Valorisation of agroindustrial waste for the production of energy, biofuels and biopolymers

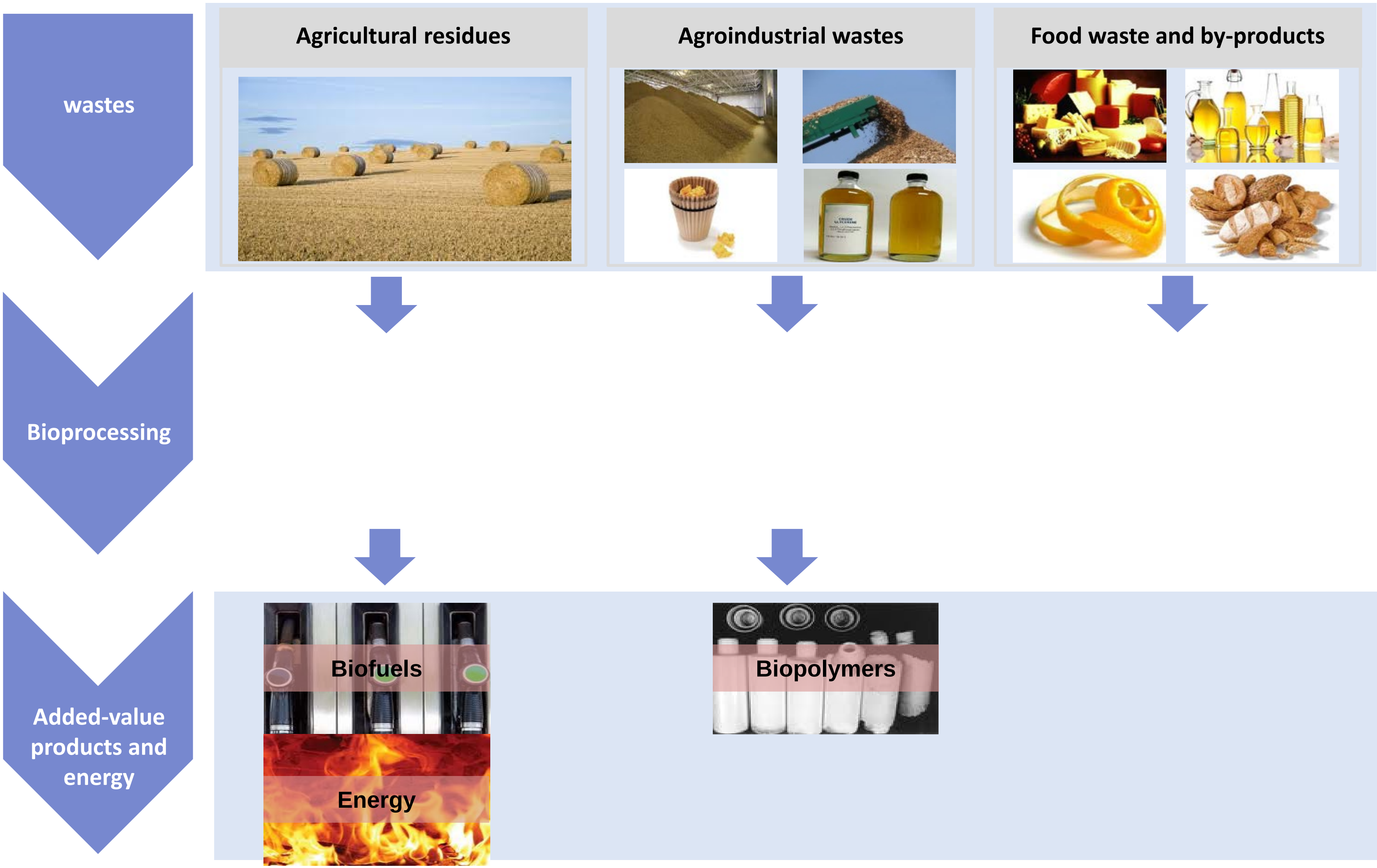
Prof. Gerasimos Lyberatos
National Technocal University of Athens

Industrial Waste & Wastewater Treatment & Valorisation
Athens, 21-23 May 2015

Biomass

- Biomass Organic and animal wastes, wastewaters, energy crops, agricultural and industrial residues
- Biomass: is the oldest and most promising source of energy

Valorization of agroindustrial wastes



Biomass utilization for energy

- First generation (energy crops)
  - Serious concern as it replaces food resources
- Second generation (residues, mainly lignocellulosic)
- Third generation (algal biomass)

Biomass Conversion to Biofuels

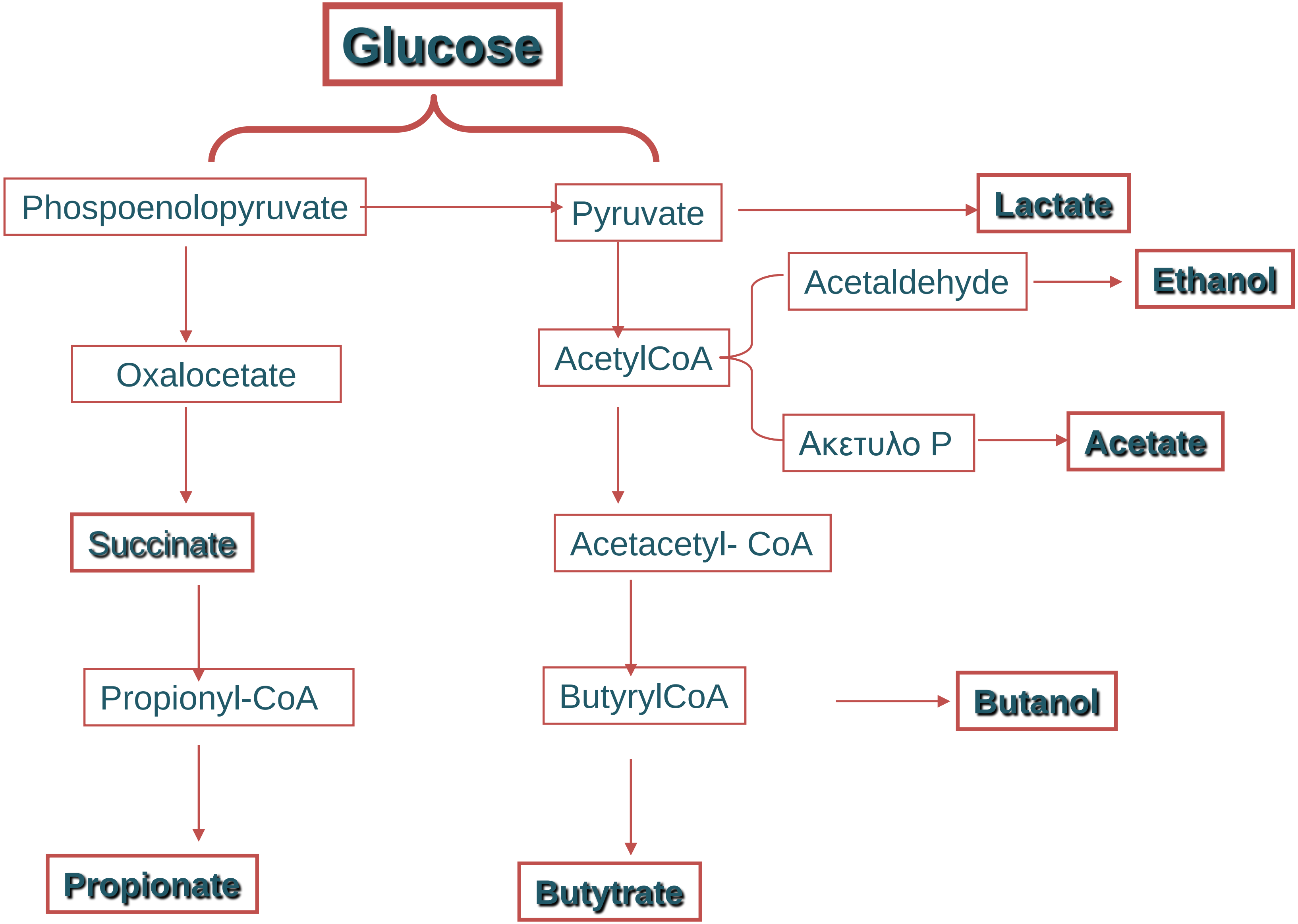
Technologies:

- Chemical (biodiesel)
- Thermal (direct combustion, pyrolysis, gasification)
- Biological (anaerobic digestion, hydrogen fermentation, alcoholic fermentation etc)

- **An emerging new possibility:**

Direct Electricity Generation: Microbial fuel cells (MFCs)

Anaerobic metabolism



What will be produced depends on:

1. Feedstock characteristics
2. Microbial species present (pure and mixed cultures)
3. Operating conditions

Anaerobic digestion

- ✓ One of the most important biochemical processes for biomass conversion
- ✓ **CH_4 and CO_2** are produced from organic substrates via mixed microbial consortia under anaerobic conditions

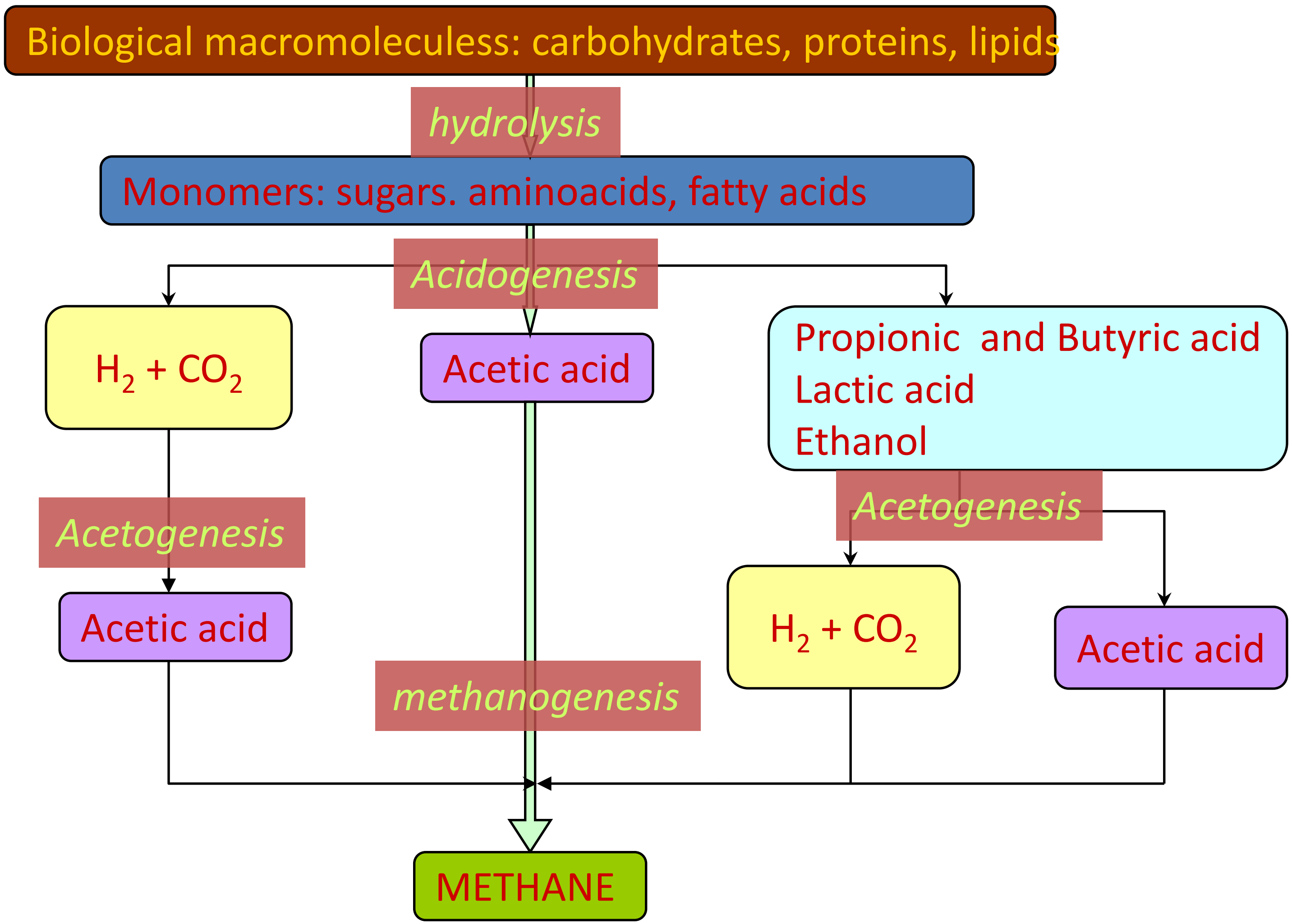
Overall reaction :

$$\text{Organic substrates} + H_2O \rightarrow CH_4 + CO_2 + NH_3 + \text{new cells}$$

Advantages:

- Methane production (gaseous biofuel)
- Suitable for wastes of high organic load
- Digestate can be composted

Anaerobic digestion



High Organic Content Industrial Wastewaters

Virtually AD is the only feasible biological process for treating agroindustrial wastewaters (e.g. dairy, piggery and olive-mill)

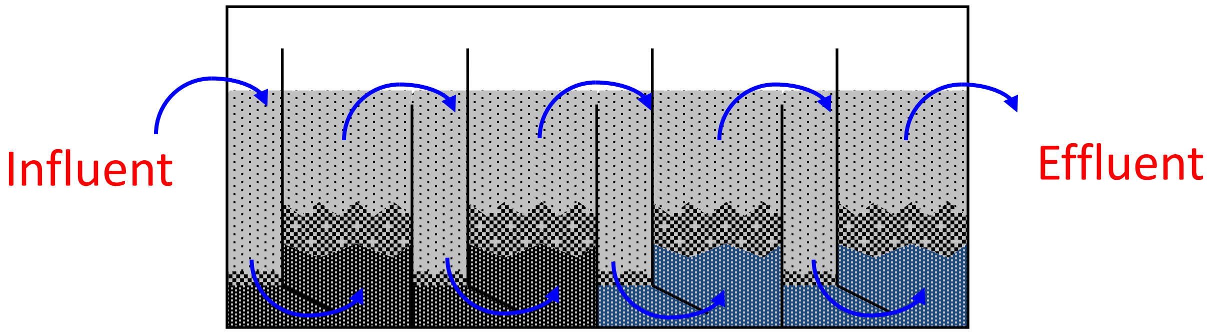
- ✓high organic load
- ✓seasonal nature
- ✓small distributed units

Normally **high retention times** are needed in standard CSTR-type reactors

High-rate reactors such the UASBR and the ABR have been developed

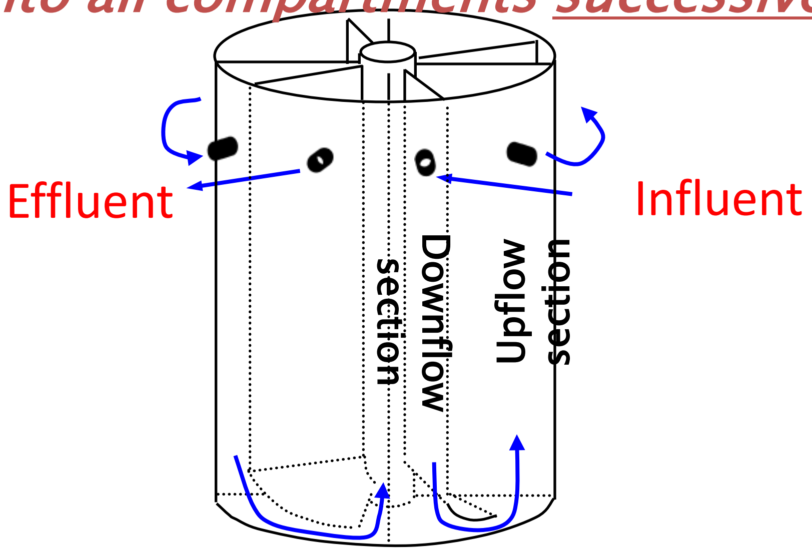
Periodic Anaerobic Baffled Reactor (PABR)

… based on the simple ABR configuration …

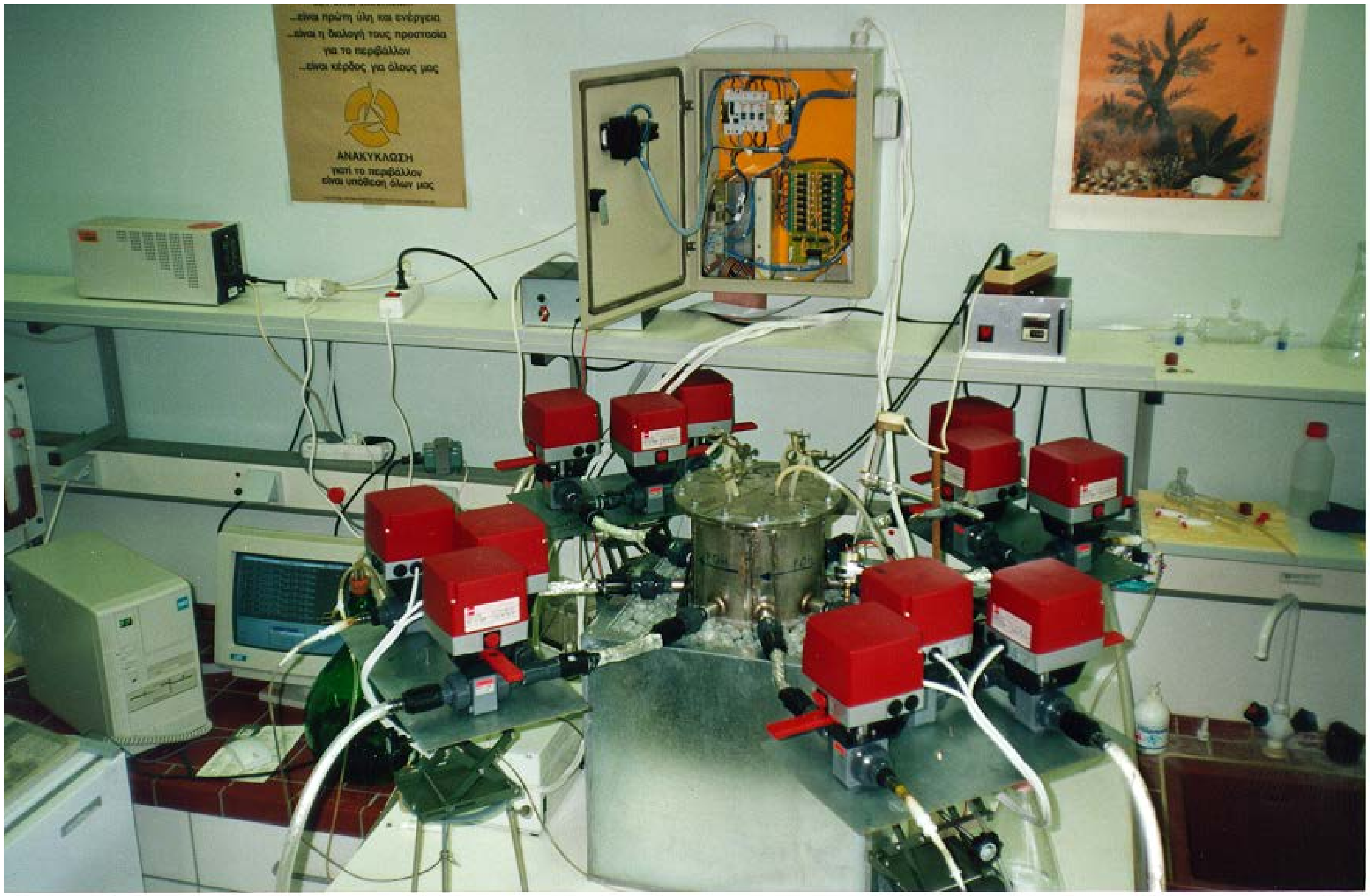


… it was made <u>flexible</u> to alternate its operation between the ABR (compartmentalized) and UASBR (homogenized) operation mode by directing the influent into all compartments <u>successively</u>.

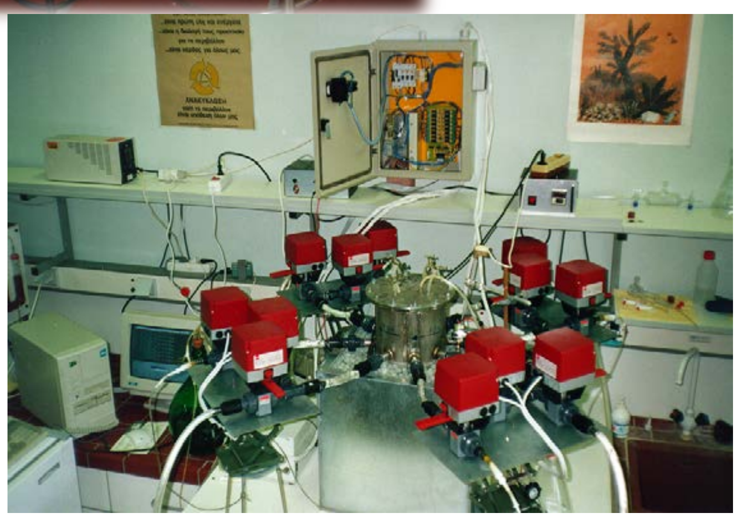
The PABR compartments are arranged in a circular manner:



The experimental PABR



Feedstocks & Conditions – CH_4

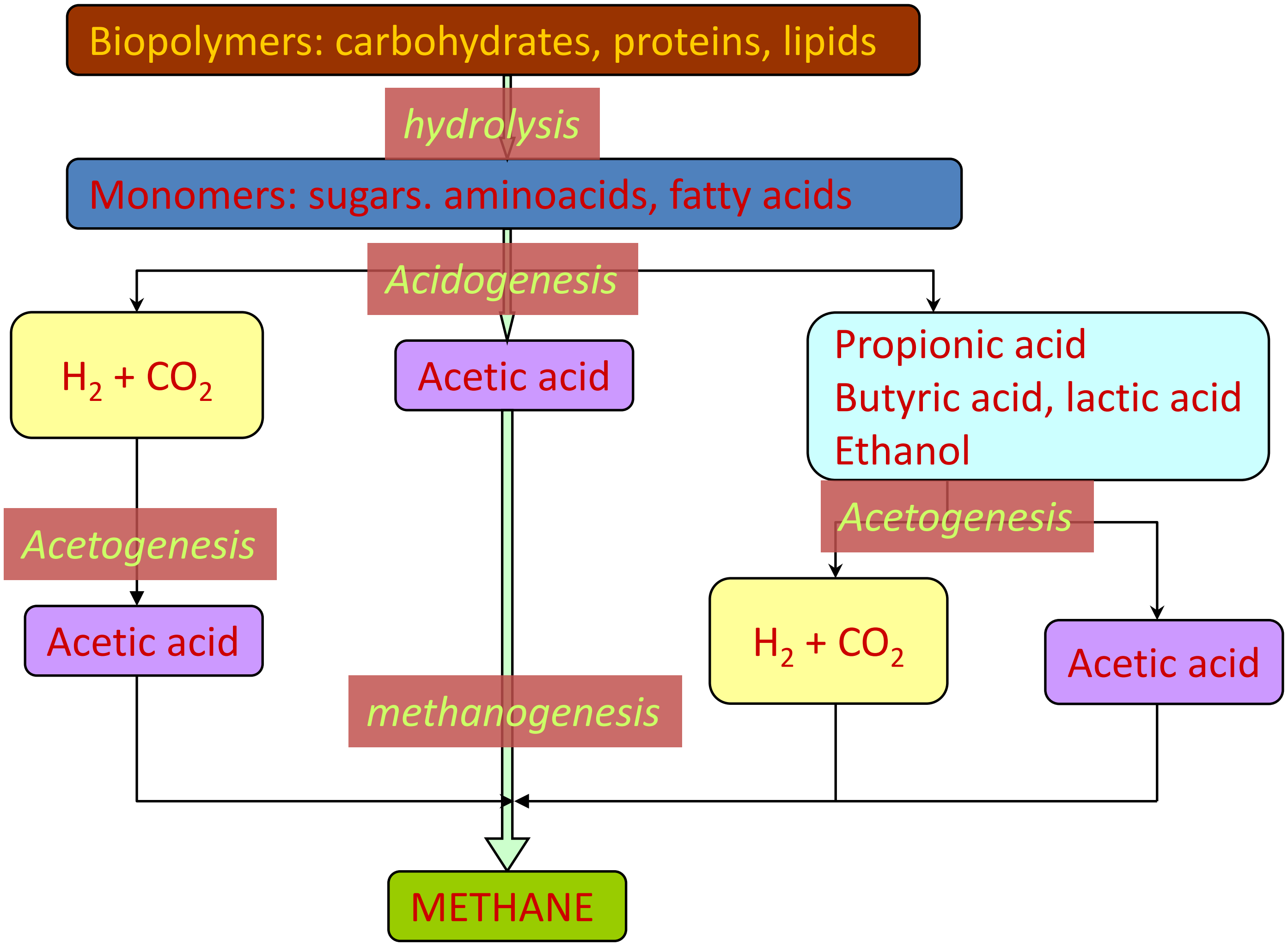


- Sorghum extract
  - 20d, 15d, 10d
- Olive Mill Waste
  - 20d, 15d, 10d
- Dairy wastewater
  - 20d, 10d, 4.4d

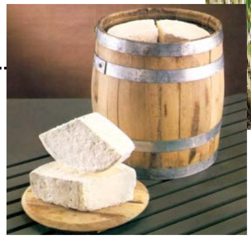
Yields and rates – CH_4

HRT (h)	CH_4 (%)	Specific rate (Lbiogas/L/d)	Specific rate (L CH_4/L/d)	Yield (LCH_4/kg TS)
20	64.4 ± 2.0	0.34 ± 0.03	0.21 ± 0.02	25.2
15	64.9 ± 1.8	0.53 ± 0.02	0.35 ± 0.02	31.2
10	63.1 ± 1.2	0.93 ± 0.02	0.59 ± 0.01	35.2
20	66.2 ± 2.0	0.64 ± 0.05	265	79.5
15	65.0 ± 2.0	0.79 ± 0.05	245	73.6
10	67.0 ± 2.0	1.13 ± 0.08	234	70
20	74.9 ± 1.0	1.7 ± 0.3	1.3 ± 0.2	26
10	73.6 ± 3.0	3.5 ± 0.5	2.6 ± 0.3	26
4.4	71.8 ± 2.2	6.9 ± 0.6	5.0 ± 0.6	22

Fermentative hydrogen production

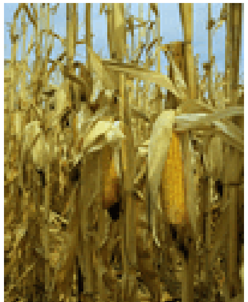



Why hydrogen ?

- A clean and environmentally friendly fuel which produces water instead of greenhouse gases, when burned
- Possesses the highest specific energy yield (122kJ/g)
- Could be used to produce electricity through fuel cells
- Can be produced by renewable raw materials, such as biomass, through biological or thermochemical processes



Fermentative hydrogen production

ACETIC ACID PRODUCTION

- $C_6H_{12}O_6 + 2H_2O \rightarrow 2CH_3COOH + 2CO_2 + 4H_2$

BUTYRIC ACID PRODUCTION

- $C_6H_{12}O_6 \rightarrow CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$

PROPIONICC ACID PRODUCTION

- $C_6H_{12}O_6 + 2H_2 \rightarrow 2CH_3CH_2COOH + 2H_2O$

LACTIC ACID PRODUCTION

- $C_6H_{12}O_6 \rightarrow 2CH_3CHOHCOOH$

ETHANOL PRODUCTION

- $C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2$

MIXED ACID FERMENTATION

↓

Intermediate H_2 yields

✓The absence or presence of hydrogen consumers in mixed consortia also affects the final distribution of metabolites and H_2 yields

✓Mixed microbial consortia need to be pretreated so as hydrogen consumers to be suppressed and hydrogen producers to dominate the consortium

Thermal pretreatment (100ºC, 15min)

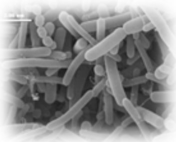
Parameters affecting fermentative hydrogen production

- pH
- H_2 partial pressure
- Hydraulic Retention Time (HRT)
- Temperature
- Nutrients concentration
- Initial carbohydrates concentration
- Organic loading

Hydrogen production from wastewaters, solid wastes and energy crops

In this framework several bioreactors of **CSTR** (Continuous Stirred Tank Reactor), **SBR** (Sequential Batch Reactor) and **UFCR** (Up-flow Column Reactor) type are used for the exploitation of :

- ✓ Dairy wastewater
- ✓ 3-phase and 2-phase olive mill wastewater
- ✓ Sweet sorghum biomass
- ✓ Glycerol
- ✓ Food wastes
- ✓ Wastepaper sludge



Reactors & Conditions – H_2

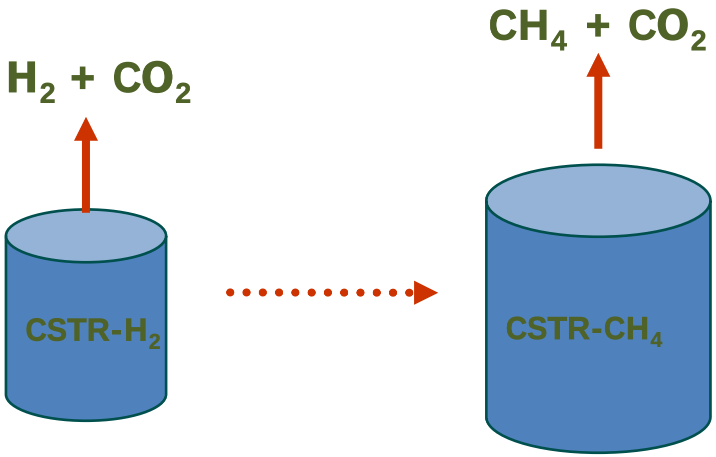
- CSTR type, 0.5 or 3 L
- T=35° C
- HRT differs according to substrate
  - Sorghum extract
    - 24h, 12h, 8h, 6h, 4h
  - Olive mill wastewater
    - 30h, 14.5h, 7.5h
  - Dairy wastewater
    - 24h

- Column bioreactor, 1,5L
- Immobilization of cells on ceramic beads
- T=35° C
- HRT 36h
  - glycerol

Yields and rates – H_2

	HRT (h)	H_2 (%)	Specific rate ($L\ H_2/L/d$)	Molecular yield ($molH_2/mol_{gluc}$)	Yield ($L\ H_2/kg$)
	24	30.4 ± 1.2	0.82 ±0.08	0.37 ± 0.02	4.9
	12	39.9 ± 1.2	3.48 ± 0.20	0.86 ± 0.04	10.4
	8	40.5 ± 1.9	4.14 ± 2.40	0.75 ± 0.05	8.4
	6	39.2 ± 0.5	5.10 ± 0.18	0.70± 0.02	7.6
	4	35.0 ± 1.5	4.36 ± 0.30	0.41 ± 0.02	4.3
	30	26.4 ± 1.7	0.26 ± 0.01	0.81	1.9
	14.5	26.7 ± 1.4	0.39 ± 0.05	0.61	1.3
	7.5	29.1 ± 1.6	0.47 ± 0.05	0.504	0.8
	24	29.3 ± 1.6	2.51 ± 0.43	0.9 ± 0.1	(LH_2/L) 2.49
	36	37.1 ± 1.2	0.35 ± 0.01	0.13 ± 0.0	3.1

Hydrogen and methane production in a two-stage process



- ✓ Stabilization of waste
- ✓ Minimization of COD
- ✓ Maximum energy generation

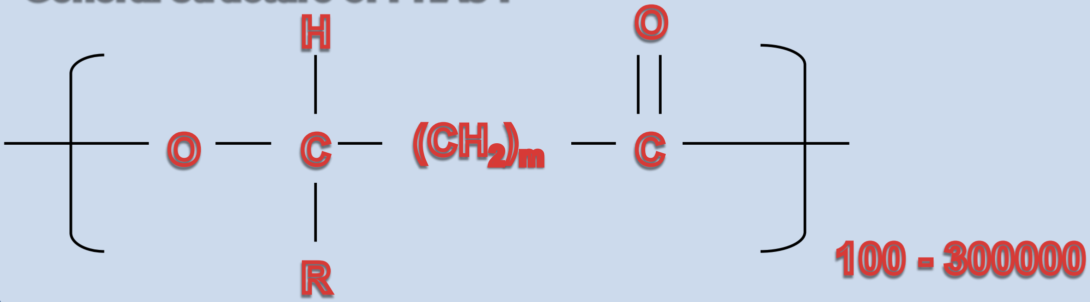
○ The effluent of hydrogen generating reactors is used directly as substrate for further stabilization and valorisation in continuous anaerobic digesters for methane recovery

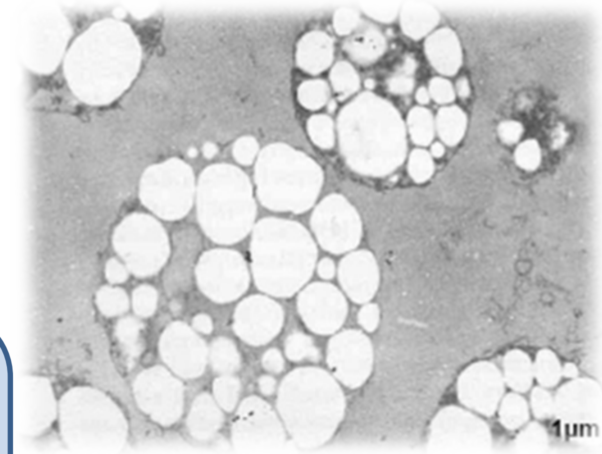
- ✓ Dairy wastewater
- ✓ 2-phase olive mill wastewater
- ✓ Sweet sorghum biomass
- ✓ Glycerol
- ✓ Food wastes

Production of polyxydroxyalkanoates

- PHAs accumulated by numerous bacteria as reserve of carbon and energy source in the form of inclusion bodies (granules) with a diameter of 0.2-0.9 μm.

General structure of PHAs :





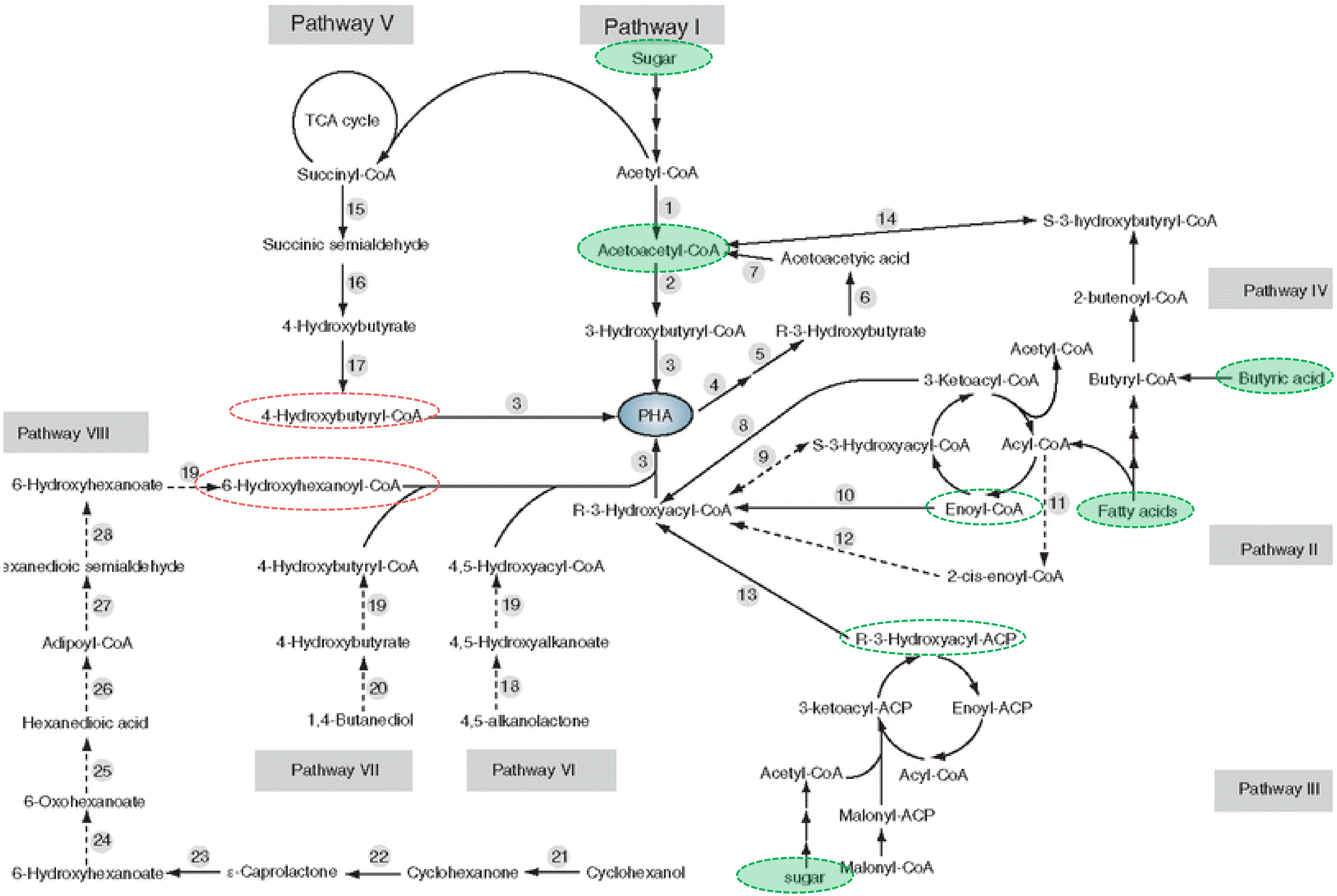
PHB intracellular granules formed in *Ralstonia eutropha* (Yu J., 2002)

Most common PHAs:

✓ **R = CH_3 ⇒ PHB poly-3-hydroxybutyrate**

✓ **R = C_2H_5 ⇒ PHV poly-3-hydroxyvalerate**

PHAs Biosynthesis



Chen, 2010, Microbiology Monographs 14: 17-37

General Approach

Alternating nutrient limitation (carbon & nitrogen) leads to PHA formation when nitrogen availability is limited

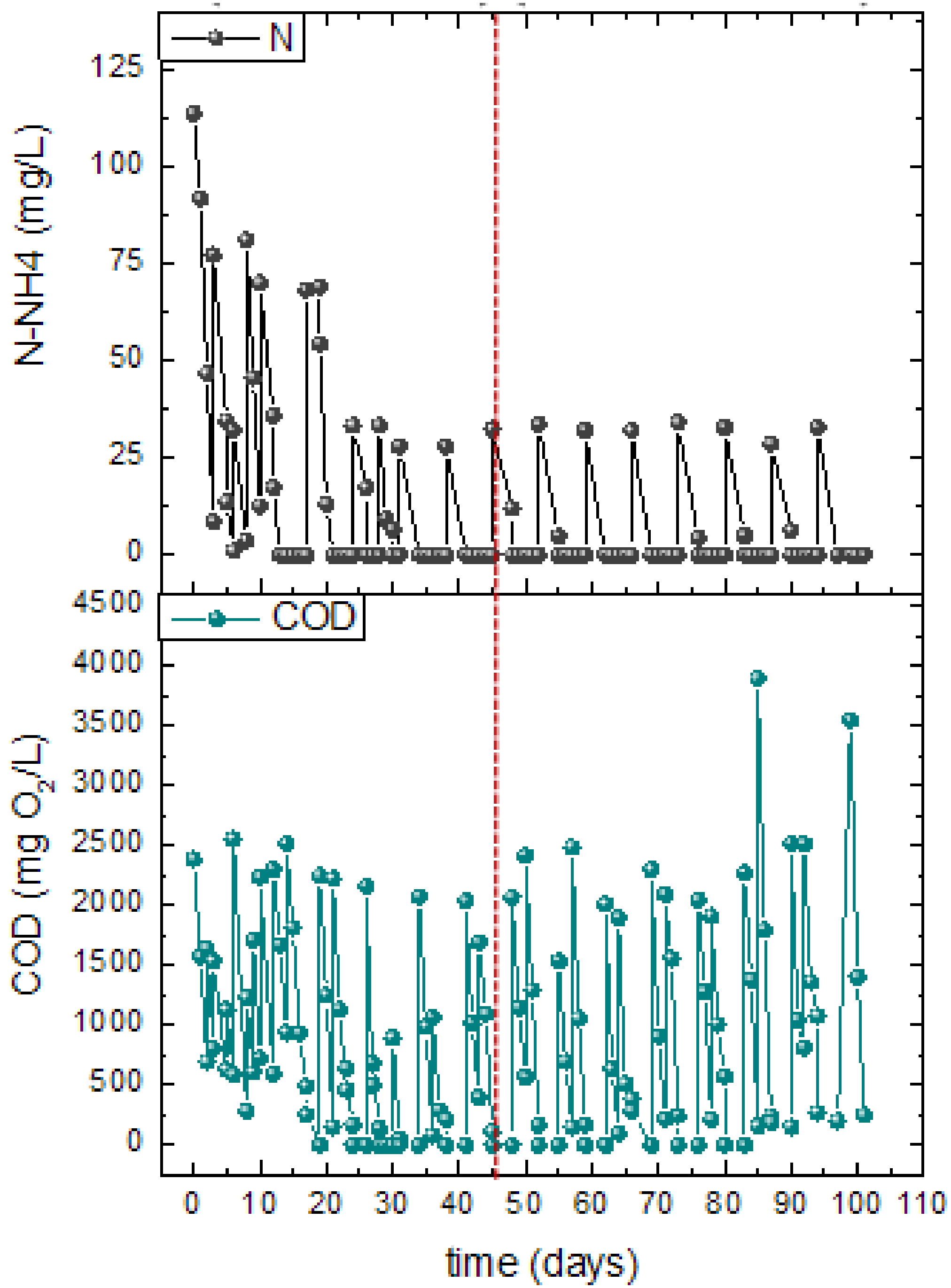
Sequencing batch reactor

SBR phases:

a) growth phase, N supply (no or limited carbon supplied),
b) biomass settling phase (no aeration and stirring)
c) supernatant withdrawal (2/3 of V_w),
d) PHA accumulation phase, C supply (nitrogen limitation)
e) withdrawal of 2/3 of the working volume under agitation (for PHAs extraction)

Wastes:

- **Olive-mill wastewater**
- **Industrial glycerol**



N
N-NH4 (mg/L)
125
100
75
50
25
0
COD
COD (mg O_2/L)
4500
4000
3500
3000
2500
2000
1500
1000
500
0
0
10
20
30
40
50
60
70
80
90
100
110
time (days)

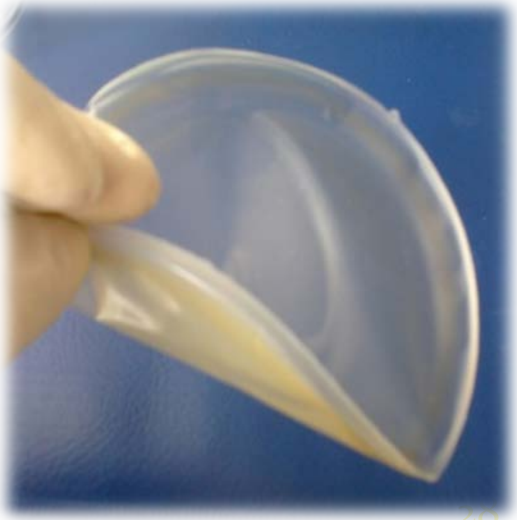
Recovery of PHAs from Cells

Collecting dry biomass by centrifugation, freezing and lyophilization

Extraction with chloroform

Purification: Mixing the extract with methanol for precipitation of bioplastic and then filtration

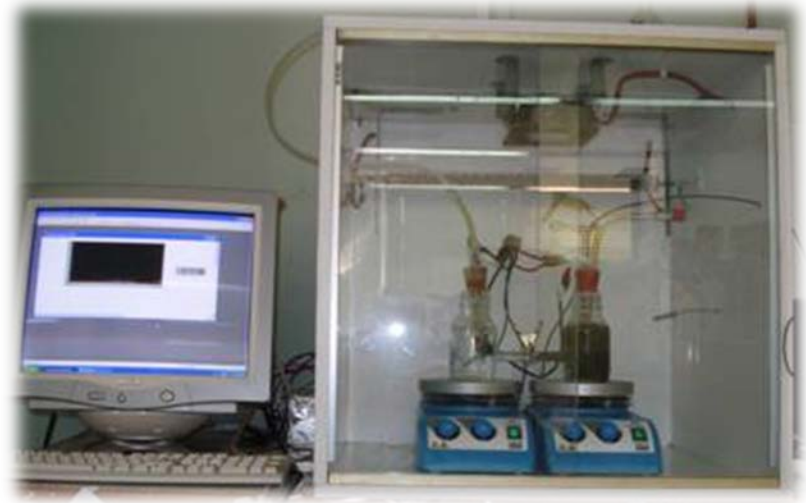
Collection of the solid and re-dissolution in chloroform to obtain bioplastic films



Electricity generation by microbial fuel cells

A **fuel cell** is an electrochemical energy conversion device that produces **electricity** from external supplies of fuel (on the anode side) and oxidant (on the cathode side).

In the **microbial fuel cell** electricity is produced via microorganisms



Substrates studied:

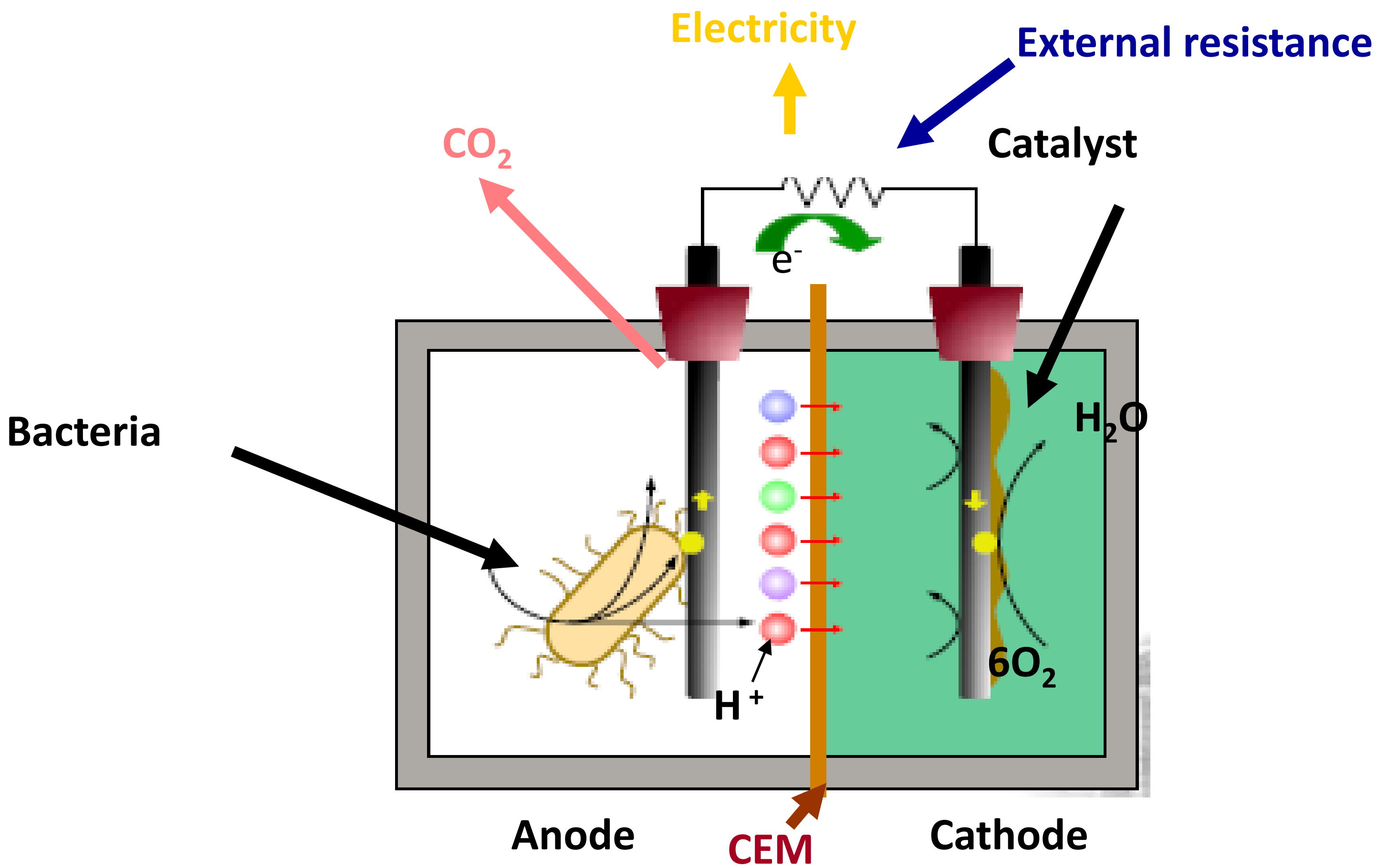
Pure substrates:

- ✓ Glucose, lactose
- ✓ Glycerol

Wastes:

- ✓ dairy wastewater
- ✓ municipal wastewater

The working principle of an MFC



<u>Chemistry of MFC</u>: As an example, glucose is used as an organic substrate.

Anode : $C_6H_{12}O_6 + 6H_2O \longrightarrow 6CO_2 + 24H^+ + 24e^-$

Cathode : $24H^+ + 24e- + 6O_2 \longrightarrow 12H_2O$

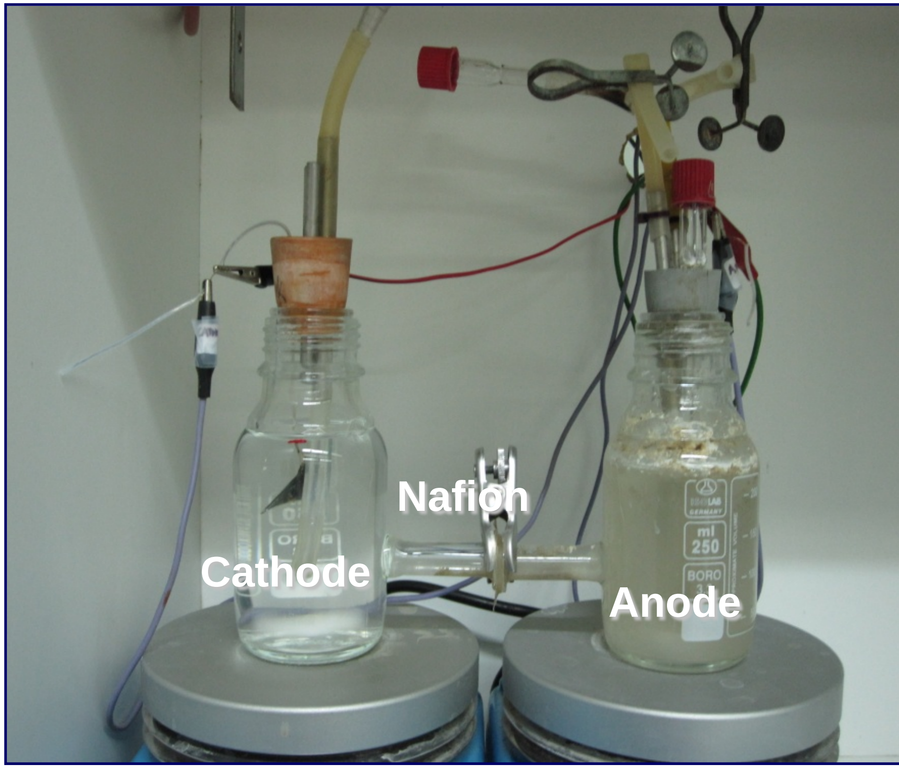
Two-chamber MFC

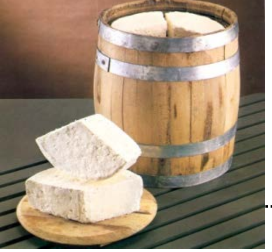
- Two bottles connected via a glass tube.

- Anode electrode: carbon fiber paper

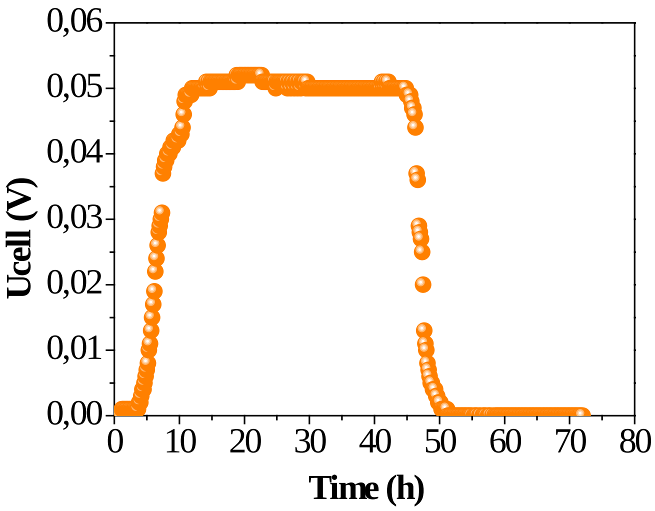
- Cathode electrode: carbon cloth coated with a Pt catalyst

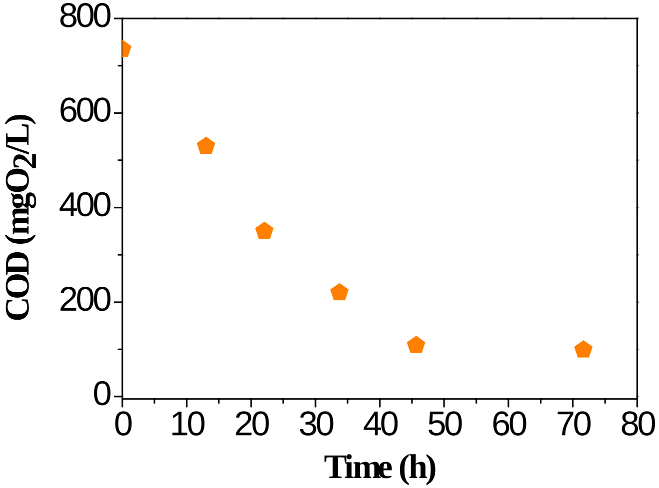
- Proton exchange membrane (Nafion 117)





Experiments using (diluted) cheese whey as substrate

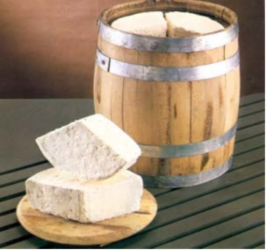


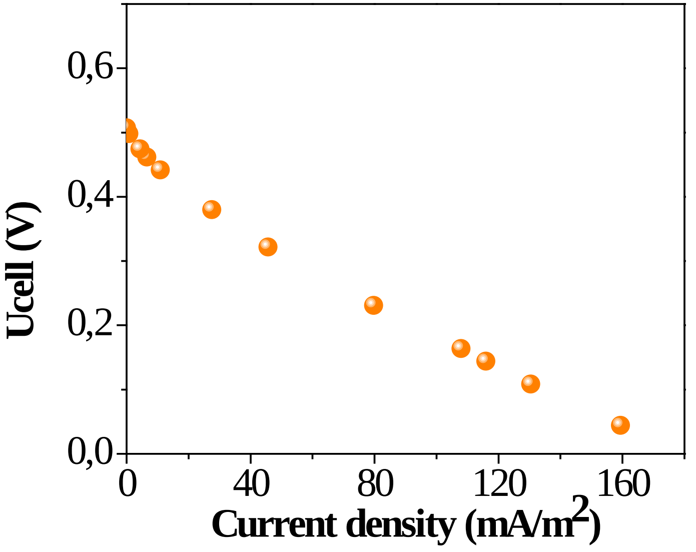


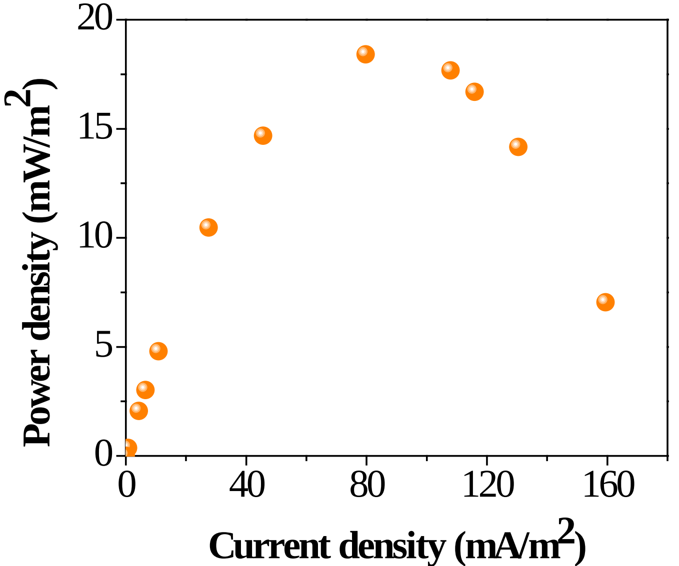
- ✓ After addition of fresh medium: the MFC voltage increased rapidly, reaching a constant value within only a few hours (approximately 50 mV for an external load of 100 Ω)

- ✓COD removal completed within 50 hours, accompanied by rapid decrease in voltage

➢Diluted cheese whey (dilution 1:100) at a final concentration of 0.73 g COD/L







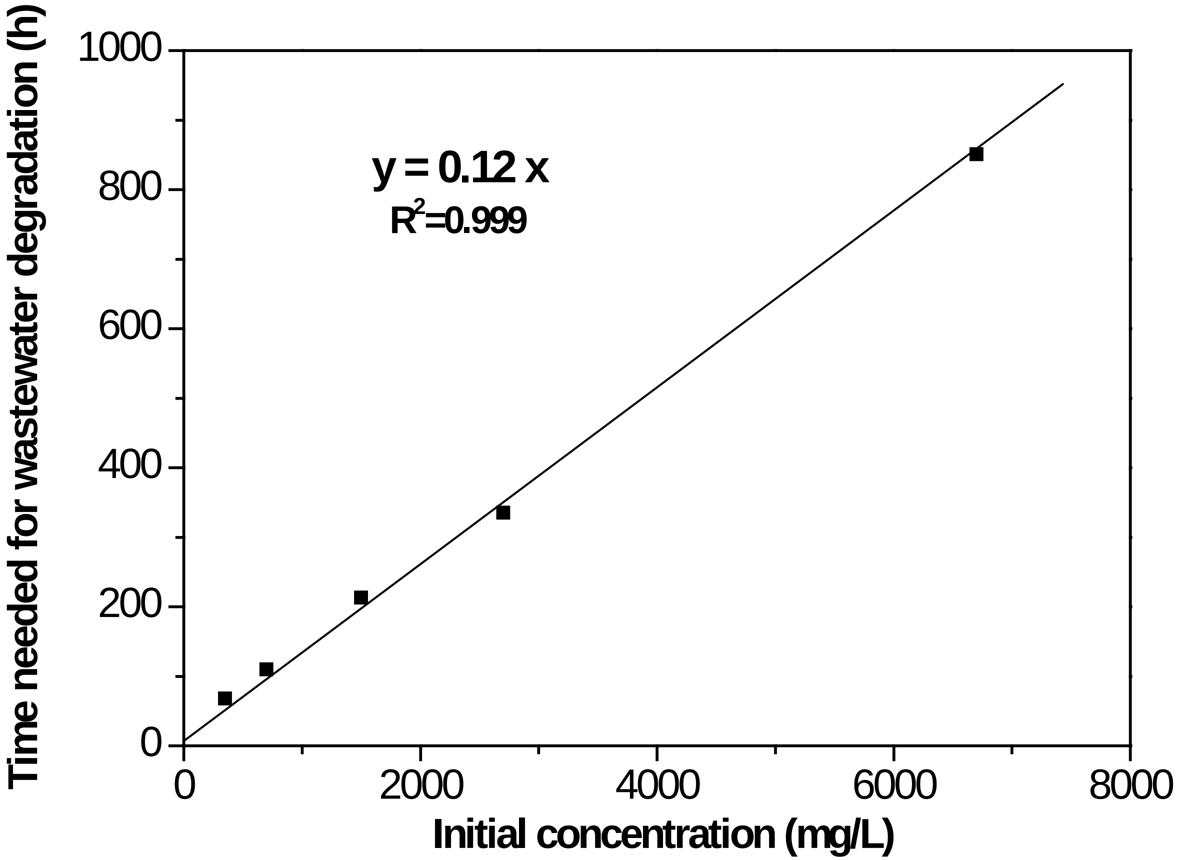
Varying the external load from 0.1 to 1000 kΩ

Maximum power density
18.4 mW/m²

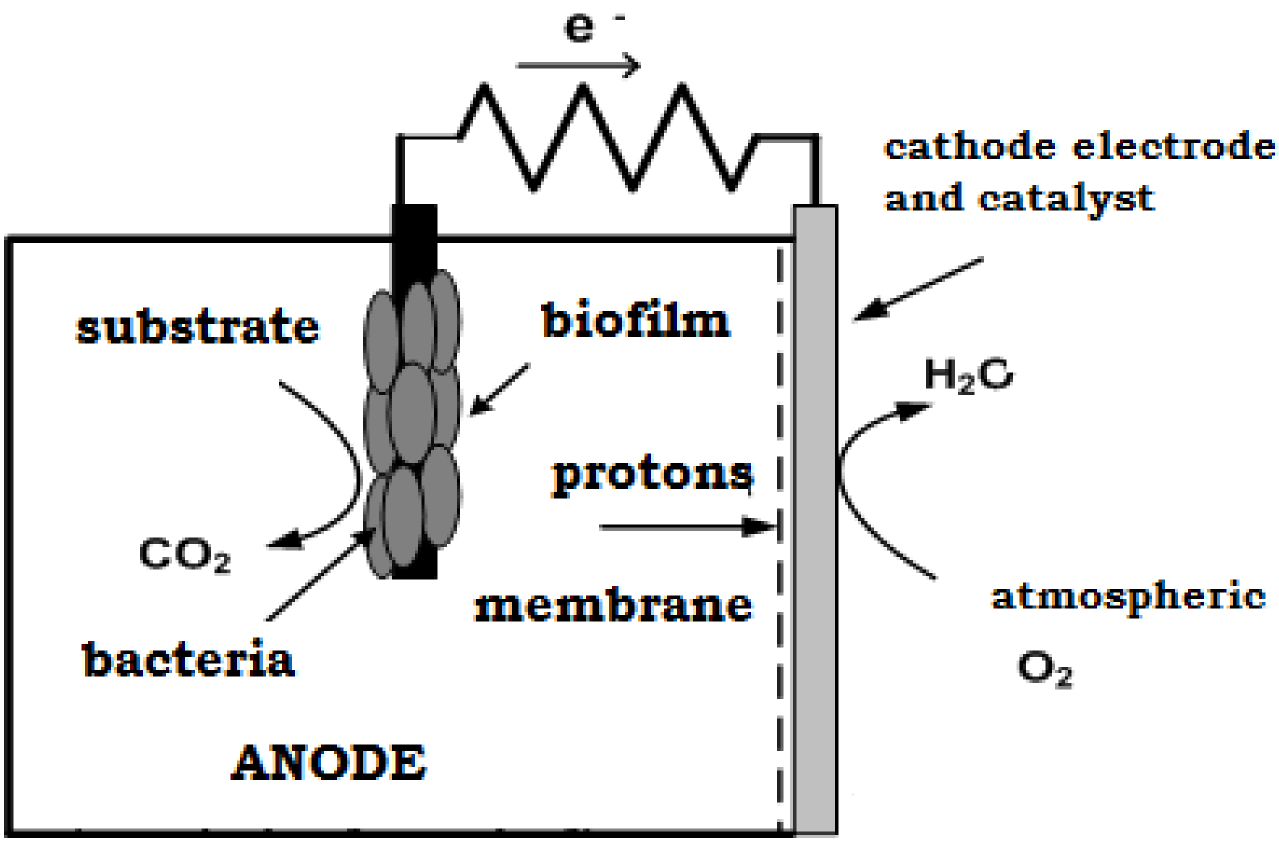
Experiments with cheese whey

Initial concentration (mg COD/L)	% COD removal	Duration of each cycle (h)	Maximum power output (mW/m^2)
350	95	68	40.5
700	96	110	39.9
1500	96	213	39.8
2700	96	335	38
6700	96	851	42

Duration as a function of initial concentration



Single cell chamber



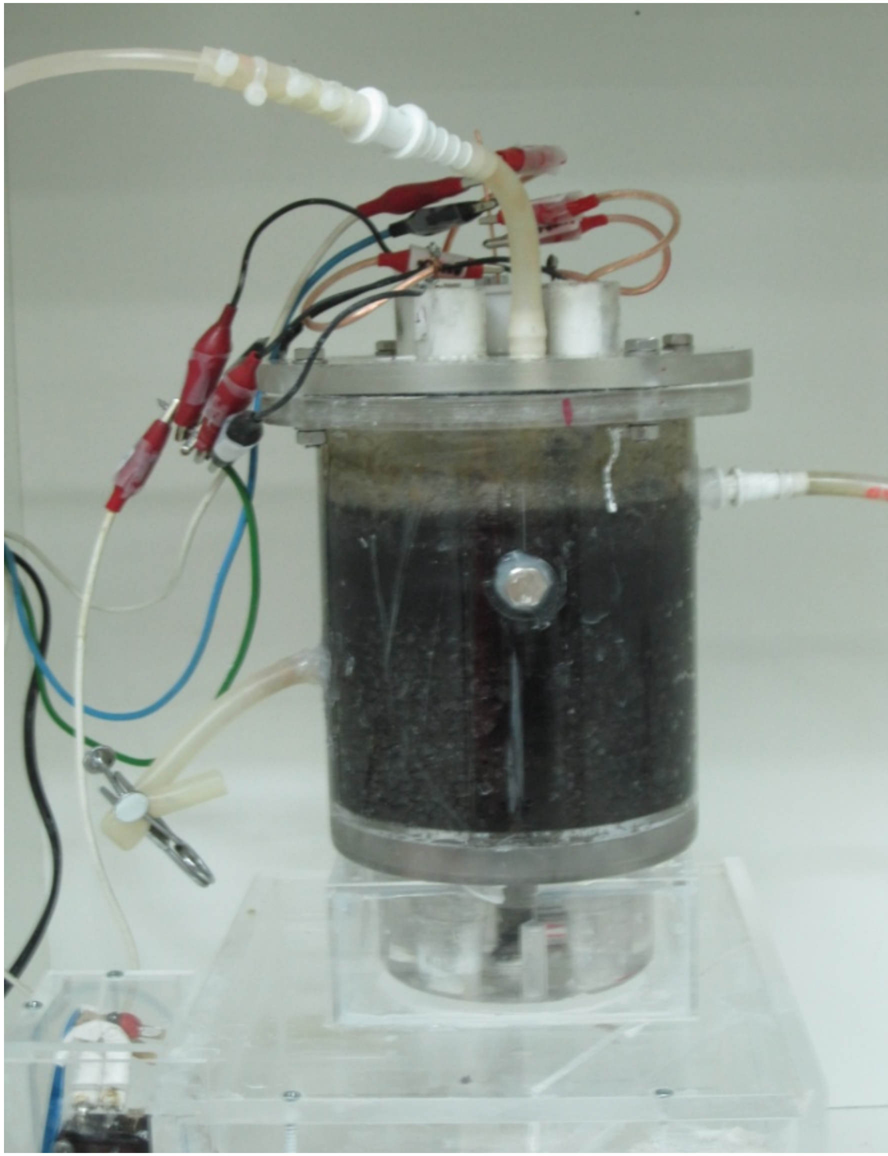
Innovative single chamber MFC

- A single cylindrical plexiglas chamber with four plexiglas tubes placed, in a concentric arrangement, inside the chamber.

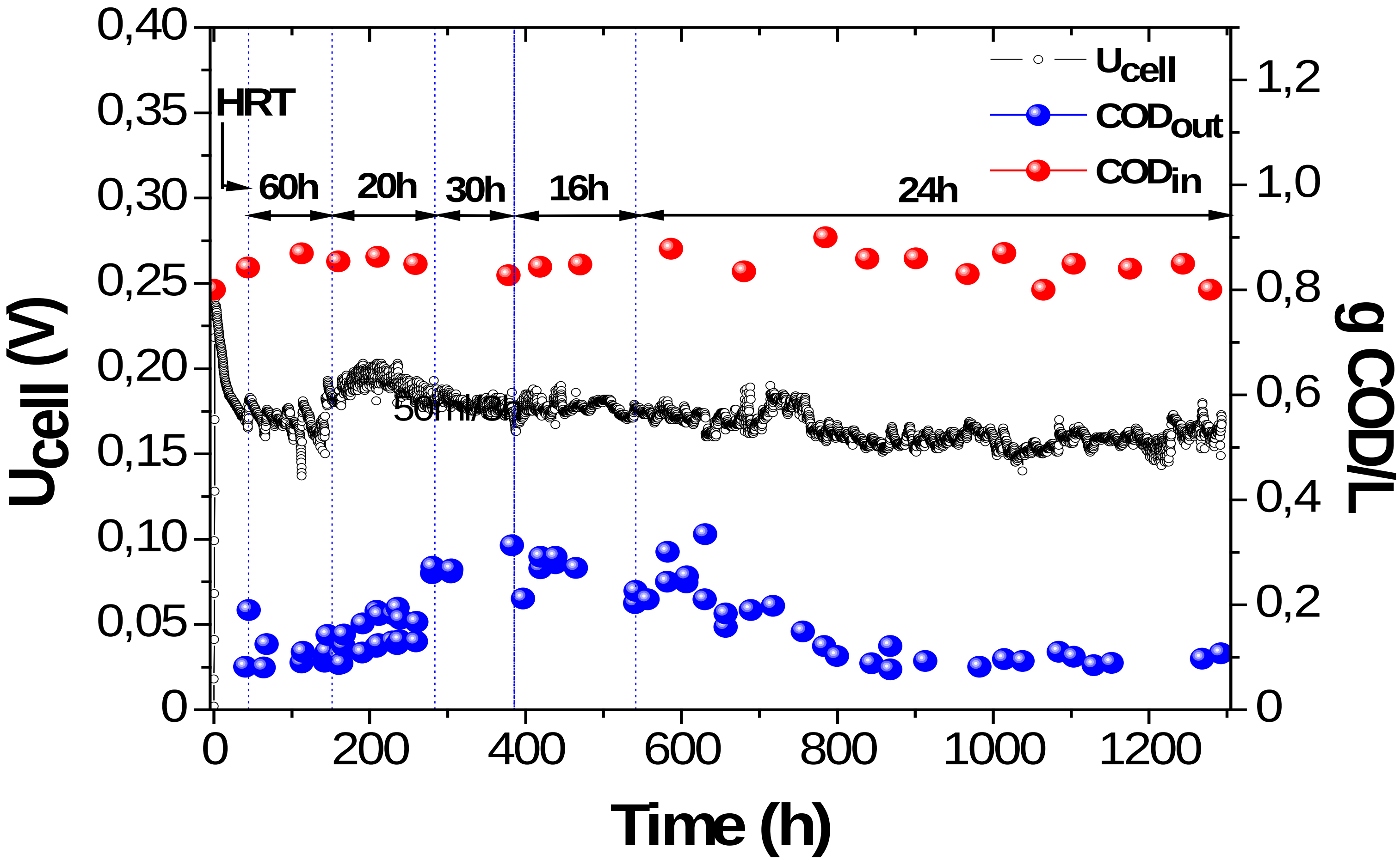
- The tubes inside the cell were homogenously drilled with holes

- Anode electrode: graphite granules.

- Cation Exchange Assembly: GORE-TEX ® cloth covered with graphite conductive paint and electrolytic manganese oxide, MnO_2.



Continuously operated Single chamber performance using glucose as substrate



Thank you for your attention !