Laboratory of Biochemical Engineering and Environmental Technology

- Founded in 1990
- Main research area is Biochemical Engineering as applied to:
  - Advanced water and wastewater treatment (nutrient removal, biofilm systems, sludge management)
  - Abatement of xenobiotics from wastewaters and sludge
  - Valorisation of wastes and energy crops for the production of electricity and energy carriers (biogas, bioethanol, biohydrogen)

Laboratory of Biochemical Engineering and Environmental Technology
Department of Chemical Engineering, University of Patras and
Institute of Chemical Engineering and High Temperature Chemical Processes

Production of gaseous biofuels and electricity from cheese whey

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SYMPOSIUM ON NEW FRONTIERS IN CHEMICAL & BIOCHEMICAL ENGINEERING
Thessaloniki, 26-27 November 2009

Biomass – Biofuels

- Global energy and environmental concerns due to the increasing use of fossil-derived fuels have led to the search for alternative energy sources

- **Biomass** is one of the oldest and the most promising sources of energy

- Biomass: Organic and animal wastes, wastewaters, energy crops, agricultural and industrial residues

- Nowadays, it provides approximately 15% of the total worldwide energy needs

Biomass → Biofuels

Technologies for the energy exploitation of biomass

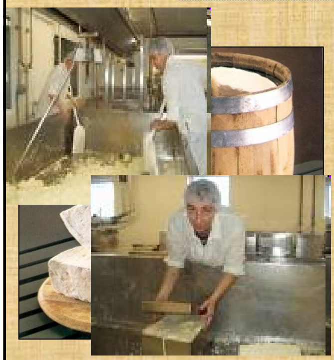
- Chemical (biodiesel)
- Thermal (direct combustion, pyrolysis, gasification)
- **Biochemical**

Fuel	Technology
Methanol	Gasification
Bio-oil	Pyrolysis
Hydrogen	Gasification, Biological conversion
Ethanol	Biological conversion
Biogas	Biological conversion
Biodiesel	Chemical conversion

- An emerging new possibility:

Direct Electricity Generation ⟹ Microbial fuel cell (MFC) technologies

Cheese whey



✓The lactose-rich watery by-product of cheese manufacturing

- ➢High organic load (60-80 g COD/L)
- ➢Low alkalinity
- ➢Tendency to acidify rapidly

✓It corresponds to 85-95% of the milk volume

➢Because of high organic content its disposal constitutes a serious environmental problem

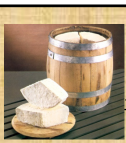
Components	% w/v
Lactose	4.5-5
Soluble proteins	0.6-0.8
Lipids	0.6-0.8

Scope of this study

To explore the possibility of exploiting cheese whey in order to produce:

a)Biohydrogen and biogas (methane) in a two-stage process

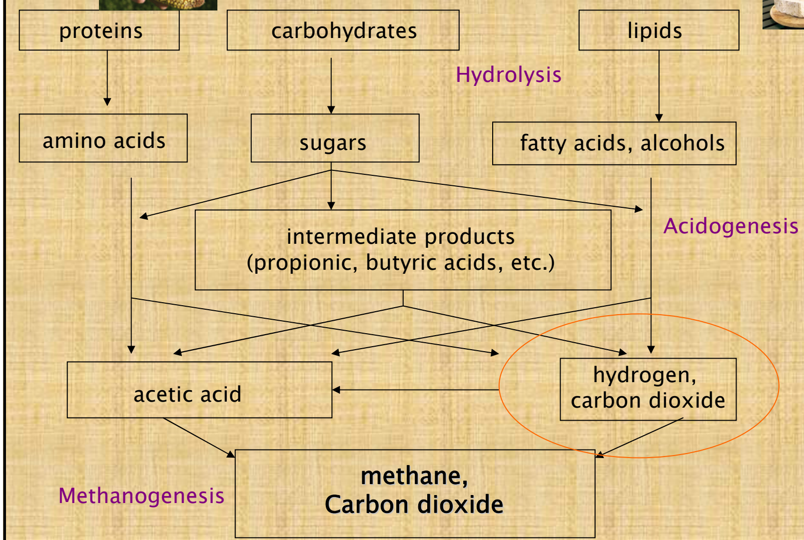
b)Direct electricity using a microbial fuel cell



Characteristics of cheese whey

Characteristic	Value
pH	6.0 ± 0.1
TSS (g/L)	6.77 ± 0.5
VSS (g/L)	6.27 ± 0.4
Total COD (g/L)	61.0 ± 1.5
Soluble COD (g/L)	52 ± 3.0
Total carbohydrates (g/L)	38.0 ± 2.1
Soluble carbohydrates (g/L)	36.0 ± 1.7
Lactic acid (g/L)	0.62 ± 0.05
Total proteins (g/L)	4.675
Oil and grease (g/L)	0.1
Total Kjendhal nitrogen (g/L)	0.826
Inorganic nitrogen (g/L)	0.078
Total phosphorus (g/L)	0.02
Total alkalinity (mg $CaCO_3$/L)	90

Anaerobic Digestion




Why hydrogen ?

- A clean and environmentally friendly fuel which produces **water** instead of greenhouse gases, when burned
- Possesses a high-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



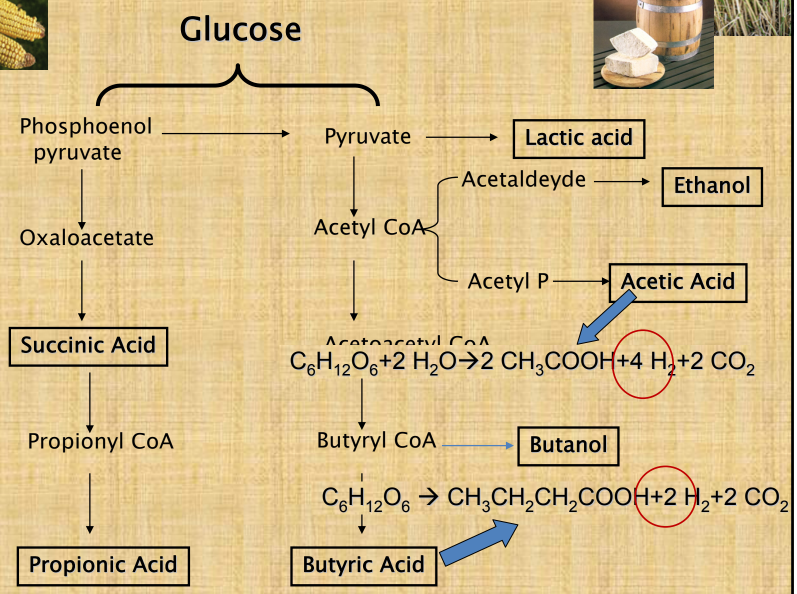


Biological hydrogen production

- Biophotolysis of water using cyanobacteria and algae
- Photodecomposition organic compounds by photosynthetic bacteria
- Hybrid systems using photosynthetic and fermentative bacteria
- **Fermentative hydrogen production from organic compounds**

carbohydrates {
- wastes/wastewaters
- agricultural residues
- energy crops

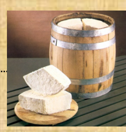
Metabolic pathways

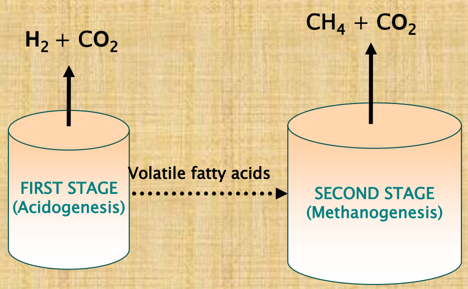


Factors influencing fermentative hydrogen production

- pH
- Hydraulic retention time (HRT)
- Temperature
- Nutrients and organic carbon concentration
- Hydrogen partial pressure and stirring conditions
- Absence of hydrogen consuming microorganisms

Hydrogen and methane production in a two stage process





✓Remaining organic content → **BIOGAS** → fuel for the production of electricity

Experiments for hydrogen production

✓ CSTR type

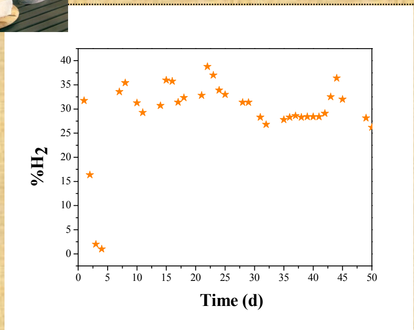
✓Active volume 3 L

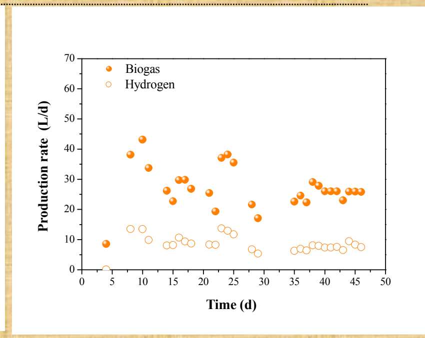
✓T=35.5° C

HRT (h)	24
Flow (mL/d)	3000
Organic load (g carbohydrates/d)	114

✓Alkalinity addition: 20 g/L $NaHCO_3$
✓Start -up: with the indigenous microflora contained in raw cheese whey

Results (H_2-CSTR)



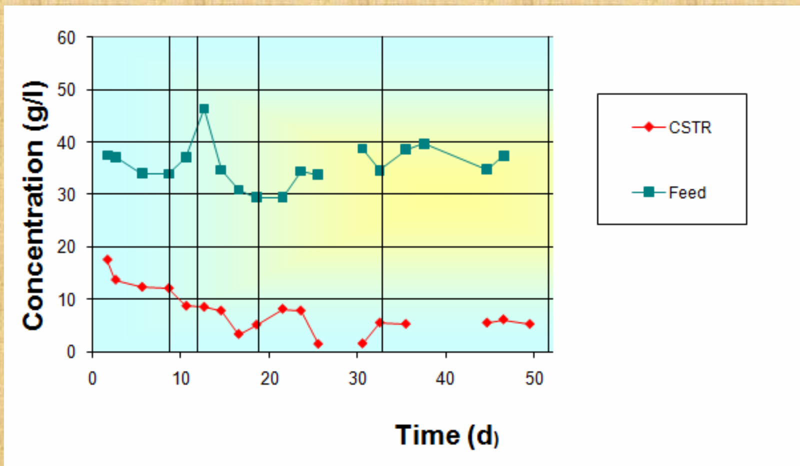


HRT, h	Hydrogen in the gas phase (%)	Hydrogen production, L/Lreactor/d	Hydrogen yield $\frac{mmolH_2}{mmol_{consumed\ carbohydrates}}$	Hydrogen yield $\frac{LH_2}{L\ cheese\ whey}$
24	29.3 ± 1.6	2.51 ± 0.43	0.9 ± 0.1	2.5

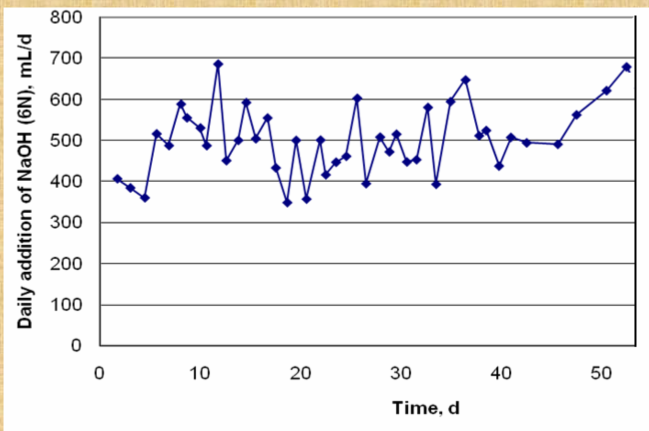
Pilot – scale reactor

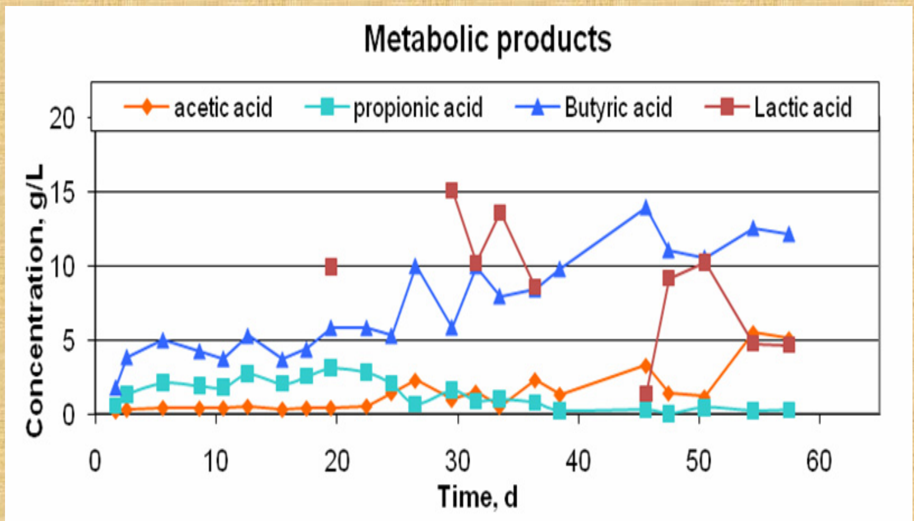
14 l reactor
Controlled pH (s.p. 5,2)
Controlled T
HRT 24 h

Carbohydrates

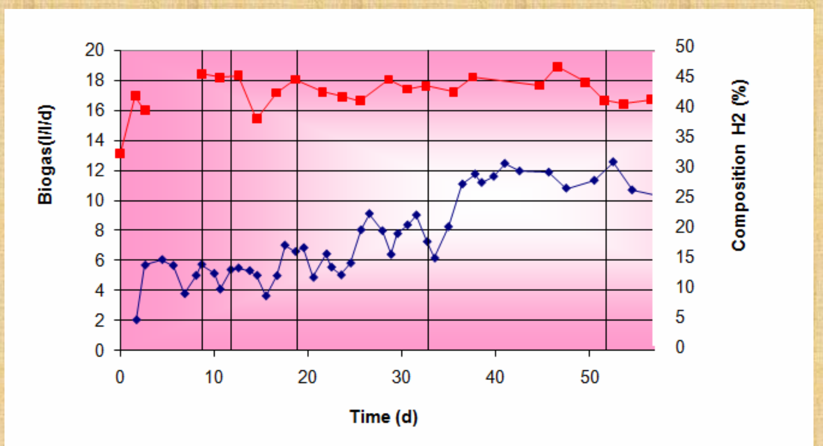


Requirement for base addition

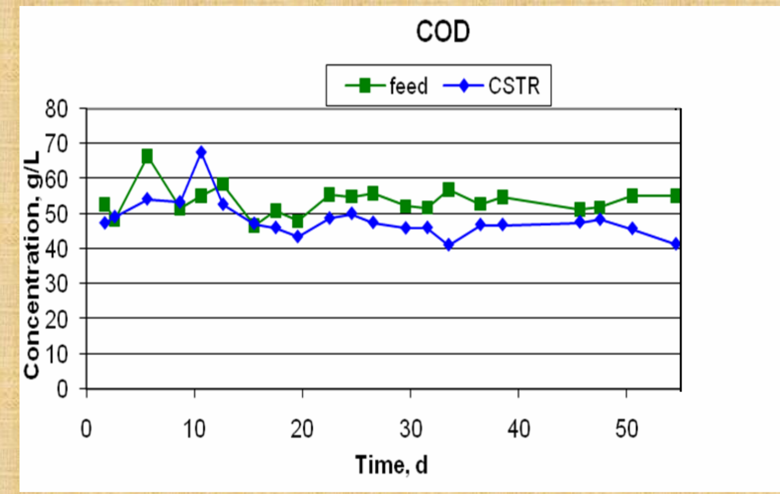




Biogas (4.8 l/l/d)

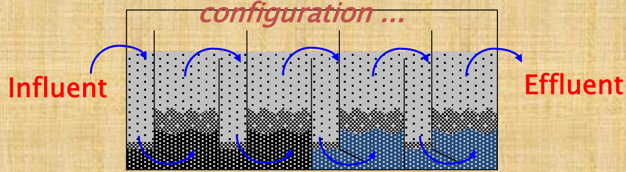


Small decrease in organic load



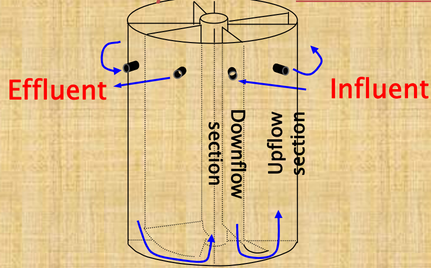
Periodic Anaerobic Baffled Reactor (PABR)

… based on the simple ABR configuration …

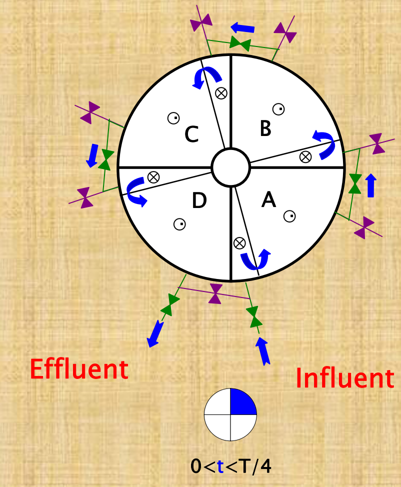


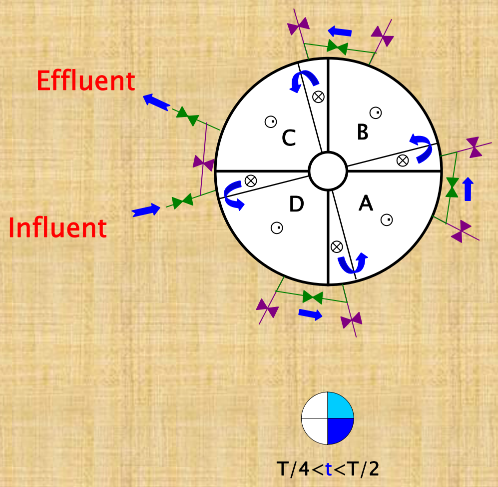
… it was made <u>flexible</u> to alternate its operation between the ABR (compartmentalized) and UASBR (homogenized) operation mode by directing the influent into all compartments <u>successively</u>.

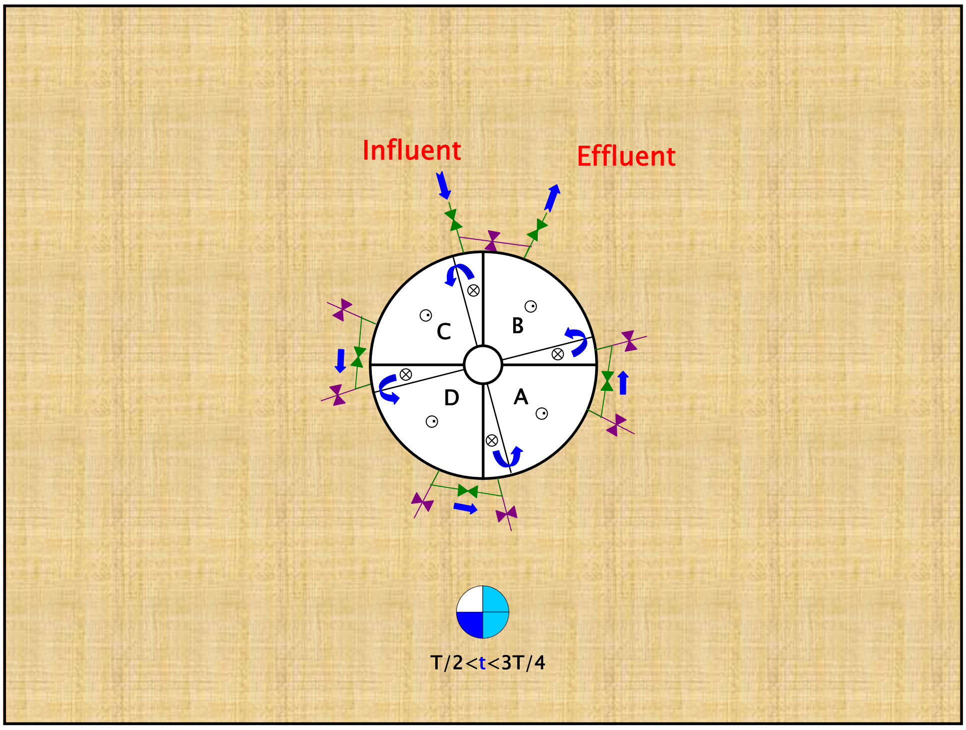
The PABR compartments are arranged in a circular manner:

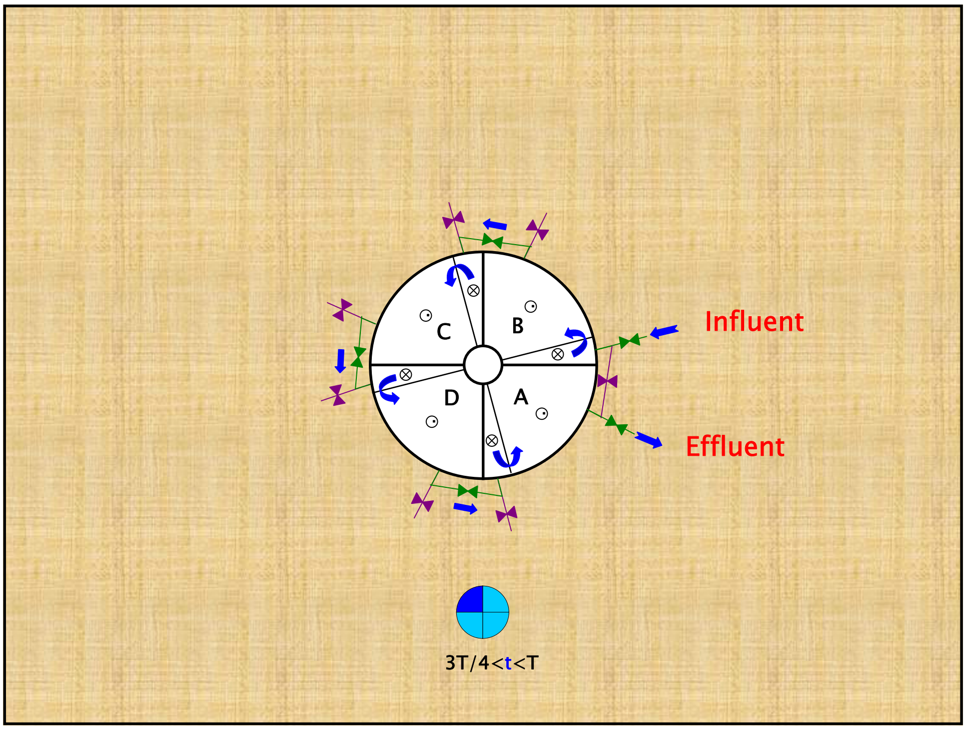


Operation of PABR during a period T

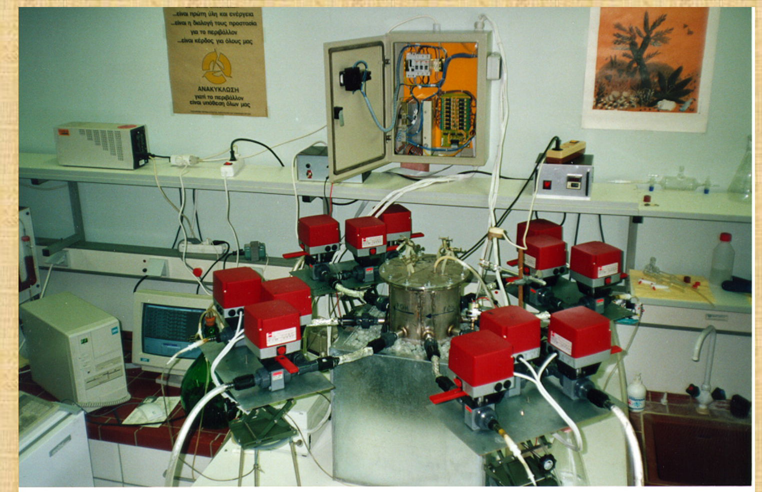





Influent
Effluent
C
B
D
A
T/2<t<3T/4


Influent
Effluent
C
B
D
A
3T/4<t<T

The experimental PABR



Characteristics of the influent of PABR

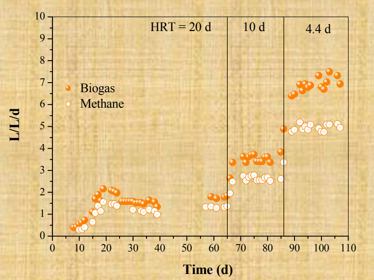
Characteristics	Value
pH	4.8 ± 0.1
TSS (g/L)	8.43 ± 1.9
VSS (g/L)	6.78 ± 1.2
Total COD (g/L)	58.0 ± 1.5
Soluble COD (g/L)	46.2 ± 3.0
Total alkalinity (mg$CaCO_3$/L)	3417 ± 300
Lactic acid (g/L)	9.6 ± 1.5
Total VFAs (gCOD/L)	27.4 ± 3.1

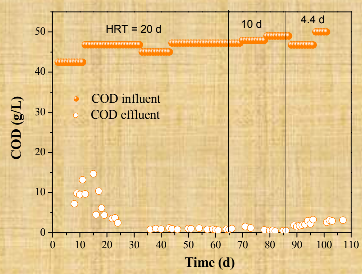
Experiments for methane production (PABR)

- ✓PABR
- ✓Active volume 15 L
- ✓T=35.5º C
- ✓Switching period 2d

HRT (d)	20	10	4.4
flow (mL/d)	750	1500	3400
Organic load (g.Total COD/d)	43.5	87	197.2

Results (PABR)





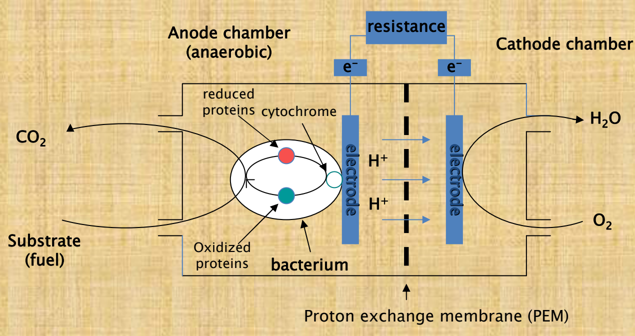
HRT (d)	% in CH_4	Methane production rate, L /Lreactor/d	Methane yield $\frac{L\ CH_4}{L\ feed}$
20	74.9 ± 1.0	1.3 ± 0.2	26
10	73.6 ± 3.0	2.6 ± 0.3	26
4.4	71.8 ± 2.2	5.0 ± 0.6	22

Microbial Fuel Cell

A MFC is a bioreactor that converts the energy stored in organic chemical bonds directly to electrical current through catalytic reactions of microorganisms under anaerobic conditions

Advantage
- Bio-energy production
- Wastewater treatment

MFC technology

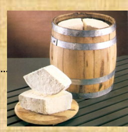


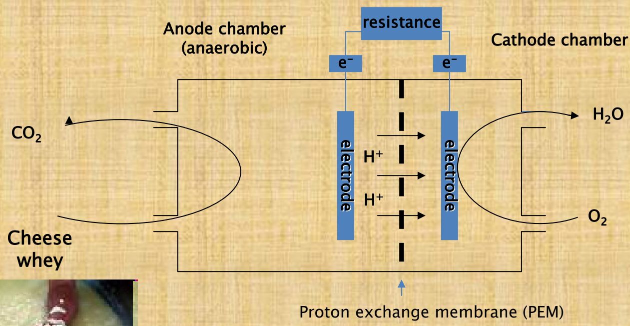
The electrochemical reactions which are carried out in a MFC using e.g. glucose as fuel are :

Anodic reaction : $C_6H_{12}O_6 + H_2O \rightarrow 6CO_2 + 24e^- + 24H^+$

Cathodic reaction: $O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$

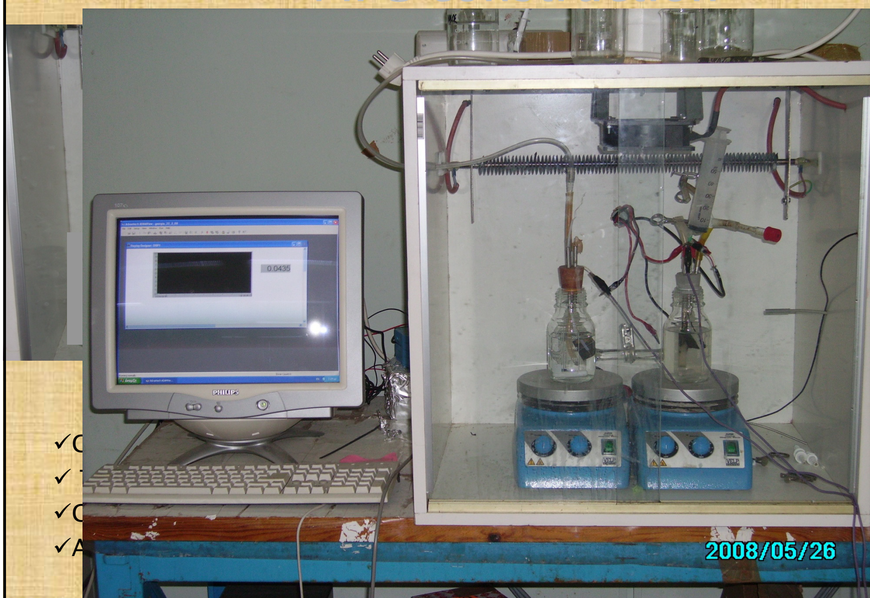
Electricity generation from cheese whey using a MFC





✓ For establishing a steady operation: **glucose** and **lactose** were used as fuels

MFC construction



lytic
wo–
rbon fiber
0, 10 wt%
.3 cm)
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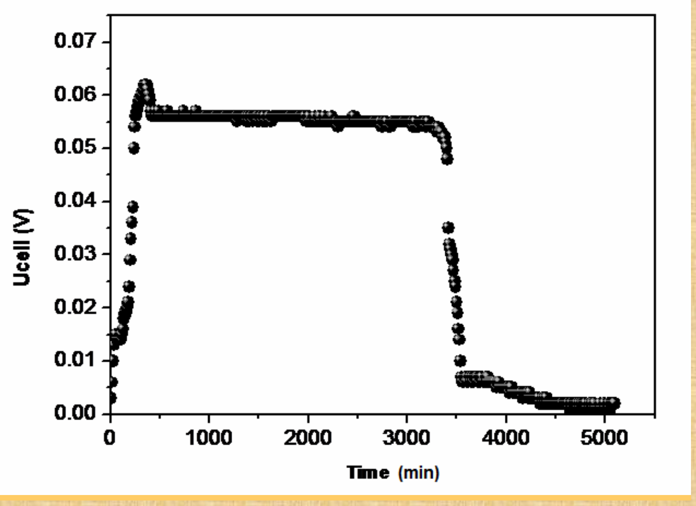
/cm²)

✓C
✓
✓C
✓A
ditions

MFC operation

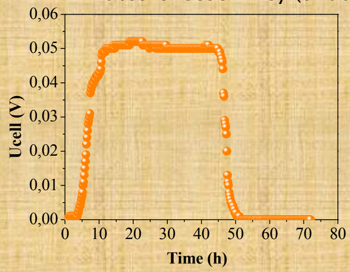
- The anode chamber was operated as a sequencing batch reactor.
- At the end of its cycle the liquid contents were emptied and the anode chamber was replenished with fresh medium

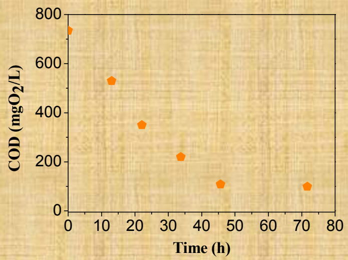
Glucose-fed MFC



Experiments using cheese whey as substrate

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



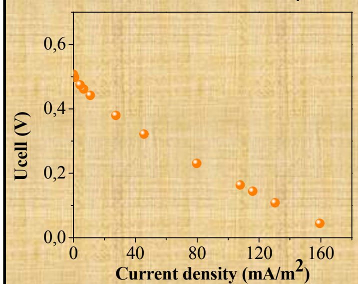


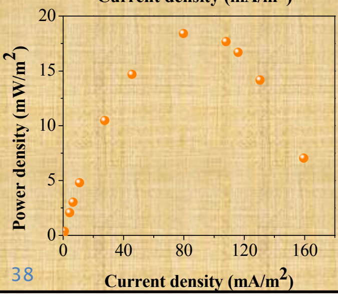
✓ After addition of fresh medium: the MFC voltage increased rapidly, reaching a constant value within only a few hours (approximately 50 mV for an external load of 100 Ω)

✓COD removal was completed within 50 hours, as also indicated by the accompanying rapid decrease in MFC voltage

Experiments using cheese whey as substrate

➢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

Current density: 80 mA/m^2

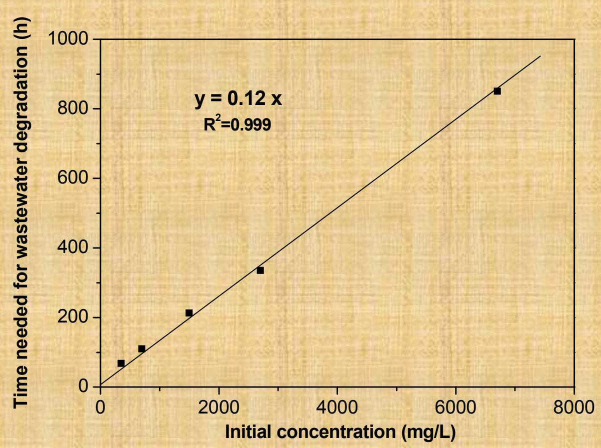
Fuel cell voltage : 0.23 V

18.4 mW/m^2

Experiments with filter sterilised 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



Conclusions

- Continuous fermentative hydrogen production from cheese whey is possible and stable using the indigenous microflora

- At an HRT of 24h, the hydrogen production rate was 7.53L/d while the yield of hydrogen produced was 0.9 ± 0.1 molH_2/mol $_{carbohydrate\ consumed}$. This yield corresponds to the production of 2.5 L H_2/L cheese whey or to an energy yield of 24.85 kJ/L cheese whey.

- pH controlled fermentative hydrogen production from cheese whey at pilot scale gave 4.8 L H_2/L cheese whey

- Further conversion of the acidified effluent of the first stage to methane may be conducted in a high rate bioreactor of PABR type.
The highest methane production rate was75.6 L/d at an HRT of 4.4 d.

Conclusions

- In overall, this work demonstrates that biohydrogen production can be very efficiently coupled with a subsequent step of methane production, and cheese whey can be an ideal feedstock for the proposed gaseous biofuels production process.

- The present study also showed that direct power generation is possible using cheese whey as energy source in a microbial fuel cell, giving a constant voltage as long as the dissolved organic matter lasts.

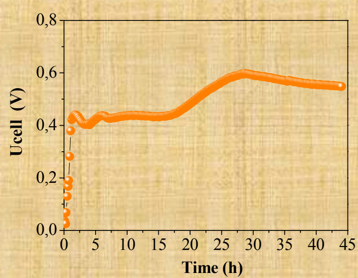
- The obtained maximum power density (normalized to the geometric area of the anodic electrode) was approximately 40 mW/m^2, and the duration was linearly correlated with the initial concentration of dissolved organic matter.

Acknowledgement

We would like to acknowledge support of this work through the programme **ΠΕΠ ΔΕΛ15**, which is funded by General Secretariat for Research and Technology

MFC start -up
Microbial acclimation

- **Glucose** was used as substrate
- **Anaerobic sludge** (10% v/v) was used as inoculum in the anodic chamber solution



✓ 1 h after inoculation: A rapid increase in the open circuit cell potential to 0.45V

✓ After nearly 45h: Stabilization of the open circuit cell potential to 0.55V

✓ After about 300h: The open circuit cell potential dropped to zero accompanied by a glucose exhaustion

In order to achieve enrichment of the anodic electrode with electrochemically active bacteria

✓ fresh nutrient medium contained glucose } Anode chamber in three successive cycles

A stable reproducible operation of the MFC was achieved while anaerobic microorganisms were firmly attached on the anodic electrode