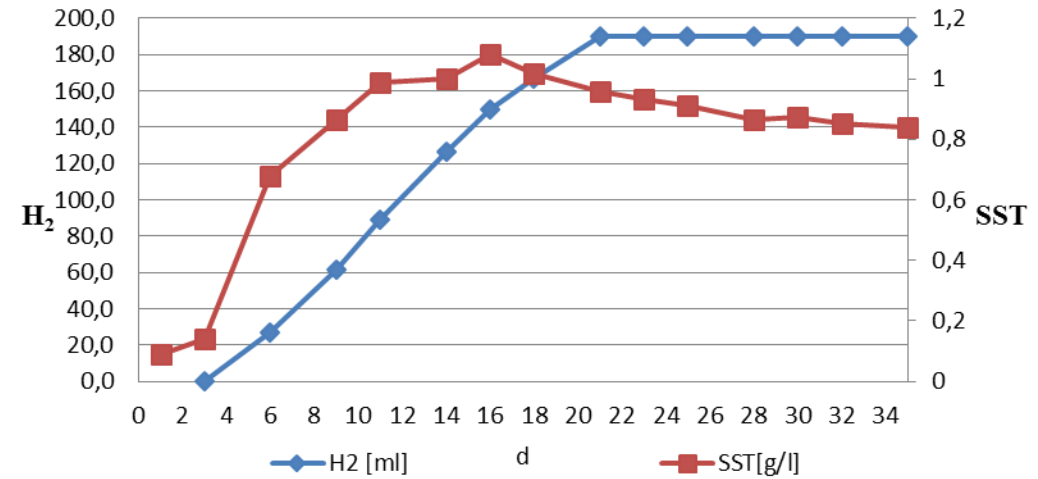


Poly(3-hydroxyalcanoate)

R alcaly or functional group



Alcune attività - Photo Fermentation



Methodology - Photofermentation

- **Pure Cultures**
(*Rhodobacter sphaeroides* AV1b)
- **Mixed Cultures**
(Native from digestate)

| Operational Parameter | Value | Unit |
|-----------------------|-------|------|
| Working Volume | 400 | mL |
| Light Intensity | 4000 | lx |
| Temperature | 25 | °C |
| Stirring Condition | 300 | rpm |
| Initial pH | 6 | ∅ |



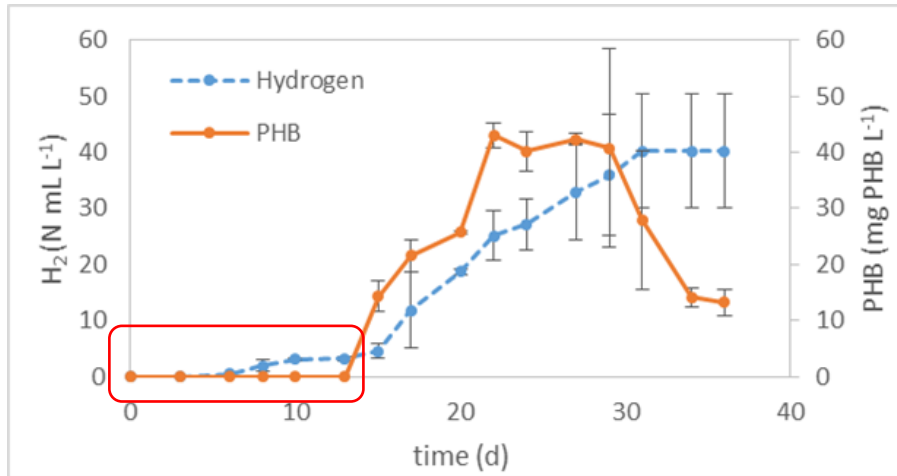
Photofermentative treatment for DFE

- **Hydrogen production (GC)**
- **PHB accumulation (GC-MS - Oehmen et al., 2005)**
- **Biomass growth (TSS - OD660)**
- **VFAs consumption (HPLC)**
- **Soluble COD removal (Standard Methods, APHA, 2005)**



H₂ and PHB Productivity for 10 min flushed test

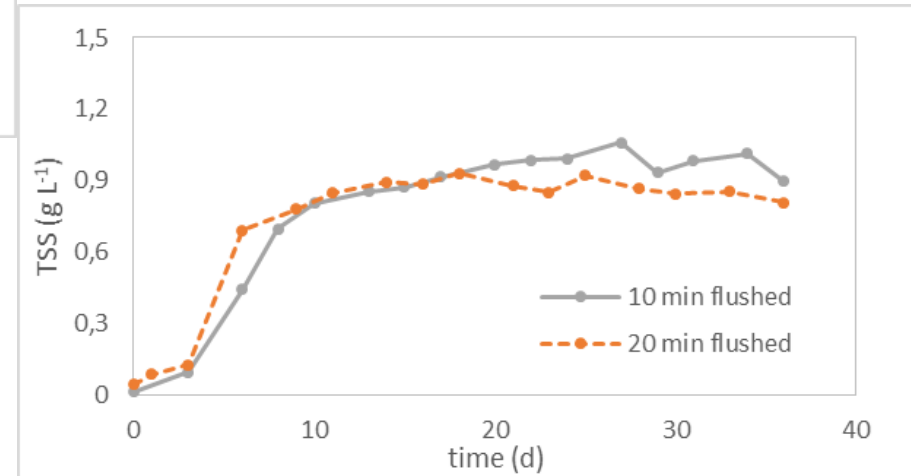
Mixed Culture



- *Long lag-phase*
- *Low Hydrogen yields*
- *Low PHB accumulation*

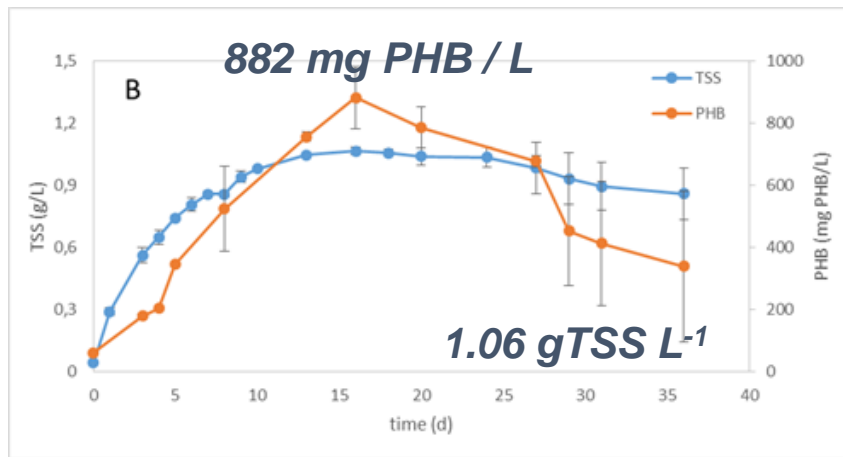
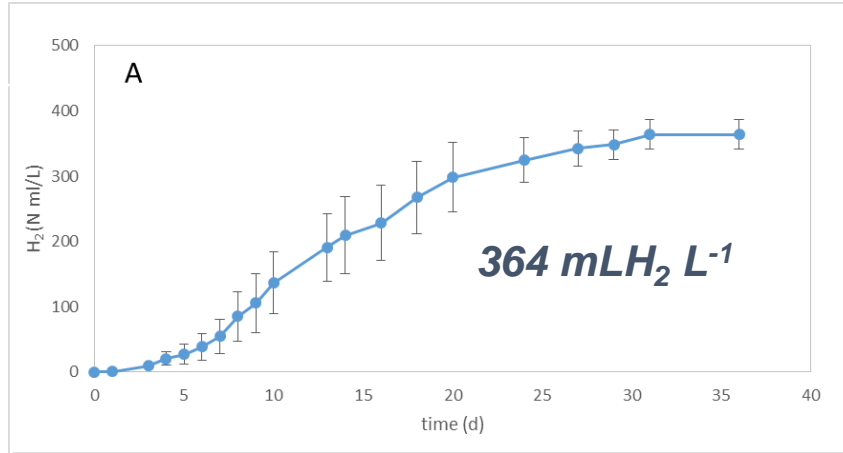
- *Comparable biomass accumulation*

- *Flushing time of 20 min*

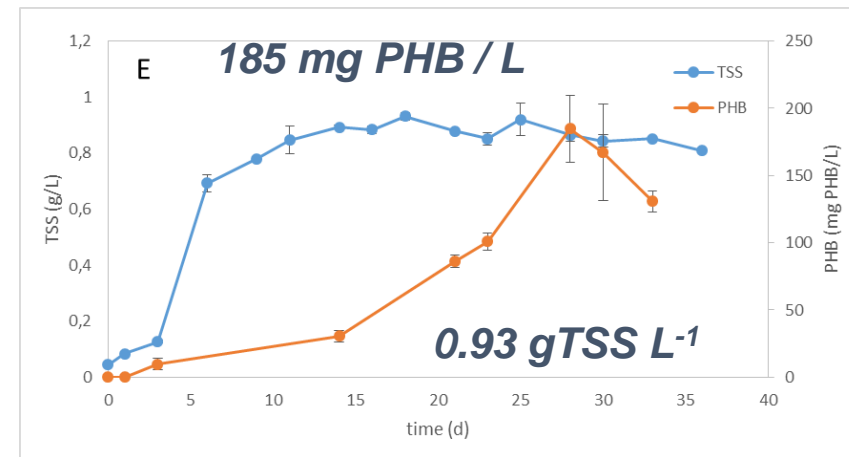
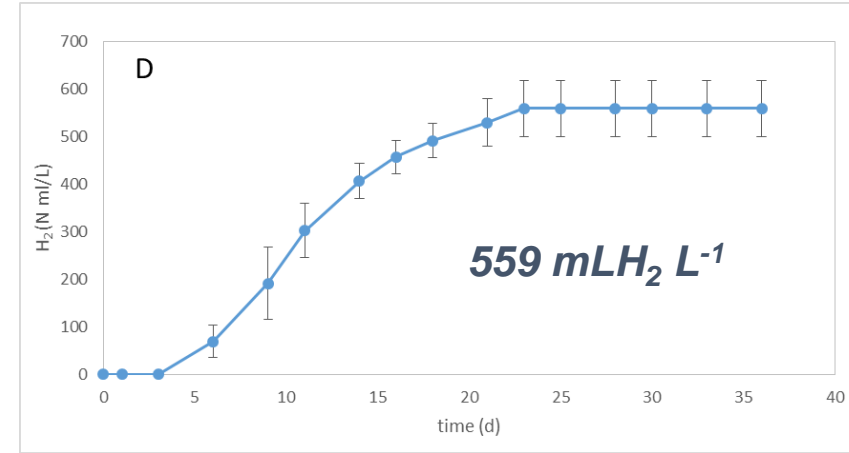


Hydrogen Productivity - PHB and Biomass accumulation

Rhodobacter sphaeroides AV1b

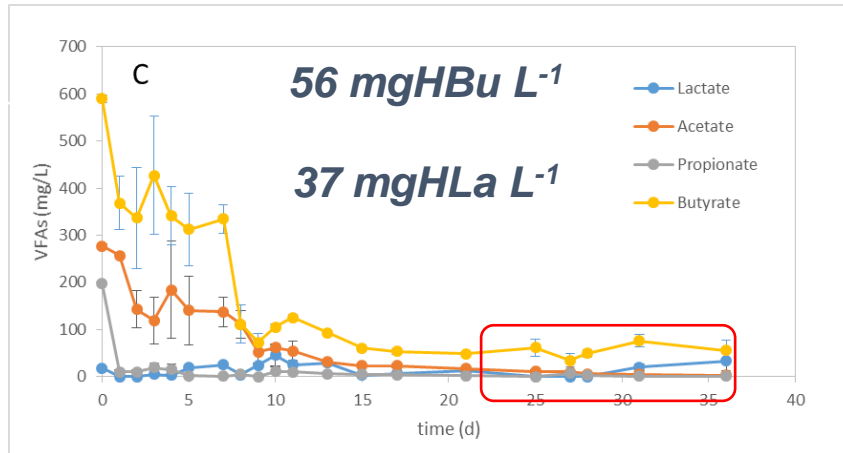


Mixed Culture

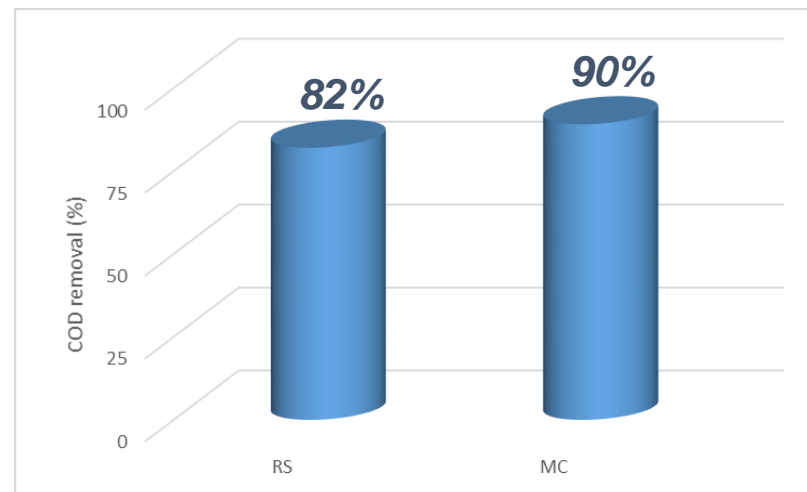
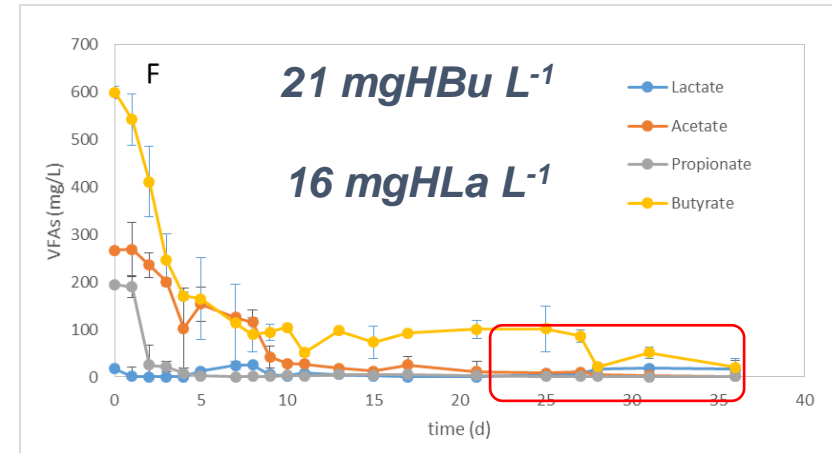


Organic Acids consumption & soluble COD removal

Rhodobacter sphaeroides AV1b

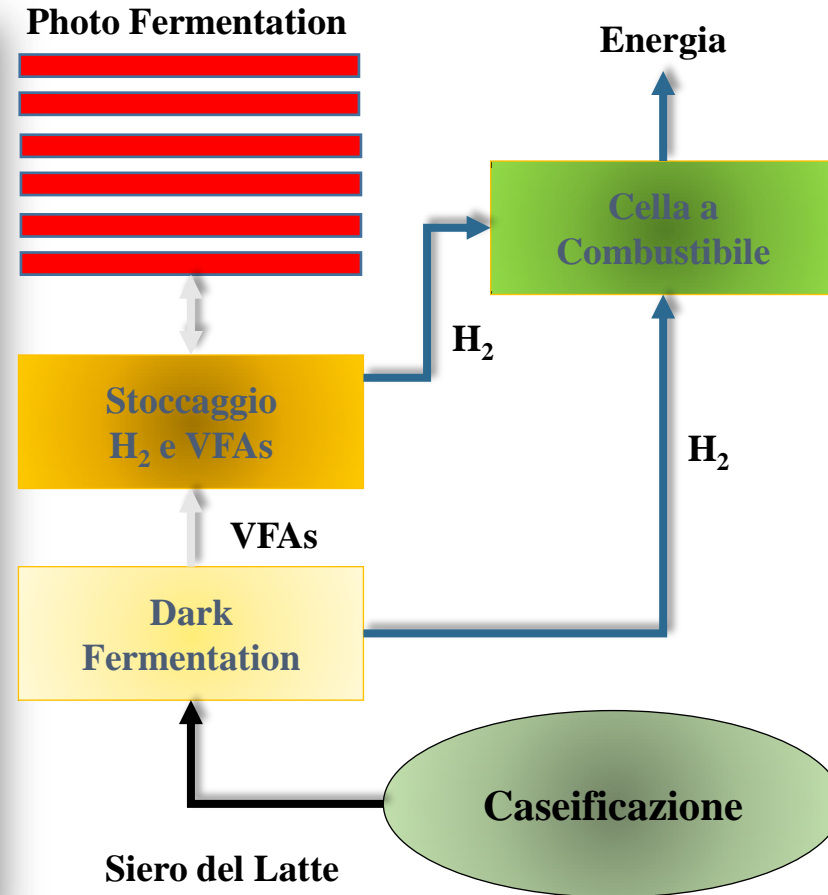
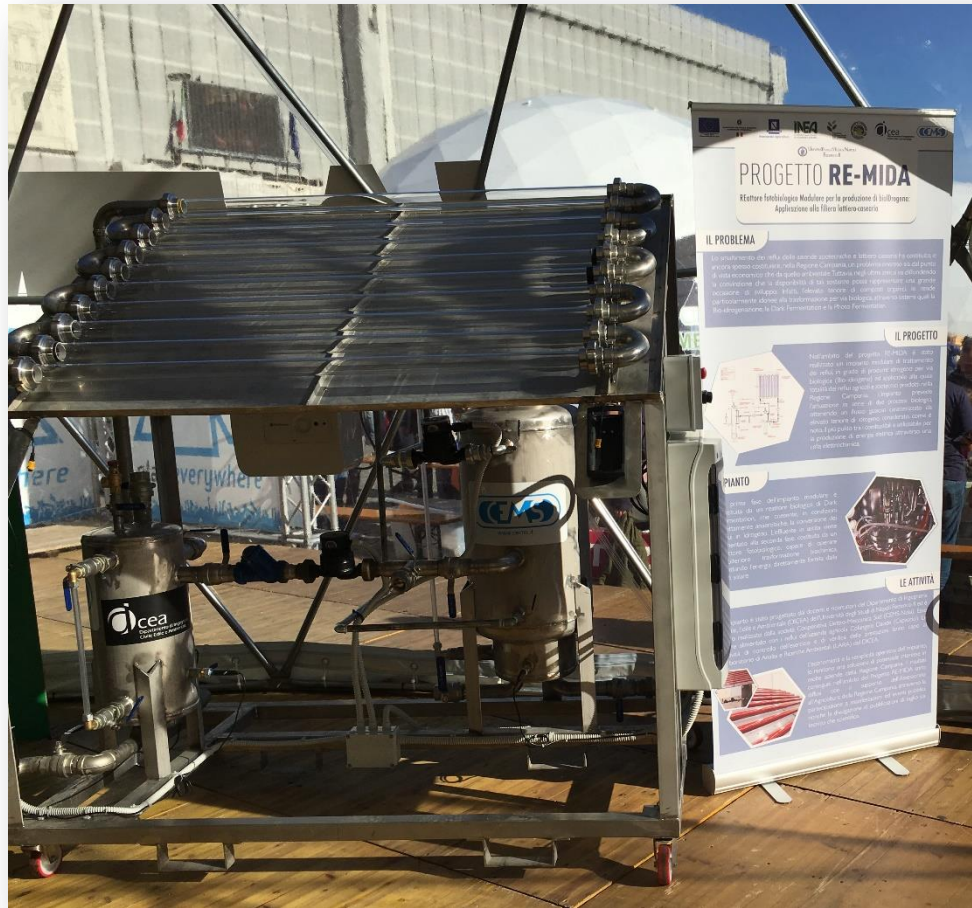


Mixed Culture



Il Progetto RE-MIDA

*RE*attore fotobiologico *M*odulare per la produzione di bio*D*rogeno: *A*pplicazione alla filiera lattiero-casearia



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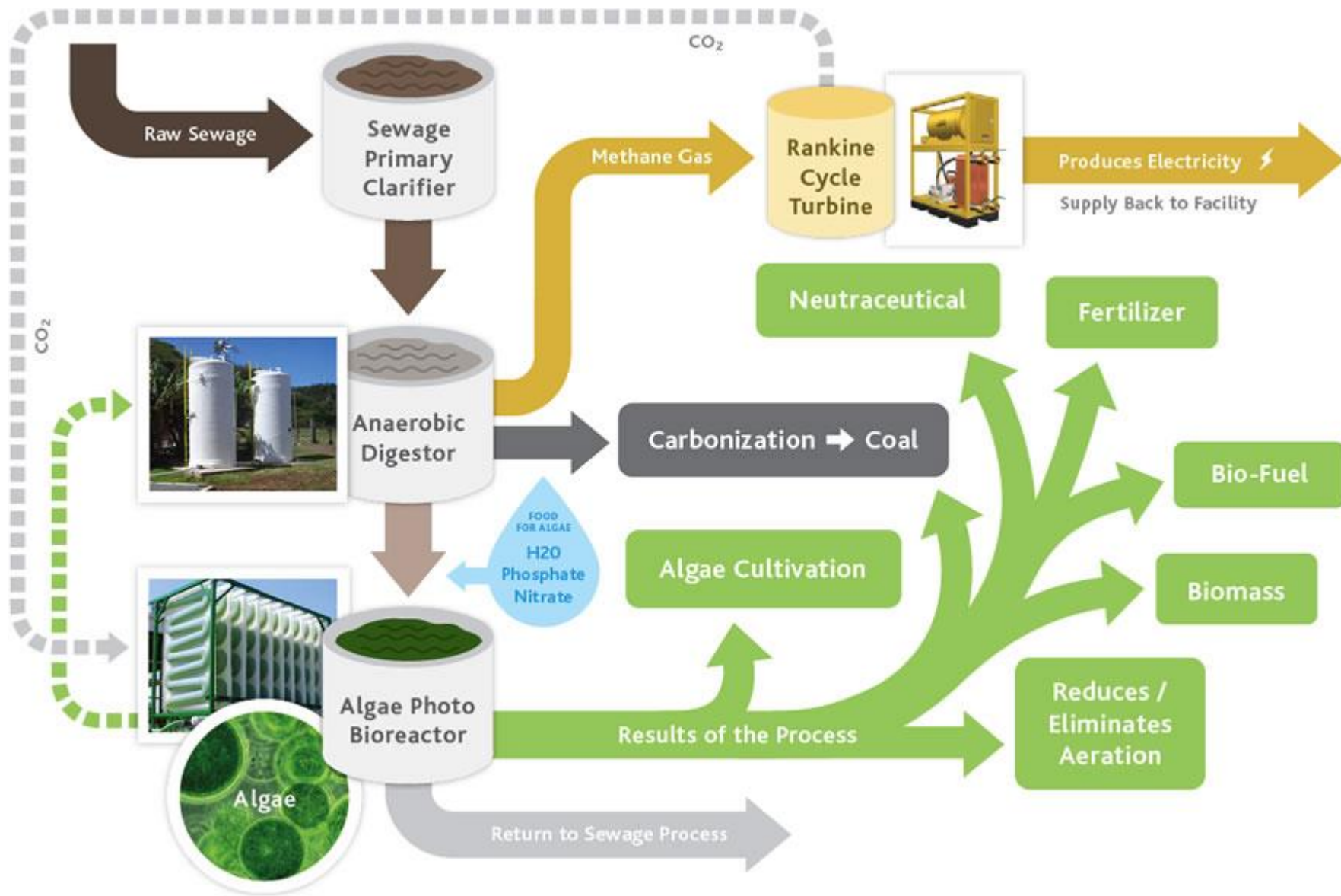
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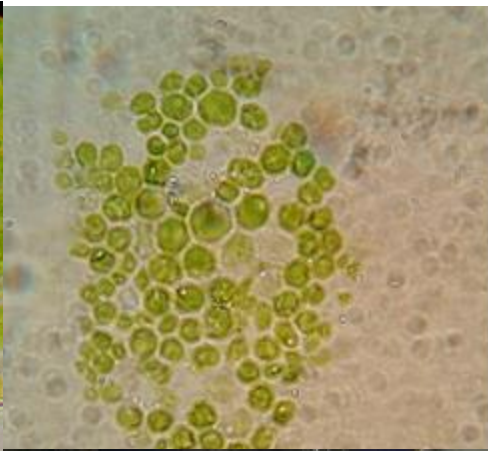
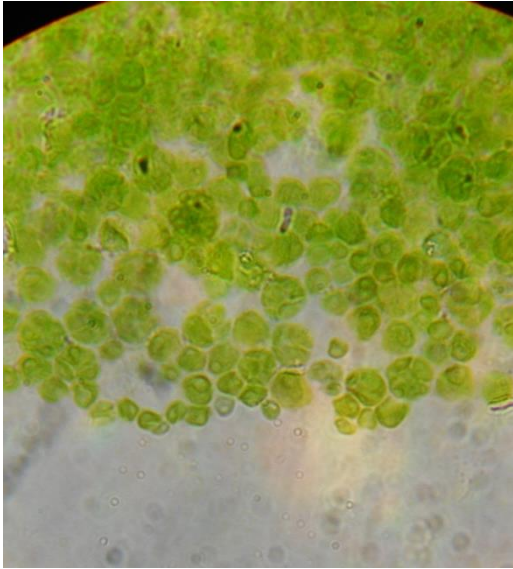
Produzione di Bioidrogeno

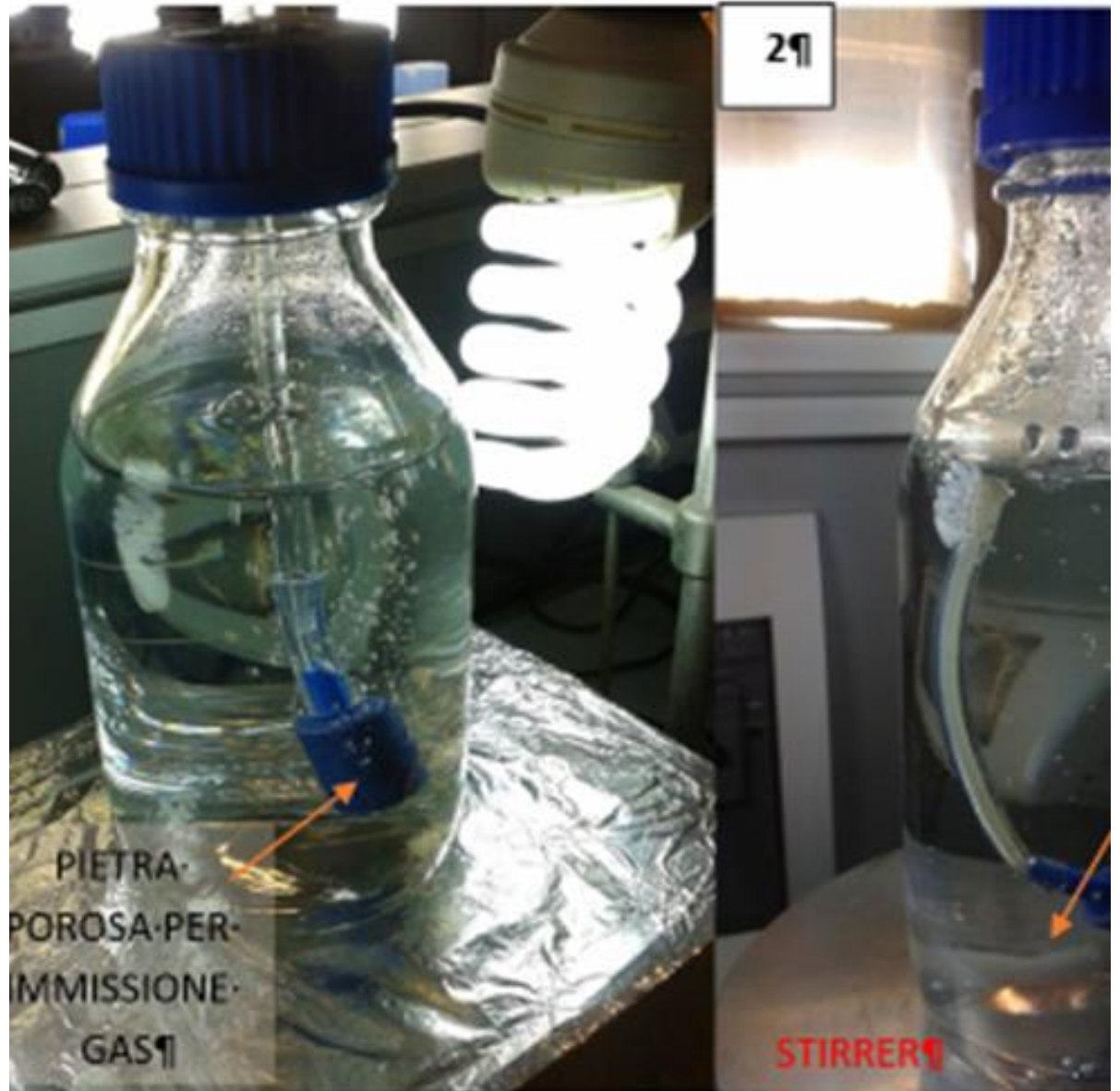
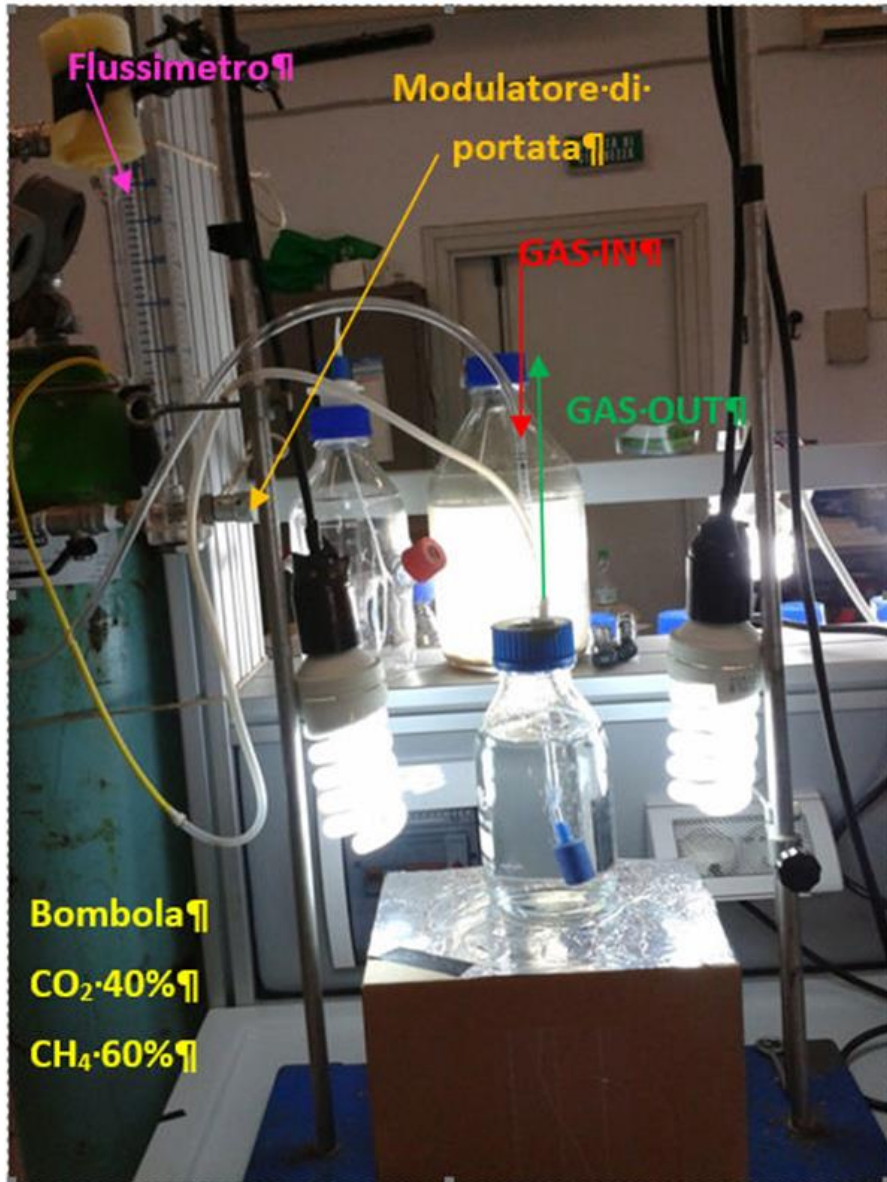
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Microalghe

Concetto di BIORAFFINERIA







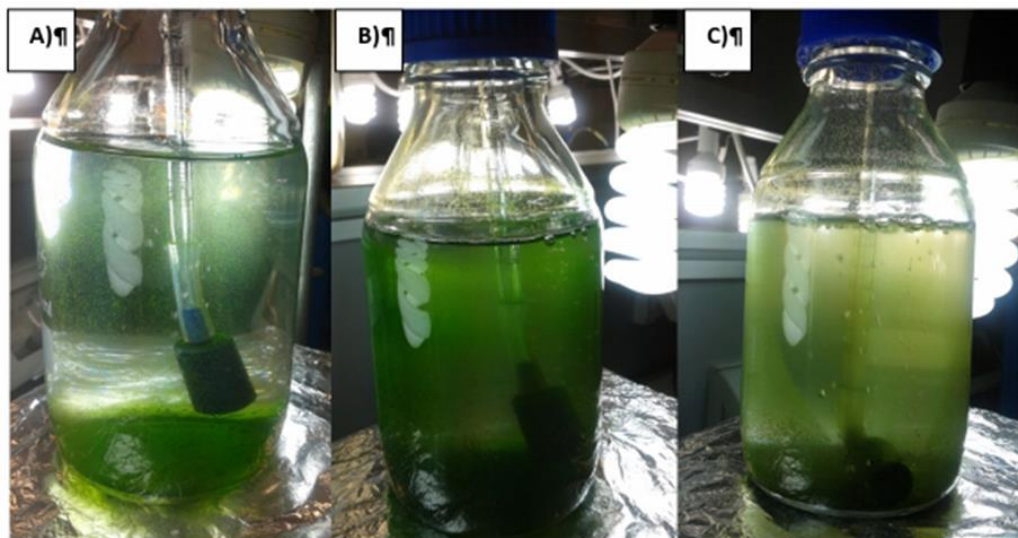
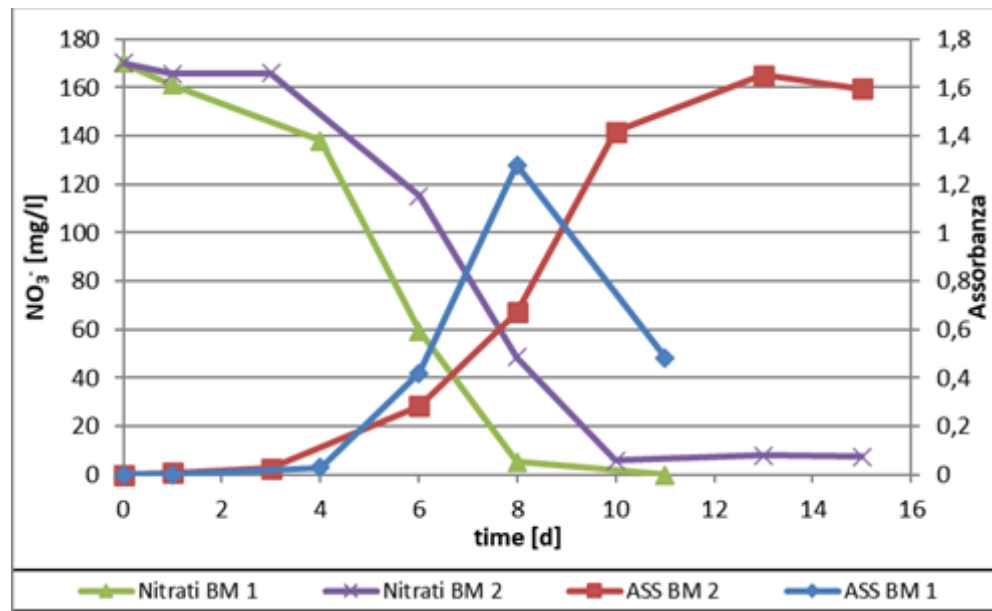


Figura 10. — Monitoraggio della prima prova nel tempo: a) 4 giorni, b) 6 giorni, c) 11 giorni. ¶

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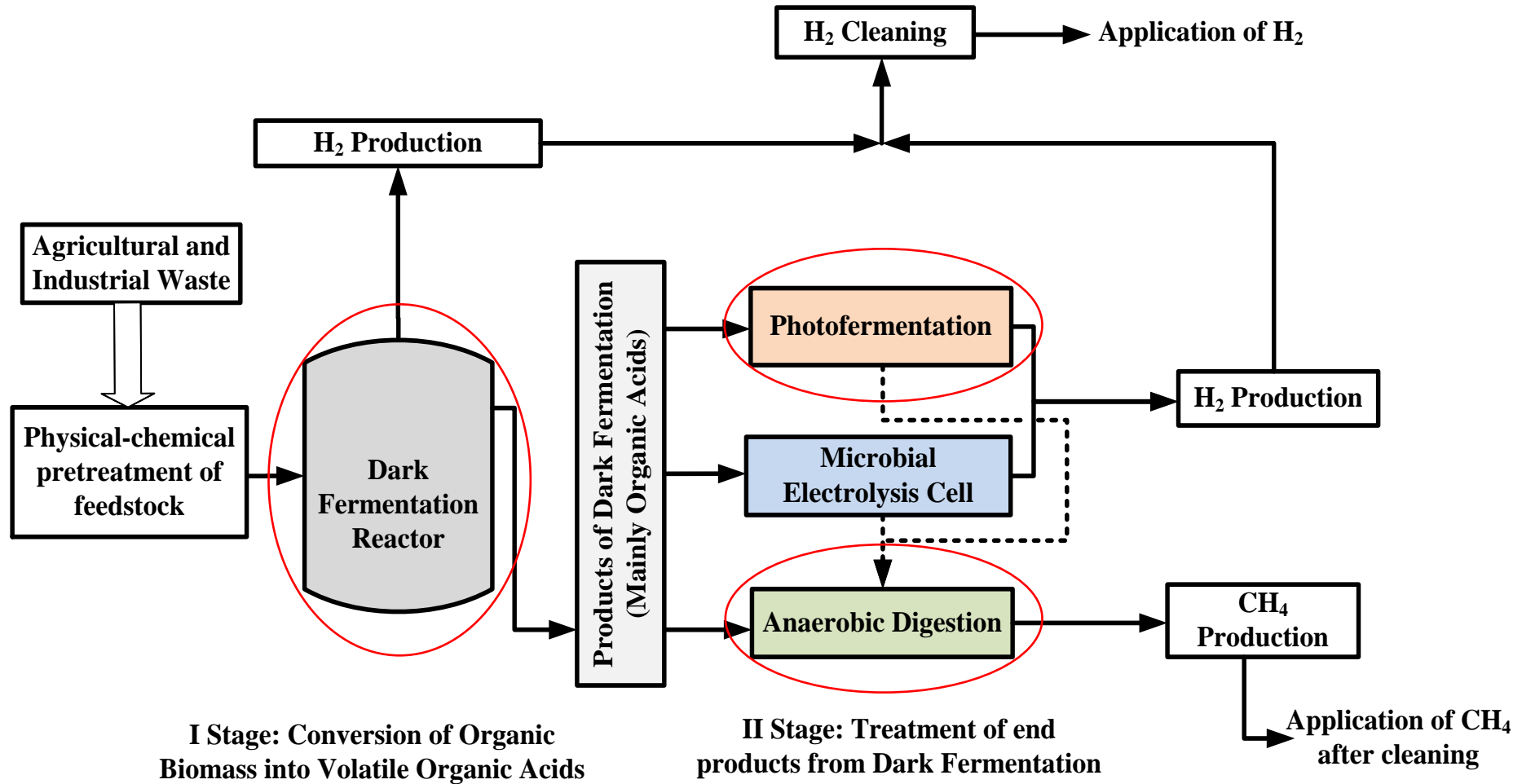
Il concetto di Bioraffineria

■ Bioraffineria

- Processo industriale in cui, attraverso l'opportuna combinazione di una pluralità di processi biologici, una biomassa (possibilmente di scarto) viene convertita in biocombustibili, idrogeno come vettore energetico, calore, energia e altri sottoprodotti chimici a valore aggiunto



Esempi di Bioraffineria



Centralità della DF per le sue capacità idrolitiche e fermentative



Ingegnerizzazione – Mathematical Modelling

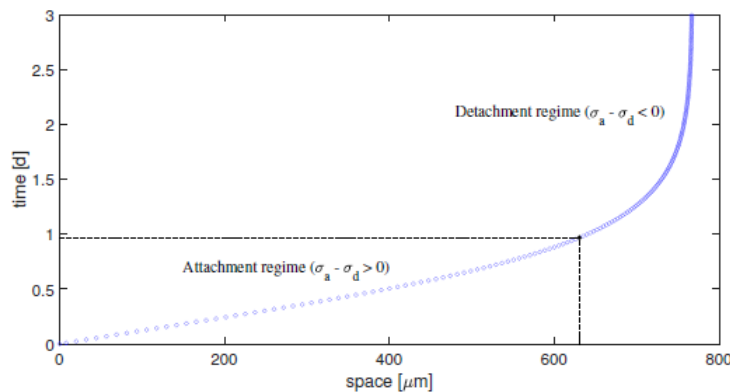
Modelling framework

- Biomass growth and transport:

$$\partial_t X_i + \partial_z(uX_i) = \rho_i r_{M,i}(\mathbf{X}, \mathbf{S}) + \rho_i r_i(\psi, \mathbf{S}), \quad 0 \leq z \leq L(t), \quad 0 < t \leq T, \quad i = 1, \dots, n,$$

$$\partial_z u = G(\mathbf{X}, \mathbf{S}, \psi), \quad 0 < z \leq L(t), \quad u(0, t) = 0,$$

$$\dot{L}(t) = u(L(t), t) + \underbrace{\sigma_a(\psi^*) - \sigma_d(L(t))}_{\text{net exchange flux}}, \quad 0 < t \leq T, \quad L(0) = 0,$$



$$\sigma_a = \sum_{i=1}^n v_{a,i} \psi_i^* / \rho_i, \quad \sigma_d = L^2 \sum_{i=1}^n \lambda_i f_i(L(t), t),$$

$$\sigma_a - \sigma_d > 0 \rightarrow \dot{L}(t) > u(L, t)$$

free boundary is a **space-like** line

$$X_i(L(t), t) = \frac{v_{a,i} \psi_i^*(t)}{\sum_{i=1}^n v_{a,i} \psi_i^*(t)} \rho_i, \quad i = 1, \dots, n$$

$$\sigma_a - \sigma_d < 0 \rightarrow \dot{L}(t) < u(L, t)$$

free boundary is a **time-like** line



Ingegnerizzazione – Mathematical Modelling

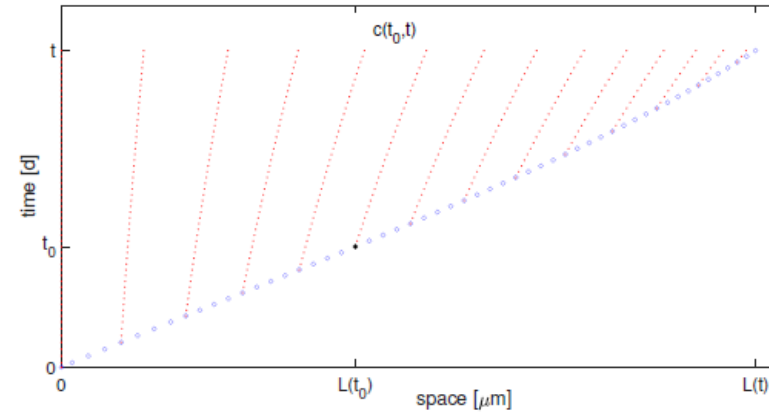
- Characteristic coordinates

$$\dot{L}(t) = u(L(t), t) + \sigma_a, \quad t > 0, \quad L(0) = 0,$$

Characteristics lines: $z(t) = c(t_0, t)$,

$$c_t(t_0, t) = u(c(t_0, t), t), \quad c(t_0, t_0) = L(t_0), \quad t > 0,$$

Hyperbolic equations \rightarrow ODEs.



- Integral equations

$$\mathbf{x}(t_0, t) = \mathbf{X}(c(t_0, t), t), \quad \mathbf{x}(x_1, \dots, x_n),$$

$$\mathbf{s}(t_0, t) = \mathbf{S}(c(t_0, t), t), \quad \mathbf{s}(s_1, \dots, s_m),$$

$$\Psi(t_0, t) = \psi(c(t_0, t), t), \quad \Psi(\Psi_1, \dots, \Psi_n),$$

$$x_i(t_0, t) = X_{i,0}(t_0) + \int_{t_0}^t F_i(\mathbf{x}(t_0, \tau), \mathbf{s}(t_0, \tau), \Psi(t_0, \tau)) d\tau, \quad 0 \leq t_0 < t \leq T, \quad i = 1, \dots, n,$$

$$s_j(t_0, t) = S_j^*(t) + \int_{t_0}^t d\theta \int_0^\theta F_{s,j}(\mathbf{x}(\tau, t), \mathbf{s}(\tau, t), c(\theta, t), c(\tau, t), \frac{\partial c}{\partial \theta}(\theta, t), \frac{\partial c}{\partial \tau}(\tau, t)) d\tau,$$

$$0 < t_0 < t \leq T, \quad j = 1, \dots, m,$$

$$\psi_i(t_0, t) = \psi_i^*(t) + \int_{t_0}^t d\theta \int_0^\theta F_{\psi,i}(\Psi(\tau, t), \mathbf{s}(\tau, t), c(\theta, t), c(\tau, t), \frac{\partial c}{\partial \theta}(\theta, t), \frac{\partial c}{\partial \tau}(\tau, t)) d\tau,$$

$$0 < t_0 < t \leq T, \quad i = 1, \dots, n,$$

$$c(t_0, t) = \Sigma(t_0) + \int_0^{t_0} d\theta \int_0^\theta F_{c,1}(\mathbf{x}(\tau, \theta), \mathbf{s}(\tau, \theta), \Psi(\tau, \theta), c(\theta, \theta), c(\tau, \theta), \frac{\partial c}{\partial \tau}(\tau, \theta)) d\tau$$

$$+ \int_{t_0}^t d\theta \int_0^{t_0} F_{c,2}(\mathbf{x}(\tau, \theta), \mathbf{s}(\tau, \theta), \Psi(\tau, \theta), c(t_0, \theta), c(\tau, \theta), \frac{\partial c}{\partial \tau}(\tau, \theta)) d\tau, \quad 0 < t_0 < t \leq T.$$

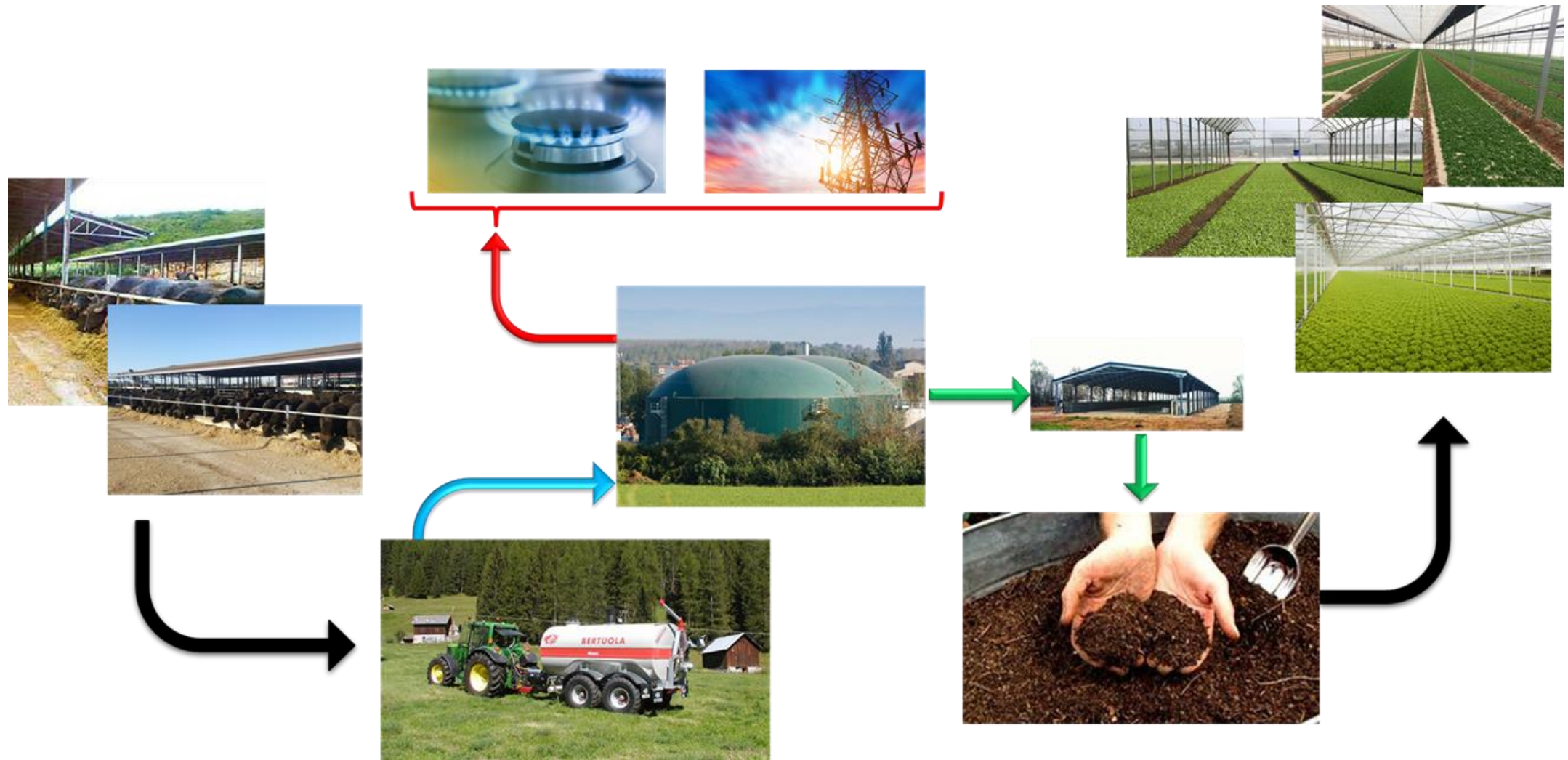


Ingegnerizzazione – Mathematical Modelling

To be continued.....



Bioenergy SERRE e Bioenergy ALBANELLA



Bioenergy SERRE e Bioenergy ALBANELLA



Bioenergy ALBANELLA



Bioenergy SERRE



GRAZIE

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CONCLUSIONI

