Anodic vs cathodic potentiostatic control of a tubular pilot scale MEC for biogas upgrading

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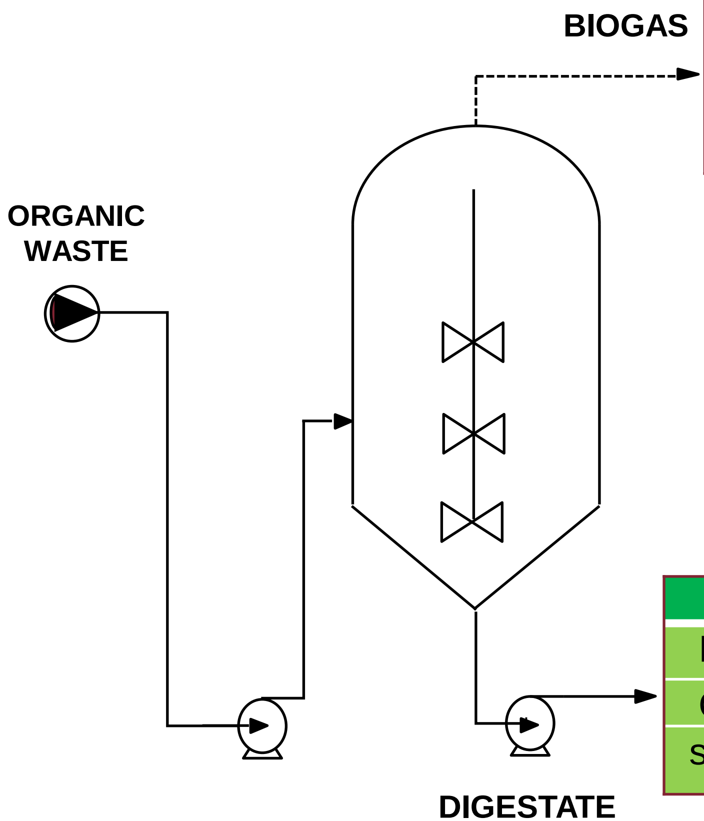
Anaerobic digestion and biogas



BIOGAS	
CH_4	50 - 75%
CO_2	25 - 45%
H_2	1 - 10%
N_2	0,5 - 3%

COGENERATION
Heat & Power
(40% electricity)

UPGRADING

BIOMETHANE
(CH_4 >95%)

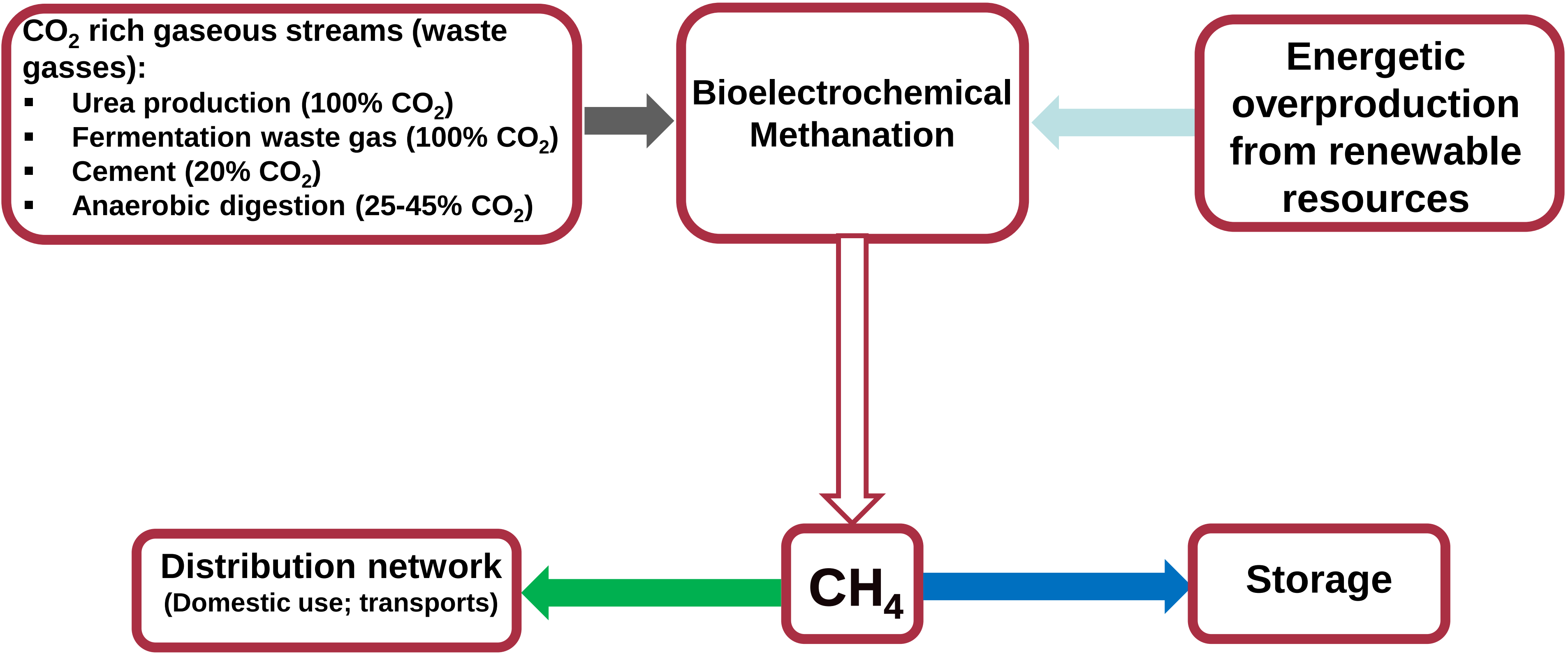
- **Physical Adsorption**
- **Chemical Adsorption**
- **Membrane technologies (among which bioelectrochemical systems)**

DIGESTATE	
NH_4^+	1 - 4 g/L
COD	4 – 10 g/L
sCOD	1 – 2 g/L

Wastewater treatment

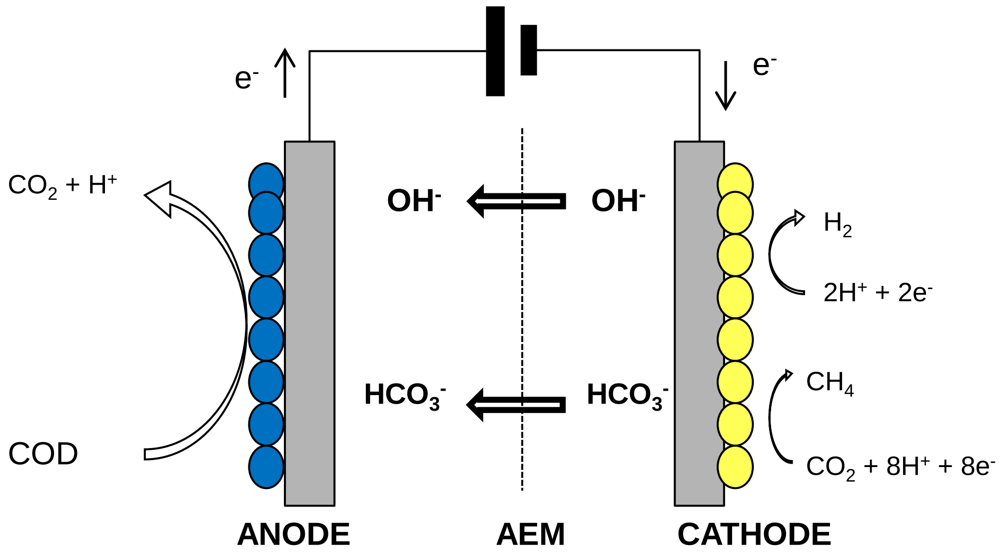
Fertilizer

POWER-TO-GAS for bioelectrochemical systems (BEP2G)



F. Geppert, D. Liu, M. van Eerten-Jansen, E. Weidner, C. Buisman, A. ter Heijne. Trends in biotechnology 34 (2016) 879-894.

Microbial electrolysis cell (MEC) for CO_2 removal



BIOANODE

$$C_xH_yO_z + (2x-z)H_2O \rightarrow xCO_2 + [y+(2x-z)]\ H^+ + e^-$$

Oxidation COD

BIOCATHODE

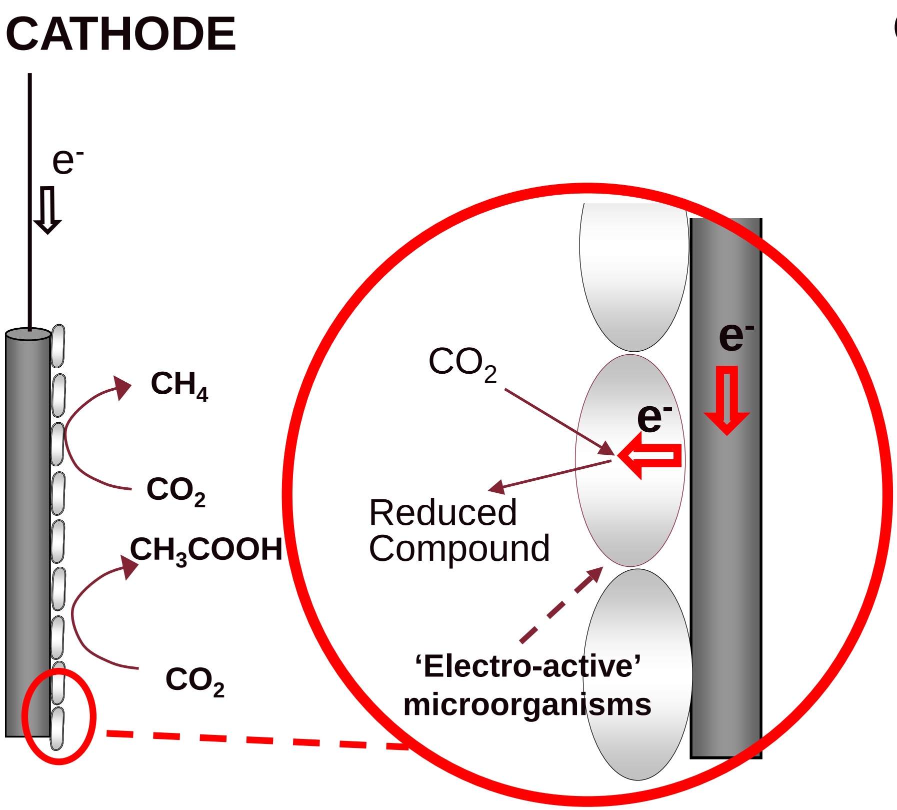
$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$$

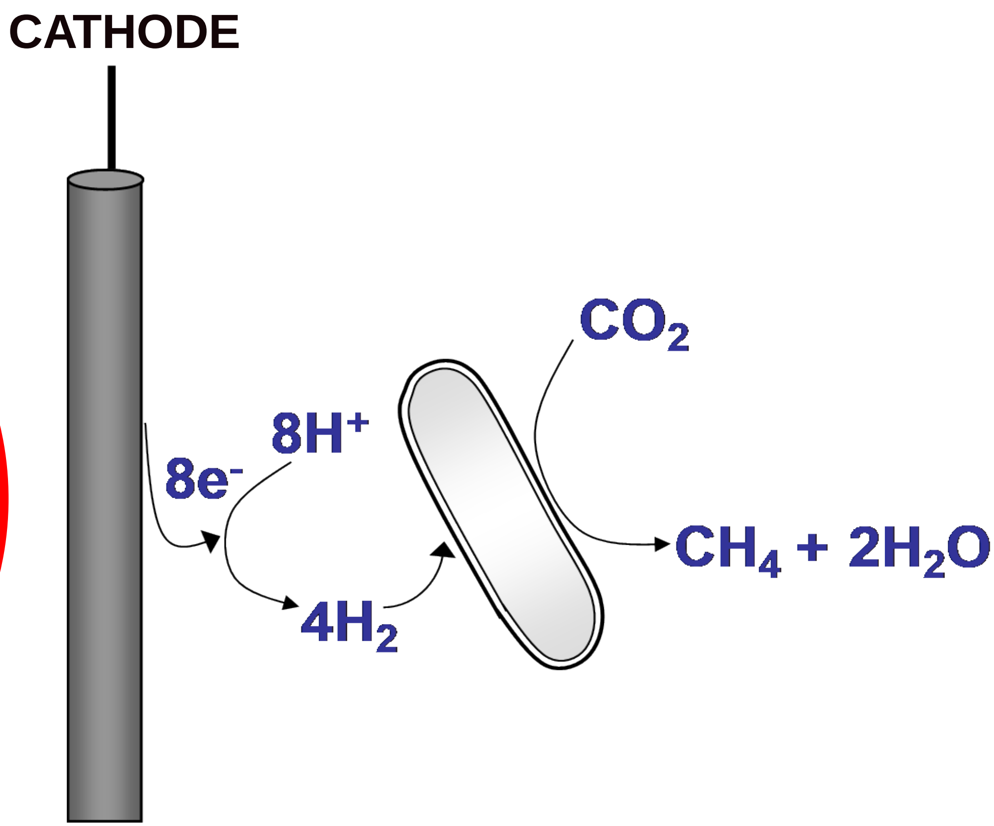
Electromethanogenesis

- **A Microbial electrolysis cell (MEC) is a particular application of bioelectrochemical systems (BES) in which an electric potential is applied**
- **Using a MEC is possible to couple the CO_2 reduction to CH_4 with the oxidation of waste COD.**
- **A MEC could be used for upgrading Biogas into Biomethane while the digestate could be used as COD source furnishing electrons to the reaction.**

The bioelectromethanogenesis

- **Direct Extracellular Electron Transfer (EET)**
- **Hydrogen mediated mechanism**





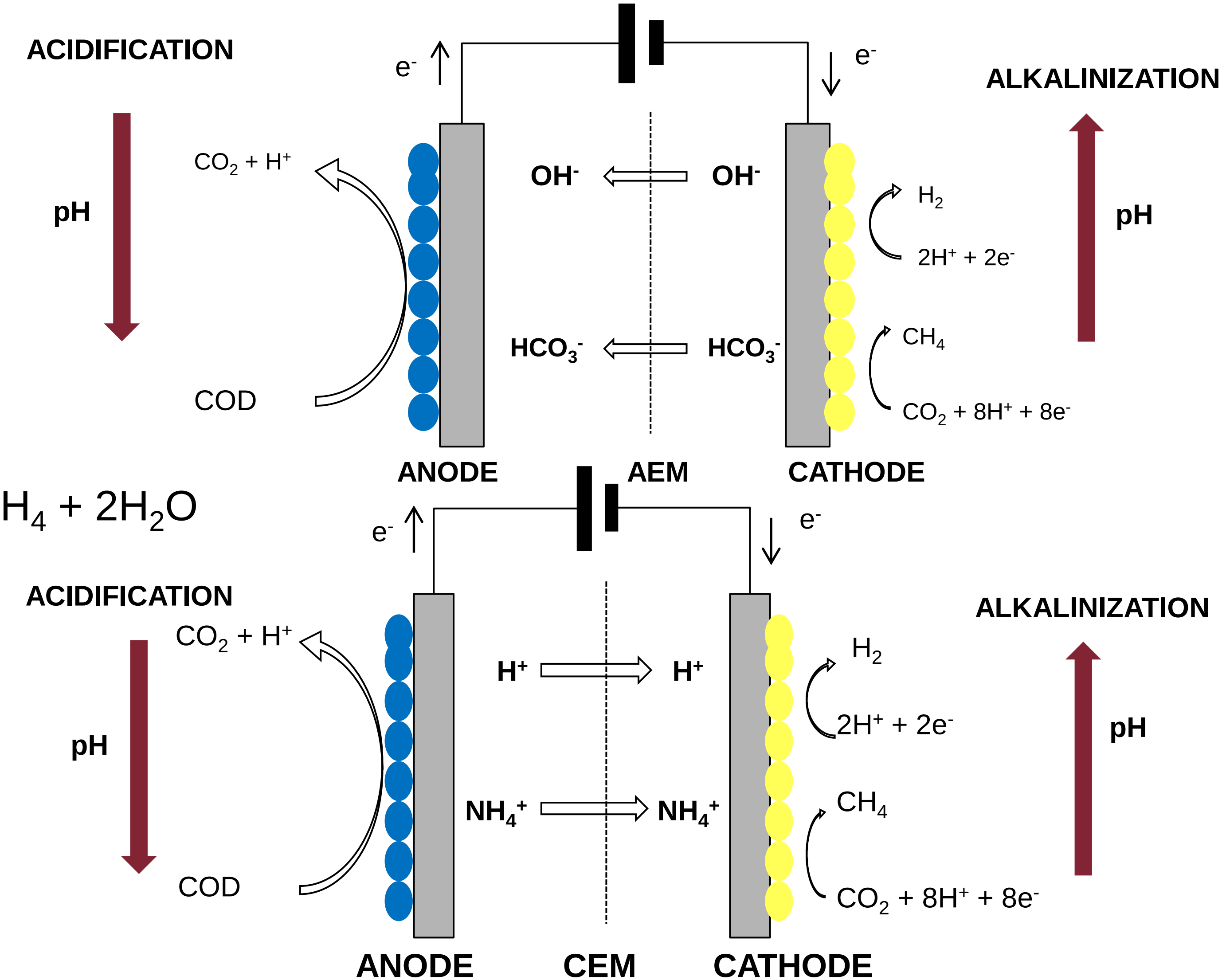
Bioelectromethanogenesis

Hydrogenotrophic methanogenesis

CO_2 removal mechanisms inside a biocathode

- The progress of the reactions generates alkalinity inside the cathodic chamber favoring the CO_2 sorption

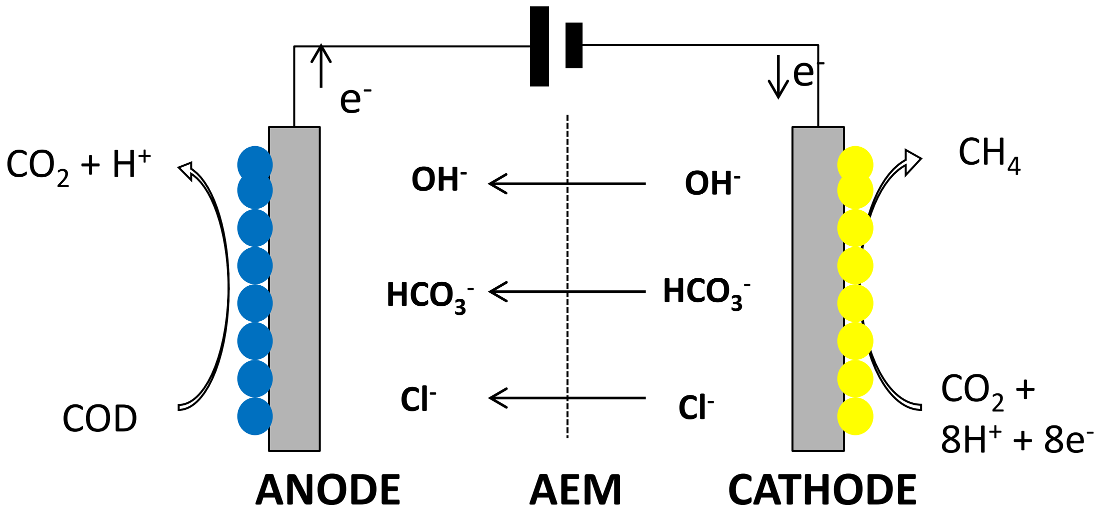
$$CO_2 + 8e^- + 8H^+ \rightarrow CH_4 + 2H_2O$$



CO_2 removal through alkalinity production

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + H_2O$$

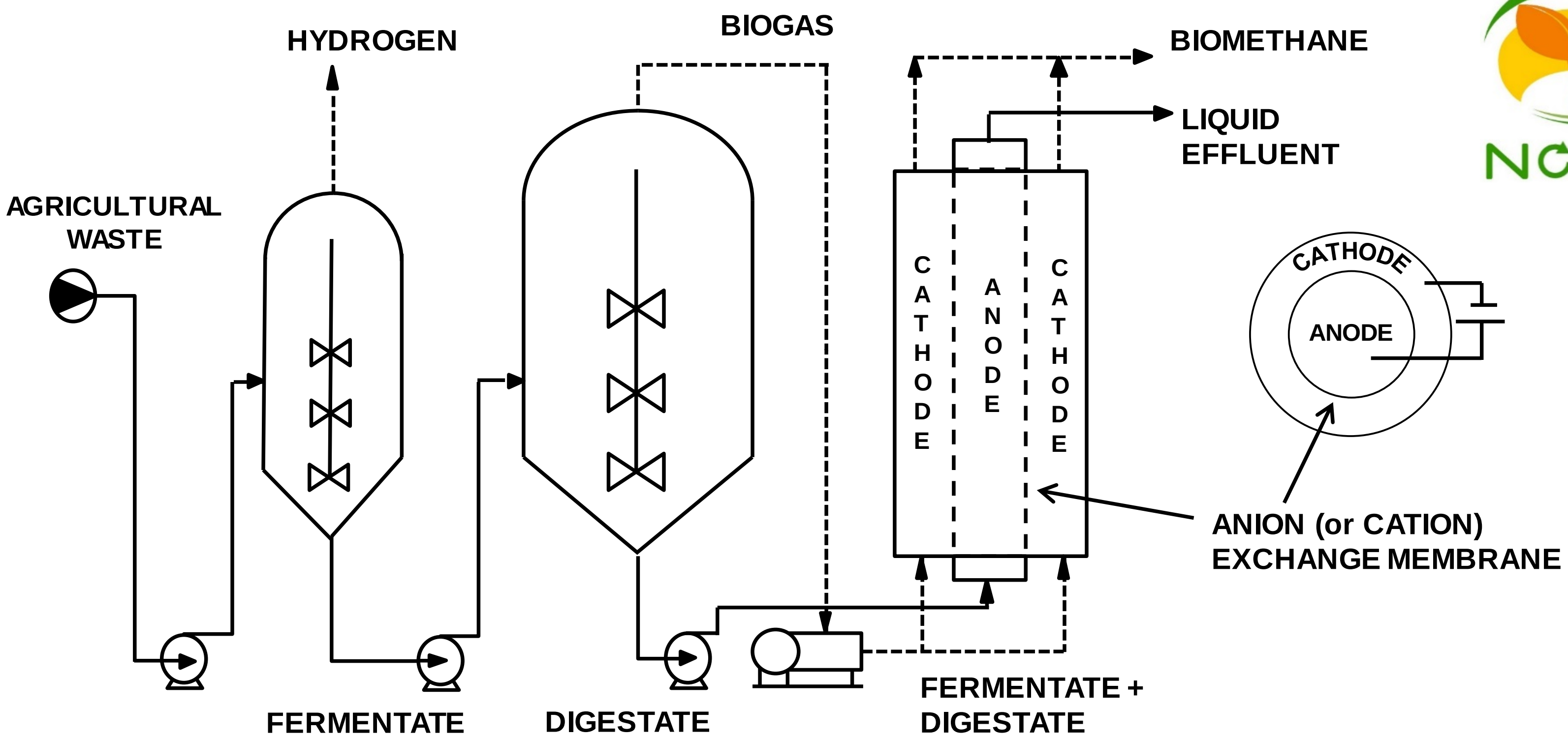
For every mole of produced CH_4, 8 moles of monovalent ions have to be transported through the ion exchange membrane in order to maintain the electroneutrality; for every species transported different from the hydroxyl, an equivalent of alkalinity is generated inside the cathodic chamber



If 8 moles of HCO_3^- are transported for the electroneutrality maintenance

For every produced mole of CH_4, a maximum of 9 moles of CO_2 is removed

Integration of a MEC with a two-stage anaerobic digestor



- One (or more) tubular MEC placed after a two-stage anaerobic digestor
- First scale up of this type of MEC

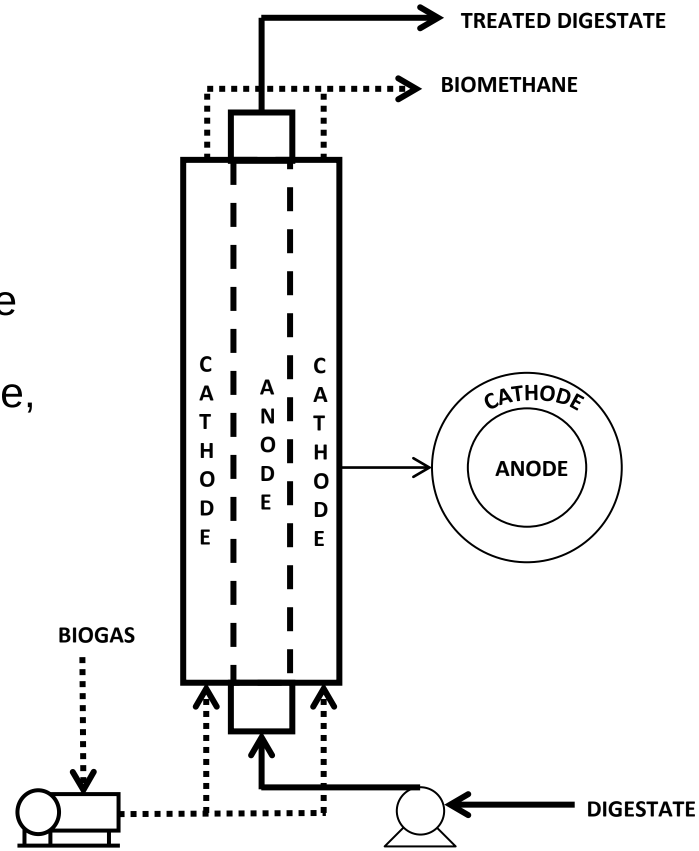
Experimental apparatus: Tubular microbial electrolysis cell

- **1.5 m high**
- **12 L total volume**
- **Granular graphite**

Anode
Inoculum activated sludge
Volume: 3.14 L
Fed with mix VFA (Acetate, propionate e butyrate)

AEM membrane

Cathode
Inoculum anaerobic digestate
Volume: 8.83 L
Fed with gaseous mix (30% v/v CO_2)

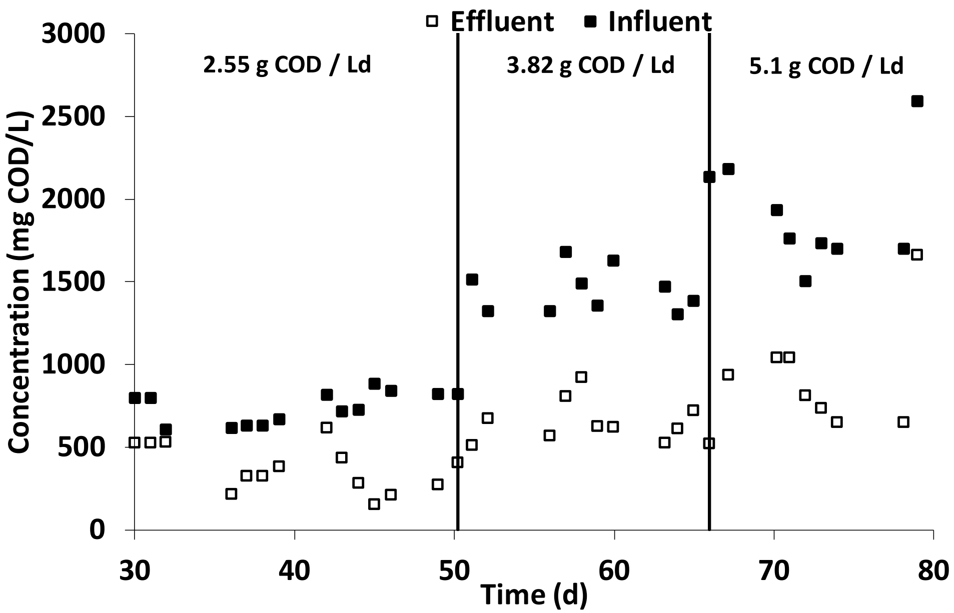


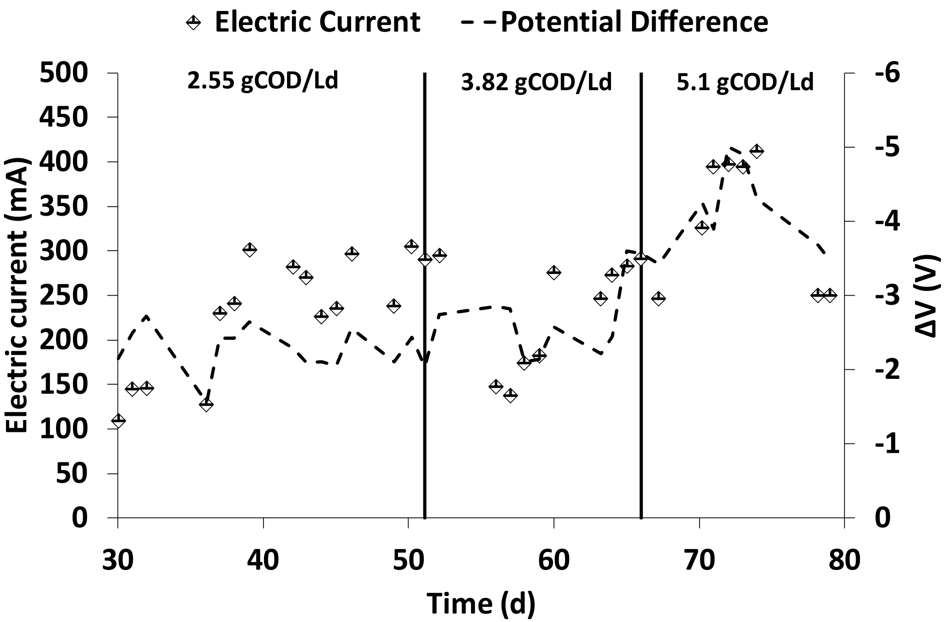
Polarization through three-electrode configuration

- Control of the anodic potential + 0.2 V vs SHE
  Changing the OLR 2.55; 3.82; 5.11 gCOD/Ld
- Control of the cathodic potential -1.3; - 1.8; - 2.3 V vs SHE
  With an OLR of 2.55 gCOD/Ld

NCAW

COD removal and electric current's production



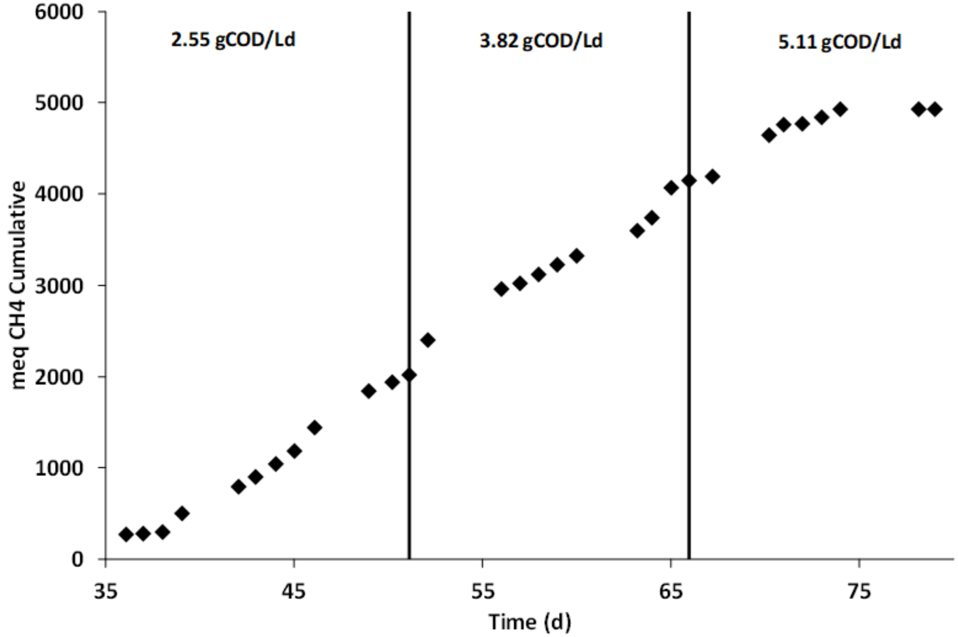


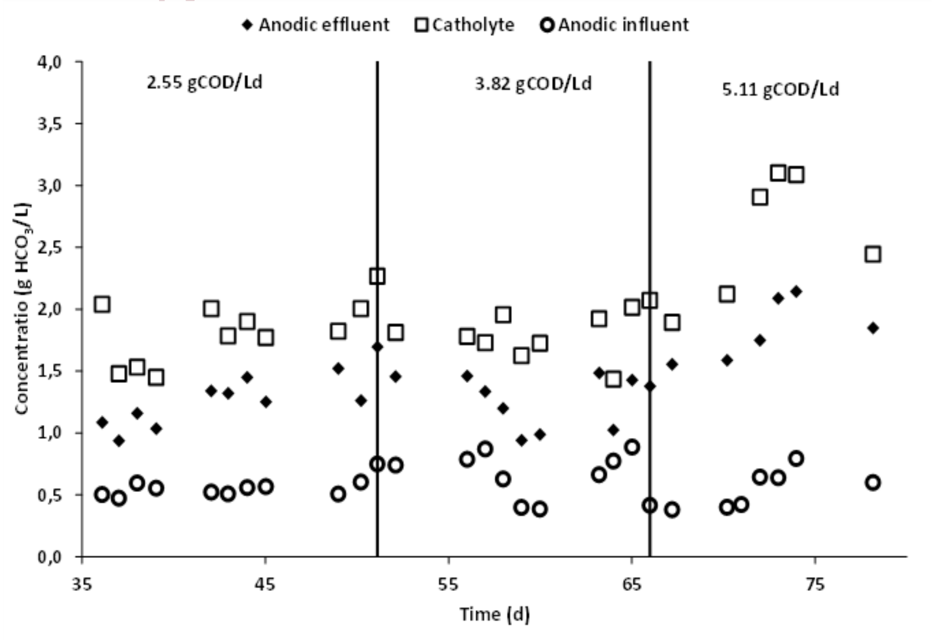
OLR	2.55 gCOD/Ld	3.82 gCOD/Ld	5.1 gCOD/Ld
Average electric current (mA)	235 ± 25	240 ± 17	311 ± 36
Average COD removal (gCOD/Ld)	0.94 ± 0.11	1.94 ±0.15	2.61 ± 0.34
CE %	54 ± 3	32 ± 2	44 ± 5

- The electric current increased with the increase of the OLR
- The increase of the produced electric current was not as high as the increase of the OLR. For this reason, the CE is lower for higher ORL.

- Probably the reason of the little increase is a kinetic limitation of the biofilm to convert COD into electric current

CO_2 production and CH_4 production



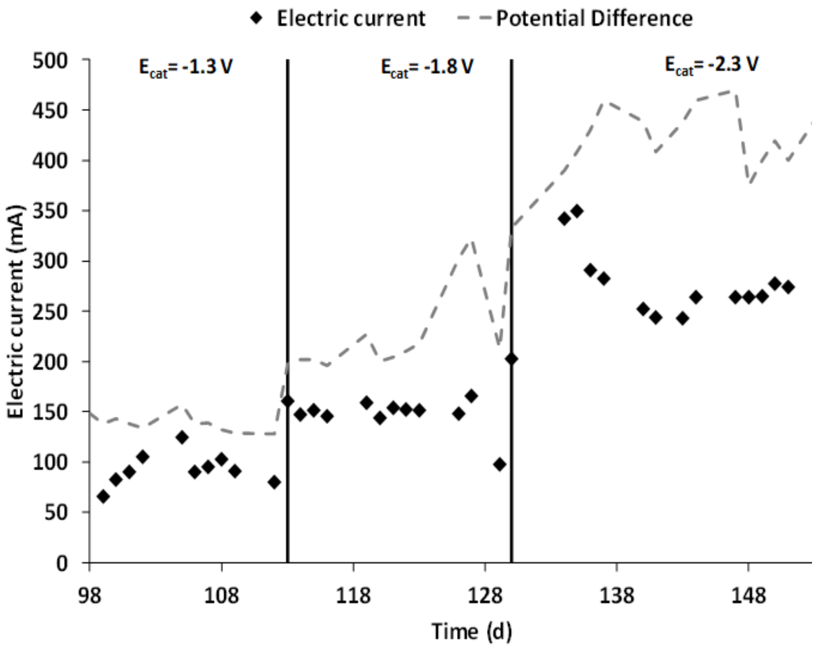


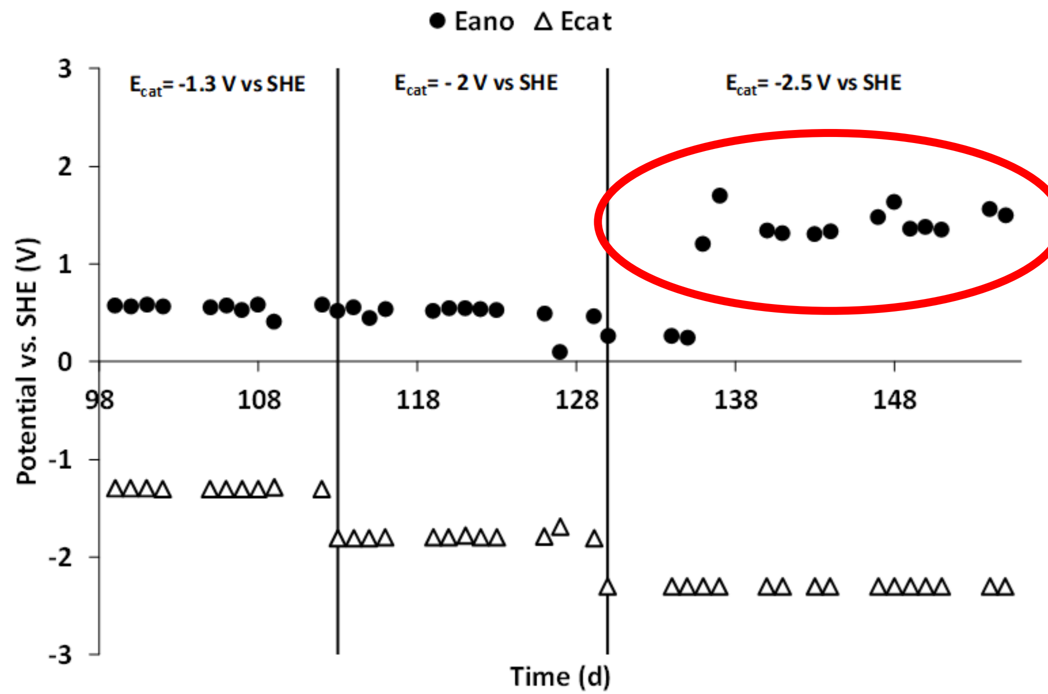
OLR	2.55 gCOD/Ld	3.82 gCOD/Ld	5.1 gCOD/Ld
ΔCO_2 (mmol/d)	243 ± 15	224± 11	270 ± 33
CH_4 production rate (mmol/d)	26 ± 4	27 ± 5	31 ± 4
CCE %	41 ± 1	59 ± 1	25 ± 1

- The CO_2 abatement did not change significantly
- The AEM membrane permits the migration of the anion bicarbonate.

- The CH_4 production did raise with the enhancement of the electric current but not as much as expected. For this reason, the CCE is significantly lower for the last period

Potential control switch





E_{cat} vs. SHE	- 1.3 V	- 1.8 V	- 2.3 V
Average electric current (mA)	91 ± 5	148 ± 5	277 ± 8
ΔCO_2 (mmol/d)	276 ± 16	215 ±13	199 ± 12
CH_4 production rate (mmol/d)	12 ± 1	32 ± 2	15 ± 1

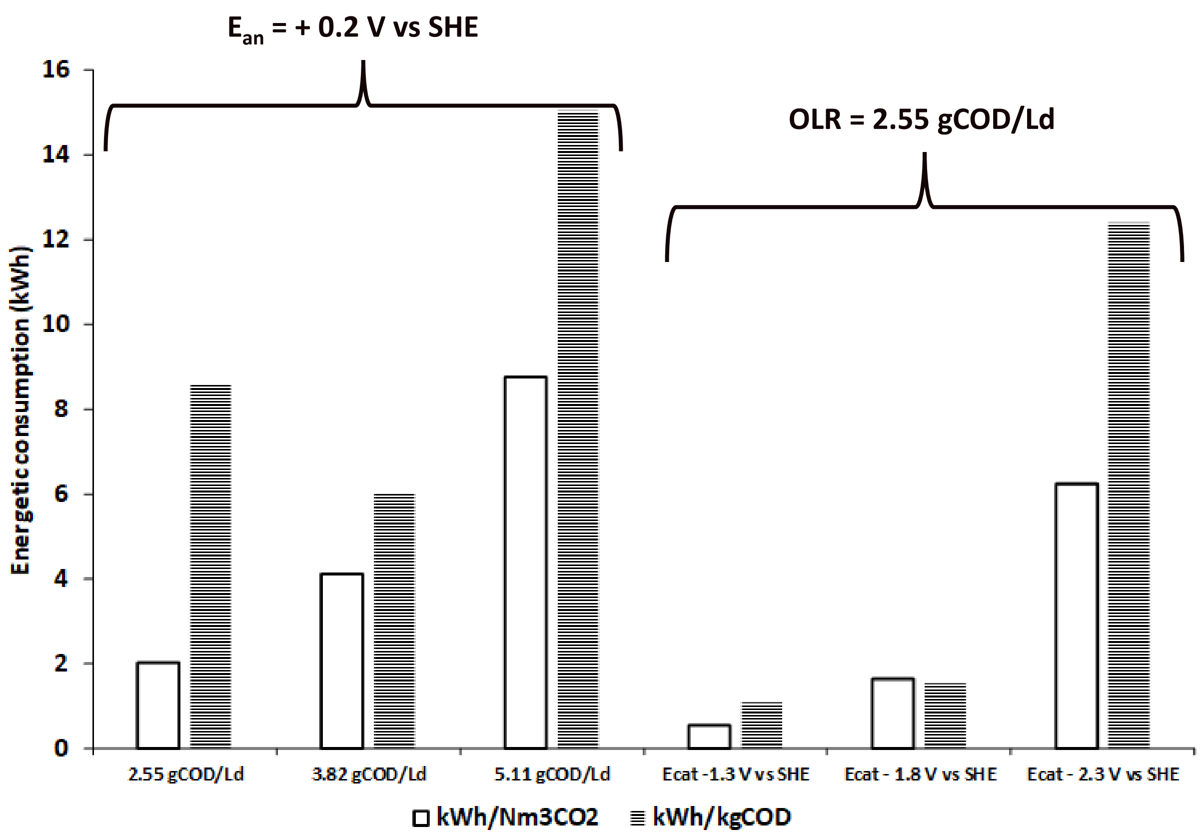
E_{an} = + 1.46 ± 0.05 V vs. SHE

Increase of the anodic potential to sustain the cathodic reaction

↓

water oxidation

Potential control switch



Potentiostatic control	Anodic	Anodic	Anodic	Cathodic	Cathodic	Cathodic
Stream	2.55 gCOD/L d	3.82 gCOD/L d	5.11 gCOD/L d	-1.3 V vs. SHE	-1.8 V vs. SHE	-2.3 V vs. SHE
kWh/kgCOD	10.7	5.6	14.1	1.2	1.4	10.9
kWh/Nm^{3}CO$_2$	2.4	3.3	7.7	0.6	1.7	6.2

Take home message

- The micro pilot scale reactors are a promising first step towards an eco-friendlier biogas upgrading.

- A higher OLR is not the better solution to enhance the current density.

- From a higher electric current production derives a higher CH_4 production rate.

- Controlling the cathodic potential minimizes the overpotential even in a micro pilot reactor.

- Further studies will be conduct using a CEM membrane.

Thank you for the attention !

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