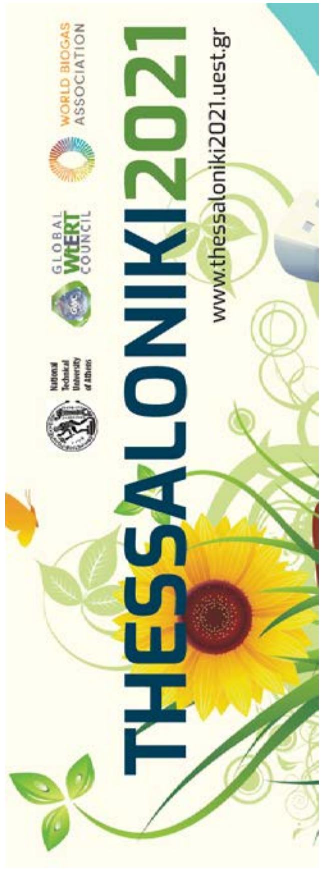
Advances in Anaerobic Biotechnology: A Core Technology for the Production of Carbon-Neutral, Sustainable and Renewable Biofuels and Bioenergy from Waste



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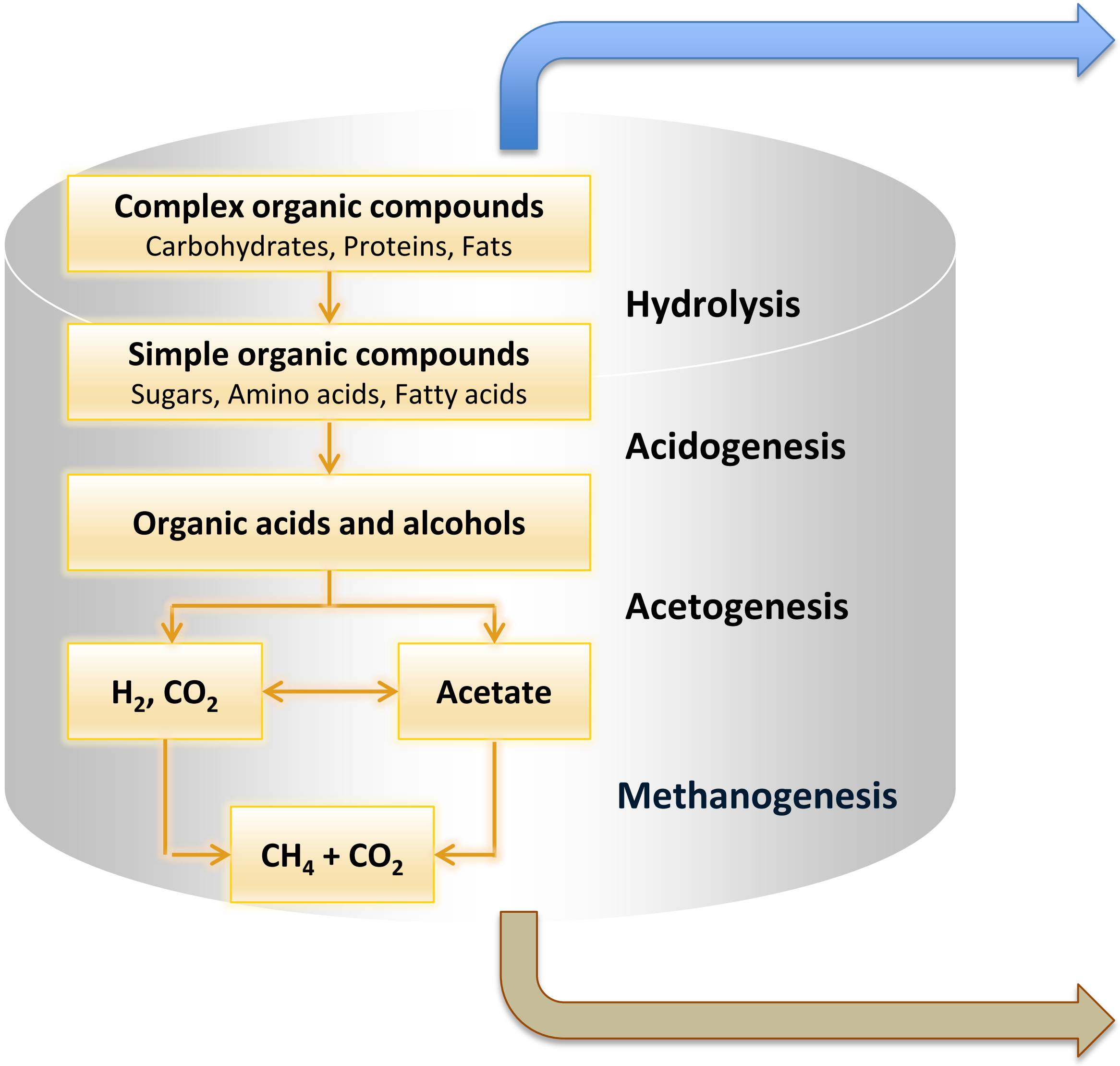
8th International Conference on Sustainable Solid Waste Management
23 – 26 June 2021

Thessaloniki, Greece

Anaerobic Digestion & Biotechnological Extensions

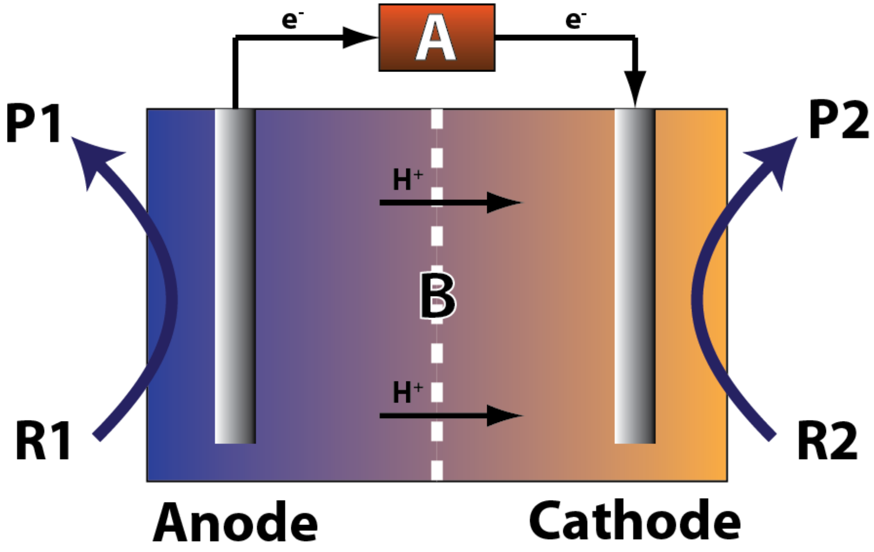


Biogas
(CH_4, CO_2, trace gases)

- **Volatile fatty acids production & C-chain elongation**
- **Hydrogen (H_2) production – "Dark fermentation"**
- **Struvite production (MgNP)**
- **Biochar production**
- **Bioelectrochemically-assisted anaerobic digestion**
- **Hydrogen (H_2) production – Microbial electrolysis cell (MEC)**
- **Biogas upgrade using MEC ($CH_4 \geq 98\%$)**
- **Anaerobic membrane bioreactor**

Liquid digestate,
Biosolids

Bioelectrochemical Systems (BES)



A	Resistor (MFC) or applied potential (MEC)
B	Proton exchange membrane
R1	Anode reactant (oxidation half reaction)
P1	Anode product
R2	Cathode reactant (reduction half reaction)
P2	Cathode product

Microbial Fuel Cell (MFC)
Produces electrical current

Microbial Electrolysis Cell (MEC)
Produces hydrogen (H_2)

Microbial Electromethanogenesis
Produces methane (CH_4)

Microbial Electrosynthesis (MES)
Produces 2+ carbon compounds (e.g., acetate, methanol, etc.)

$2H^+ + 2e^- \rightarrow H_2$
$E_H°' = -0.414$ V

$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$
$E_H°' = -0.244$ V

$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$
$\Delta E°' = 0.170$ V

At 25 °C, 1 atm, pH 7.

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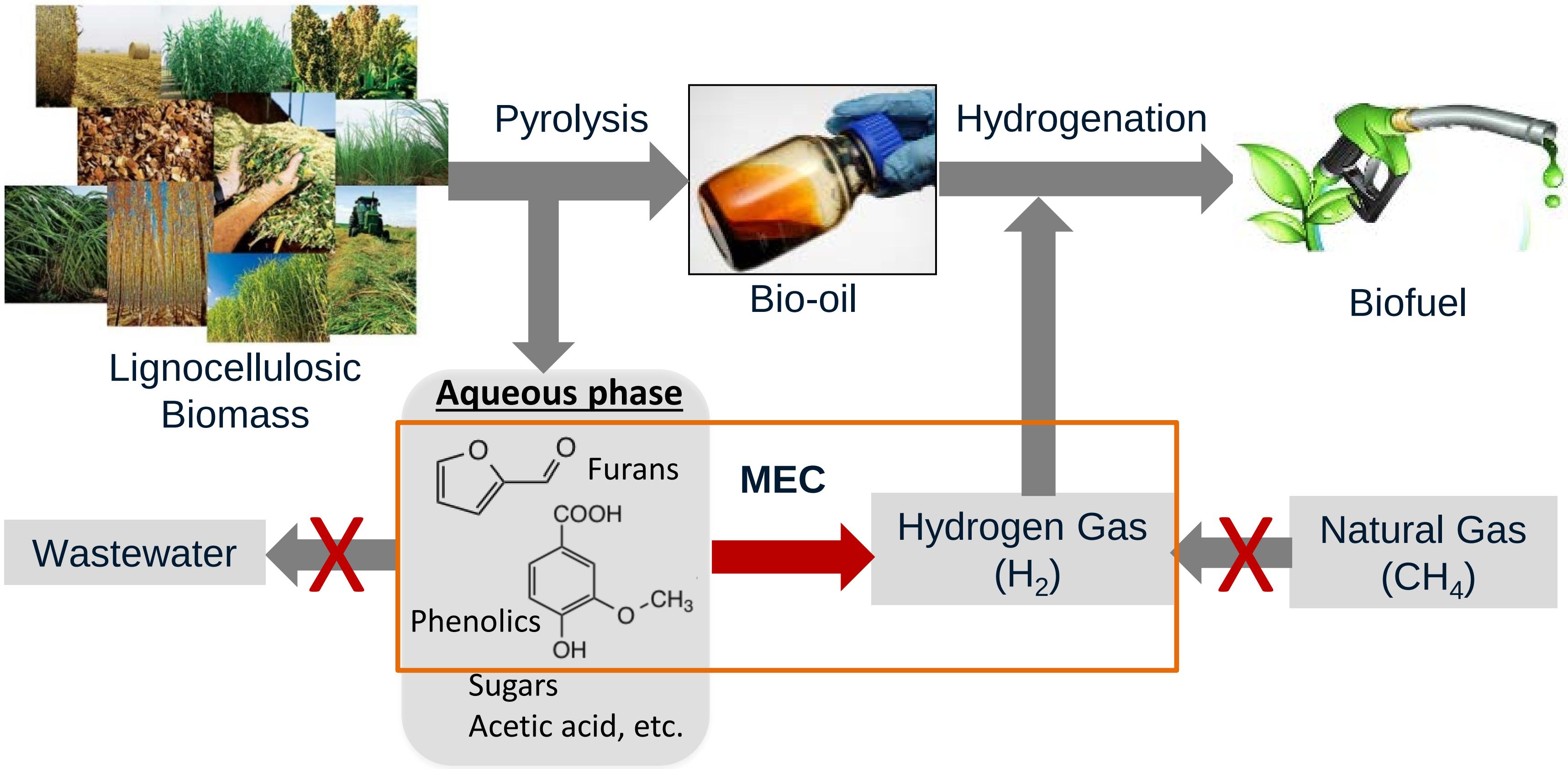
Case I: Biomass-derived Biofuels

Overall Objective

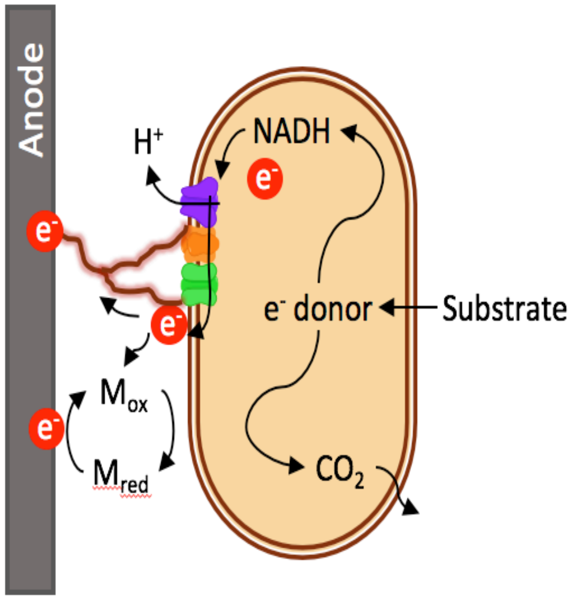
H_2 production through the biotransformation of specific furanic and phenolic compounds using MEC technology



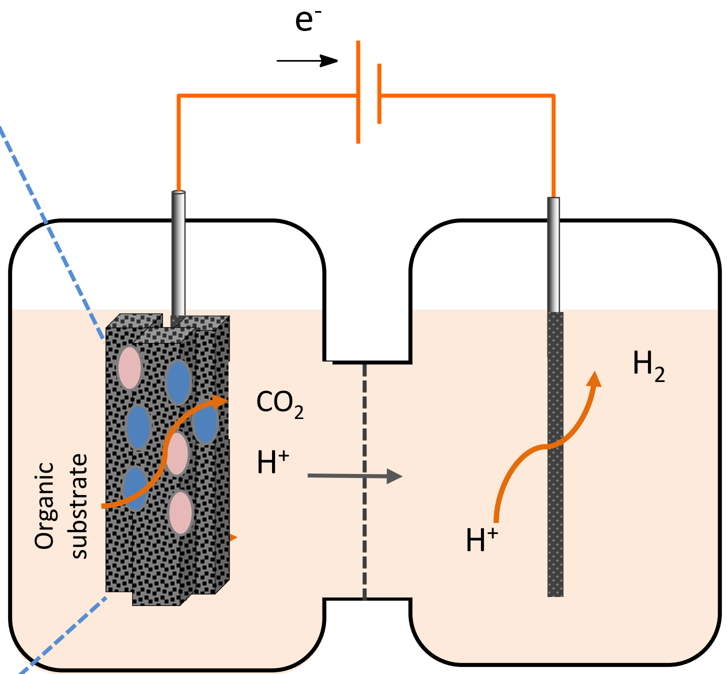
H_2 Production – Microbial Electrolysis Cell (MEC)

- **Acetate**: directly-utilized substrate
- **Fermentable, complex organic compounds**: fermentation required prior to exoelectrogenesis

Exoelectrogenesis by exoelectrogens



Geobacter spp., *Shewanella* spp., *Desulfovibrio desulfuricans*, *etc.*

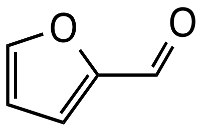


Water Electrolysis (1.7 V or higher)

Microbial Electrolysis (0.5-1.0 V)

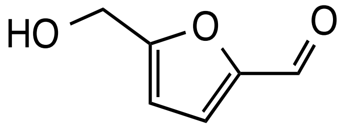
Selected Furanic and Phenolic Compounds

Furanic Compounds



Furfural

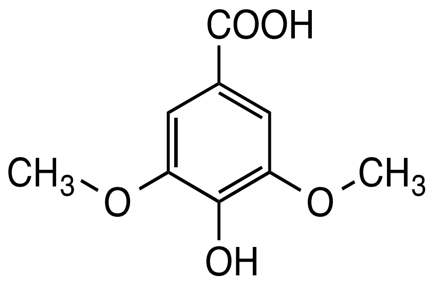
(FF)



5-Hydroxymethylfurfural

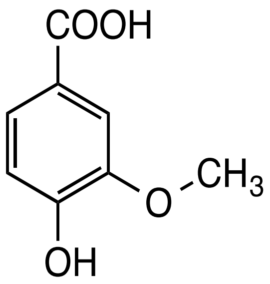
(HMF)

Phenolic Compounds



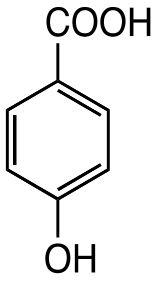
Syringic acid

(SA)



Vanillic acid

(VA)



4-Hydroxybenzoic acid

(HBA)

- Widely found in hydrolysates and pyrolysates
- Inhibitory to ethanol- and H_2-producing microorganisms in dark fermentation
- Direct conversion to hydrogen in dark fermentation has very low yield

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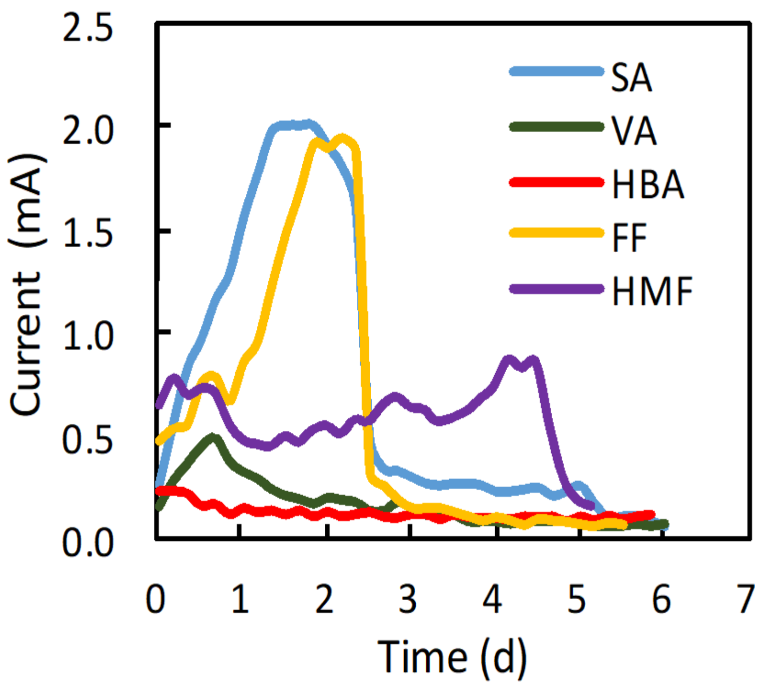
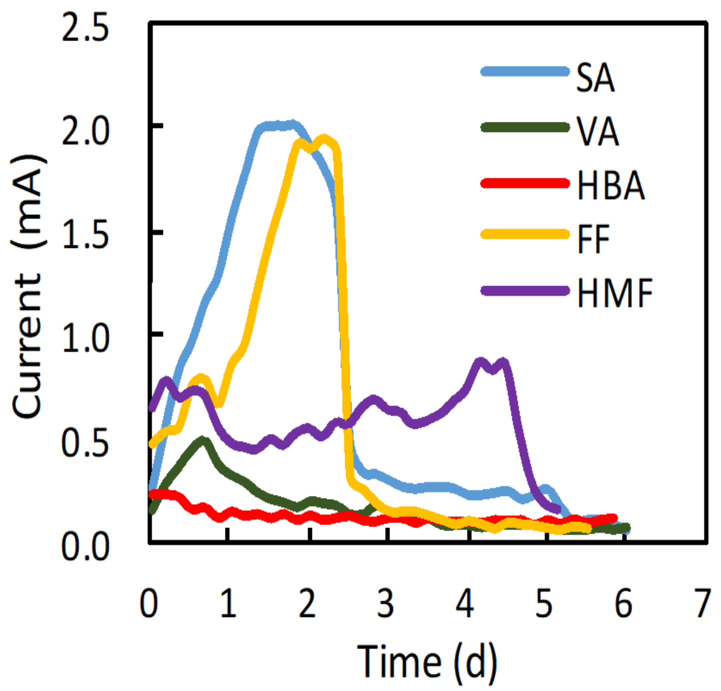
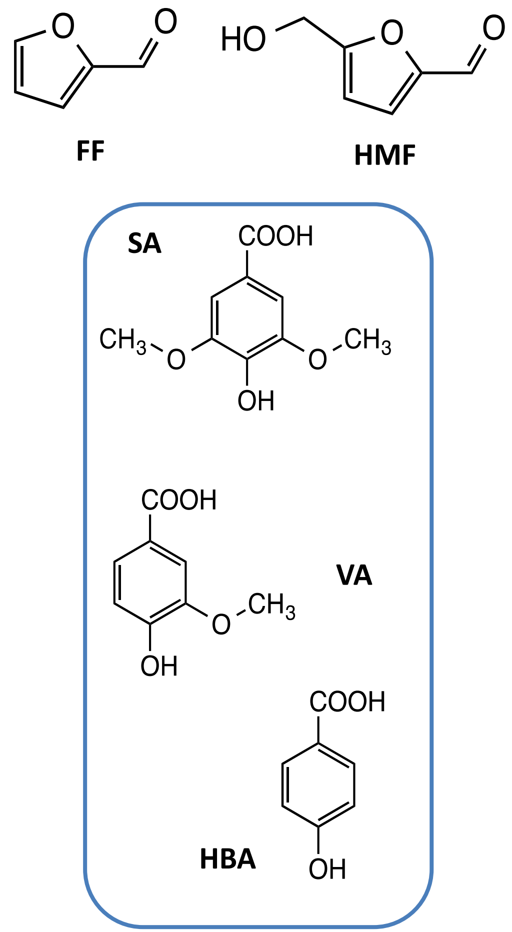
Current and H_2 Production (MEC)



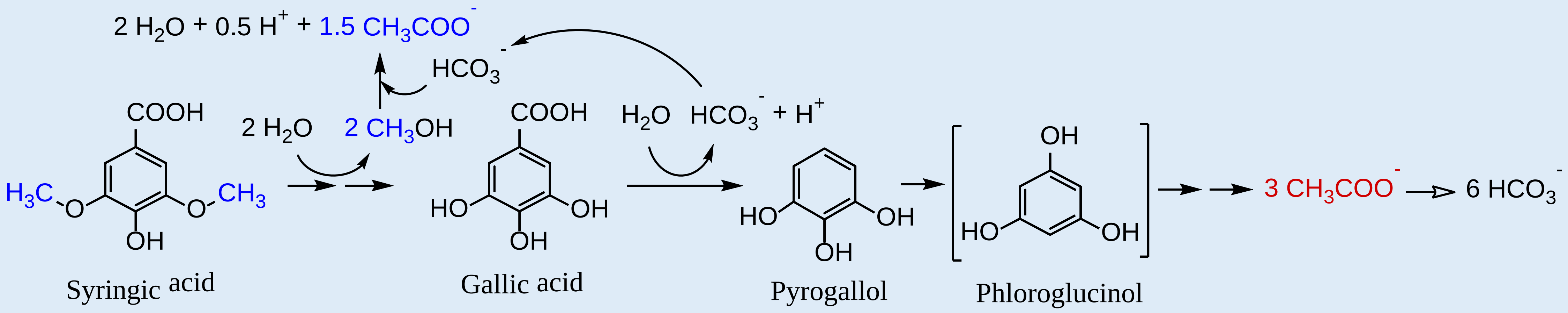


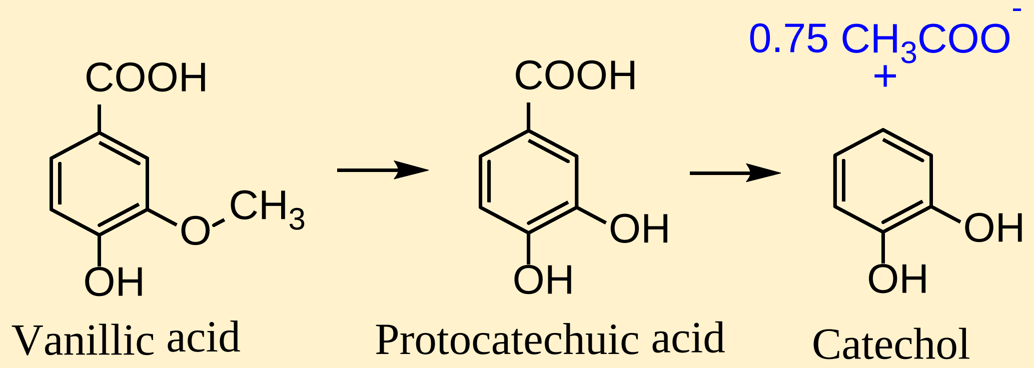


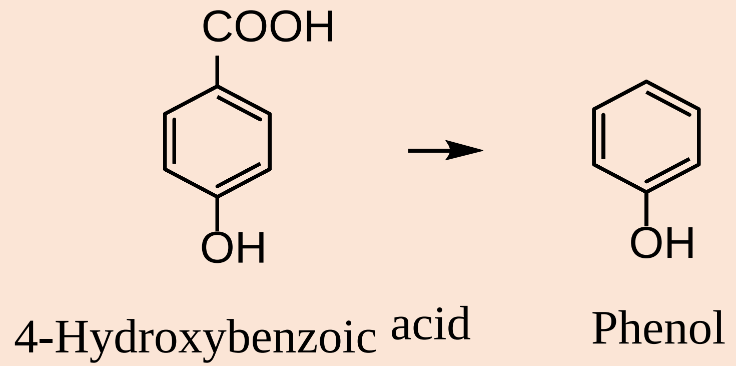
- ✓ The two furanic compounds and SA were productive substrates for H_2 generation
- ✓ VA and HBA biotransformation resulted in low current and H_2

Zeng, Collins, Borole, Pavlostathis, *Water Research*, 2017

Biotransformation Pathways







Zeng, Collins, Borole, Pavlostathis, *Water Research*, 2017

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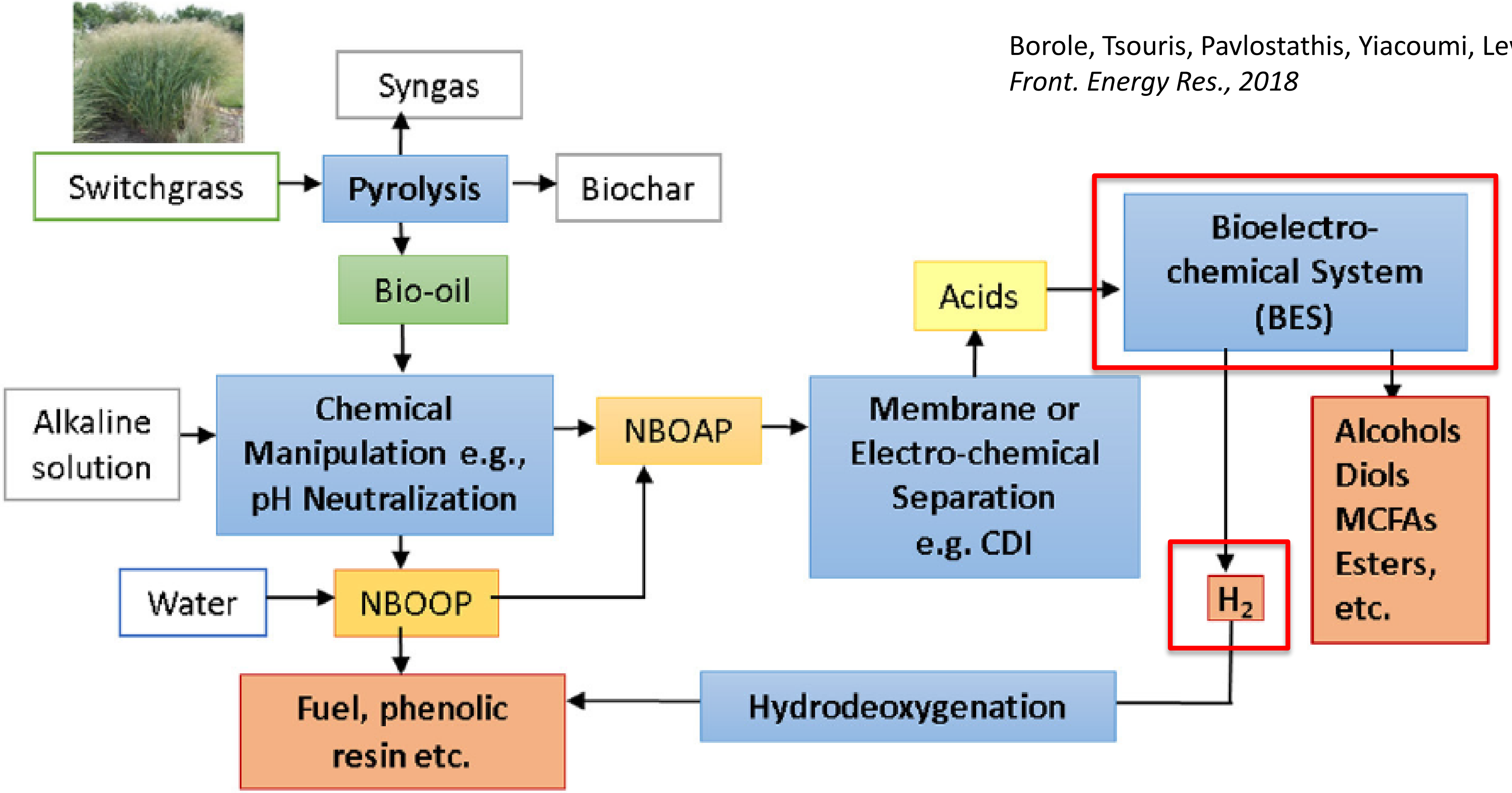
Bioanode Conversion -- MEC vs. Fermentation

Furanic and Phenolic Mixture		Sodium Acetate	MEC/Fermentation Studies
sCOD removal (%) *Extent of biodegradation*	49 - 61	76 - 87	≈ MEC-Domestic WW
Coulombic efficiency (%) *(e^- of cumulative current)/(e^- of COD removed)*	44 - 69	84 - 95	
H_2 yield (%) *(e^- of H_2)/(e^- of COD removed)*	26 - 42	55 - 58	> Dark Fermentation (~ 17%)
Cathode efficiency (%) *(e^- of H_2)/(e^- of cumulative current)*	65 - 85	66 - 88	NA
Max H_2 production rate (L/L-d)	0.09 - 0.13	0.08 - 0.14	< Dark Fermentation ≤ MEC-Domestic WW

Bio-Electro-Refinery

Bio-Electro-Refinery: production of switchgrass bio-oil, chemical manipulation followed by phase separation, and chemical production in a BES using the acid-rich aqueous phase
(NBOOP: neutralized bio-oil organic phase; NBOAP: neutralized bio-oil aqueous phase)

Borole, Tsouris, Pavlostathis, Yiacoumi, Lewis, Zeng, Park
Front. Energy Res., 2018



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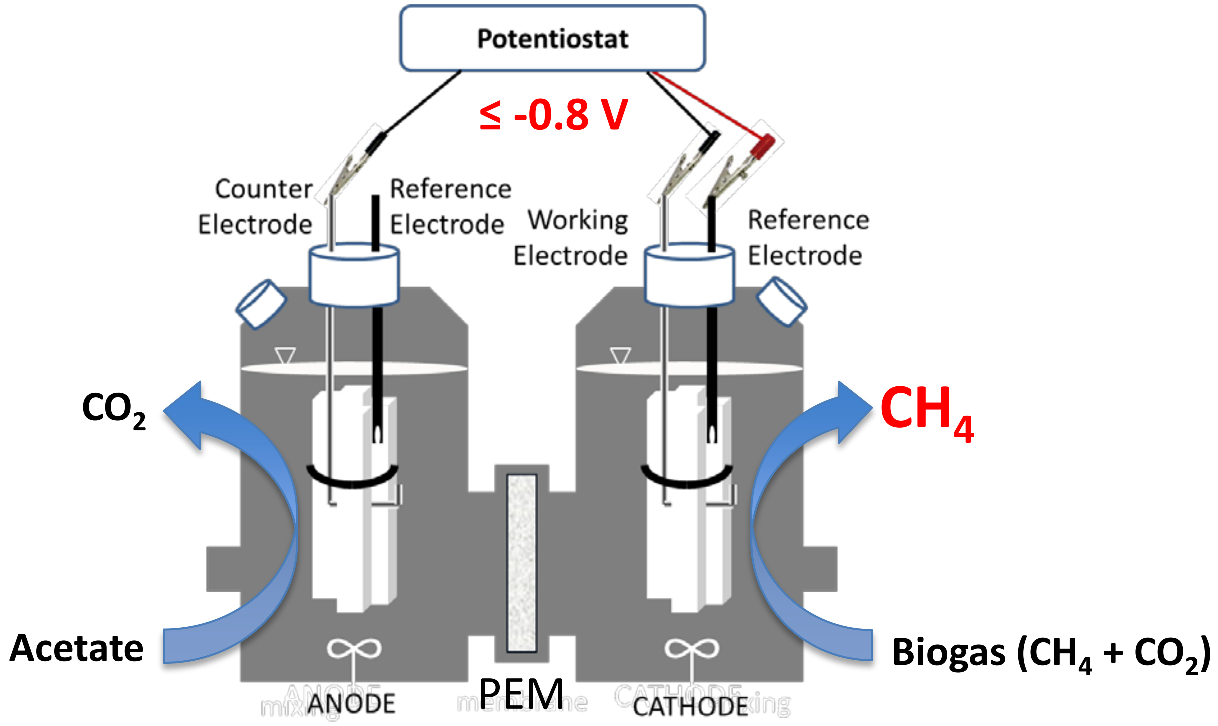
Case II: MEC Biocathode Conversion of Carbon Dioxide (CO_2) to Methane (CH_4)

Overall Objective

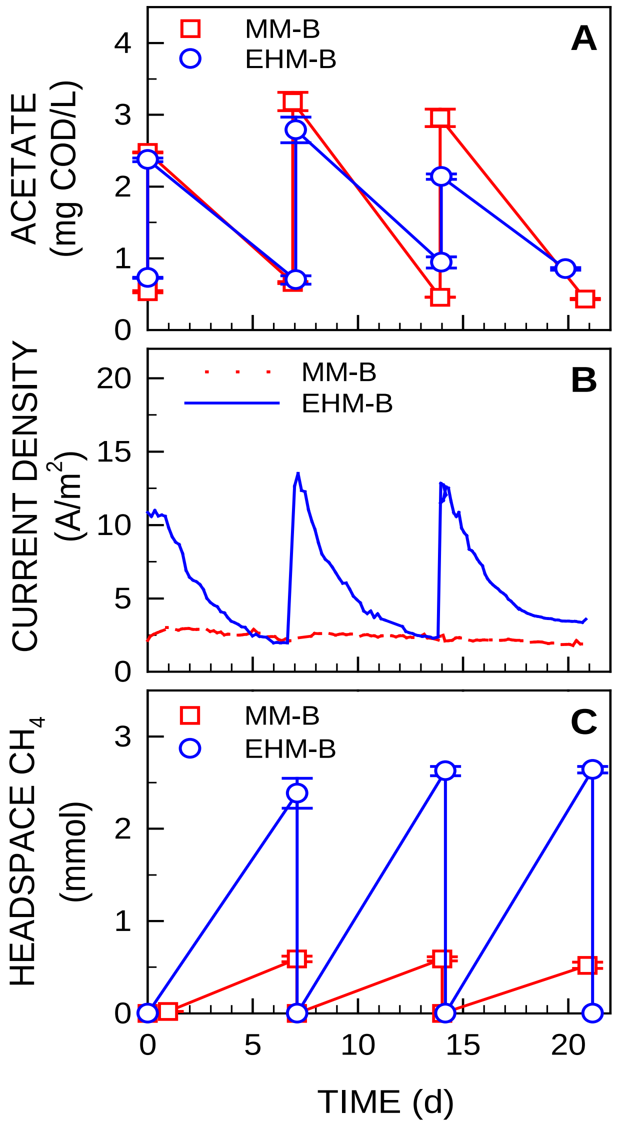
Develop and test a bioelectrochemical system (BES) designed to convert CO_2 to CH_4 for the purpose of increasing the energy content of anaerobic digester biogas (i.e., biogas upgrade)

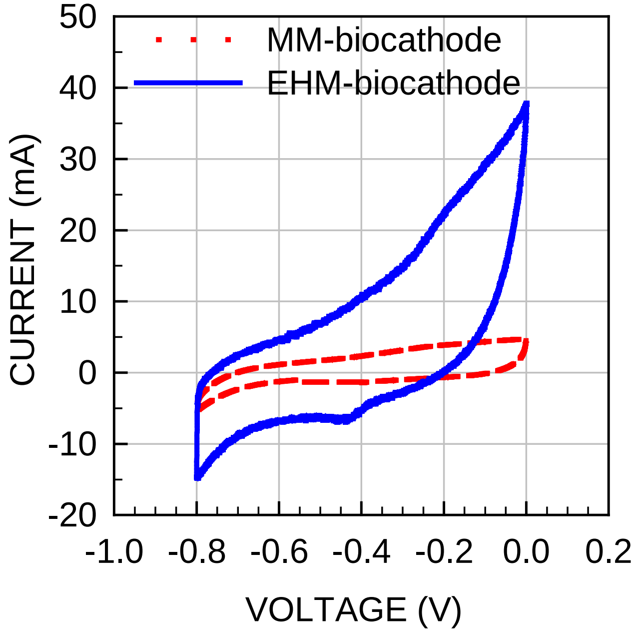


Biocathode Performance – Effect of Inoculum

Biocathode methanogenic inocula: MM, mixed; EHM, pre-enriched hydrogenotrophic

Cathode Headspace 100% CO_2 (v/v)





Biocathode	Final Biofilm Biomass (mg)	Mean CH_4 Production (mmol CH_4/mg biomass-day)
MM-inoculated	0.54 ± 0.07	0.15 ± 0.01
EHM-inoculated	0.64 ± 0.19	0.59 ± 0.03

Dykstra and Pavlostathis, *Environ. Sci. Technol.*, 2017

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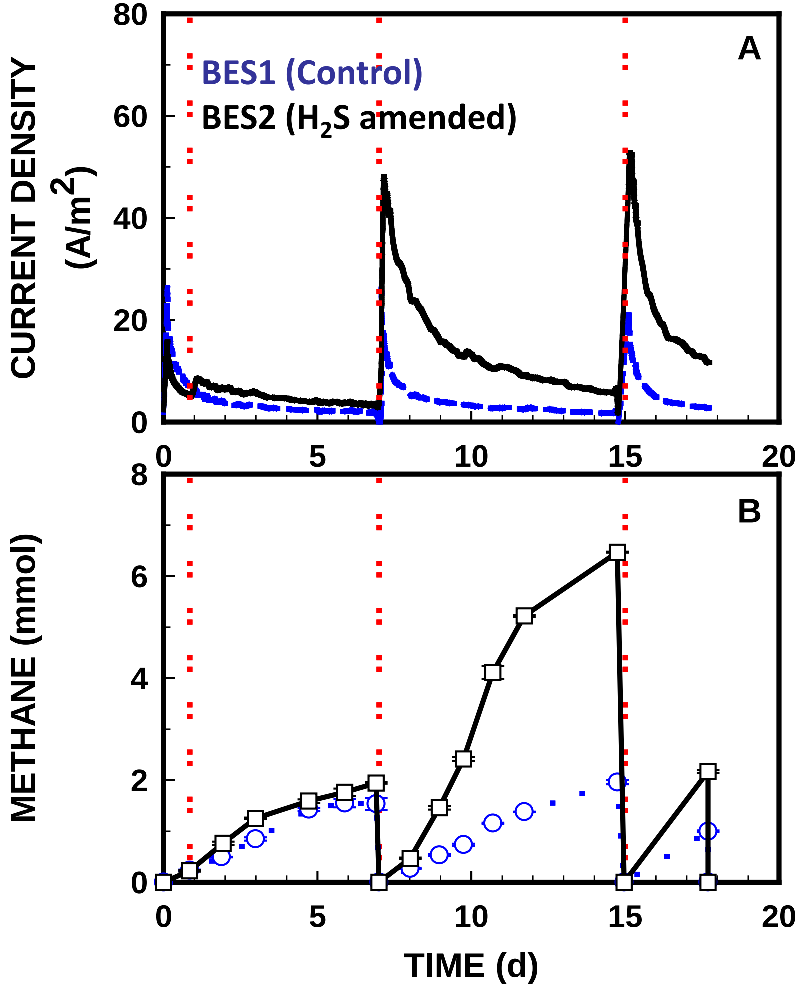
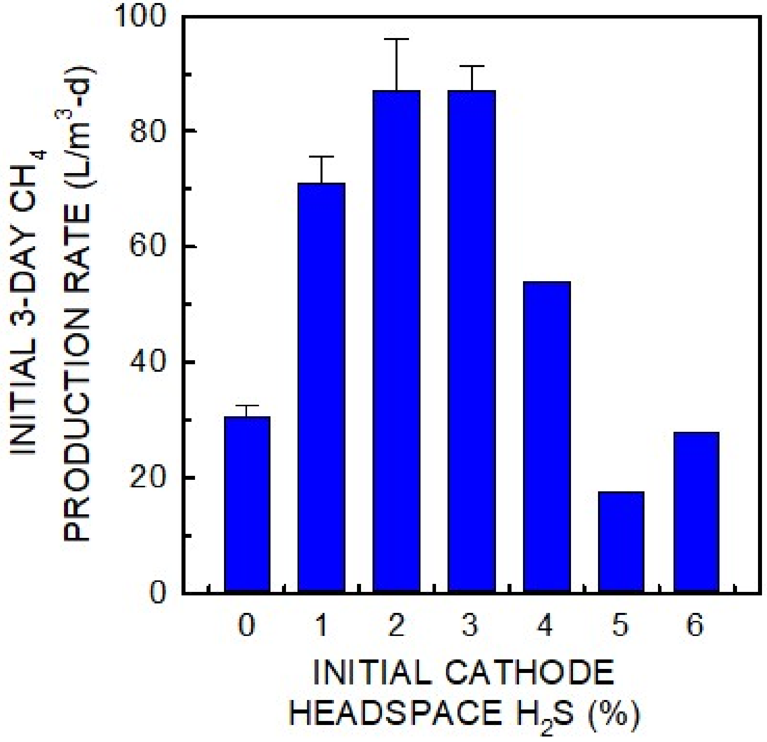
Biocathode Performance – Effect of H_2S

Cathode Headspace H_2S (1% v/v)



Cathode Headspace H_2S (0-6% v/v)



Headspace H_2S (% v/v)	CE (%)	CCE (%)
0	11	100
4	19	99
5	58	13
6	58	15

CE, Coulombic efficiency
CCE, cathode capture efficiency

Two competing effects:

- **Depression of CH_4 production (H_2S ≥4%):** Inhibition of methanogens?
- **Enhancement of CH_4 production (H_2S ≤3%):** What is/are the process(es) involved?

Dykstra and Pavlostathis, *Water Research*, 2021

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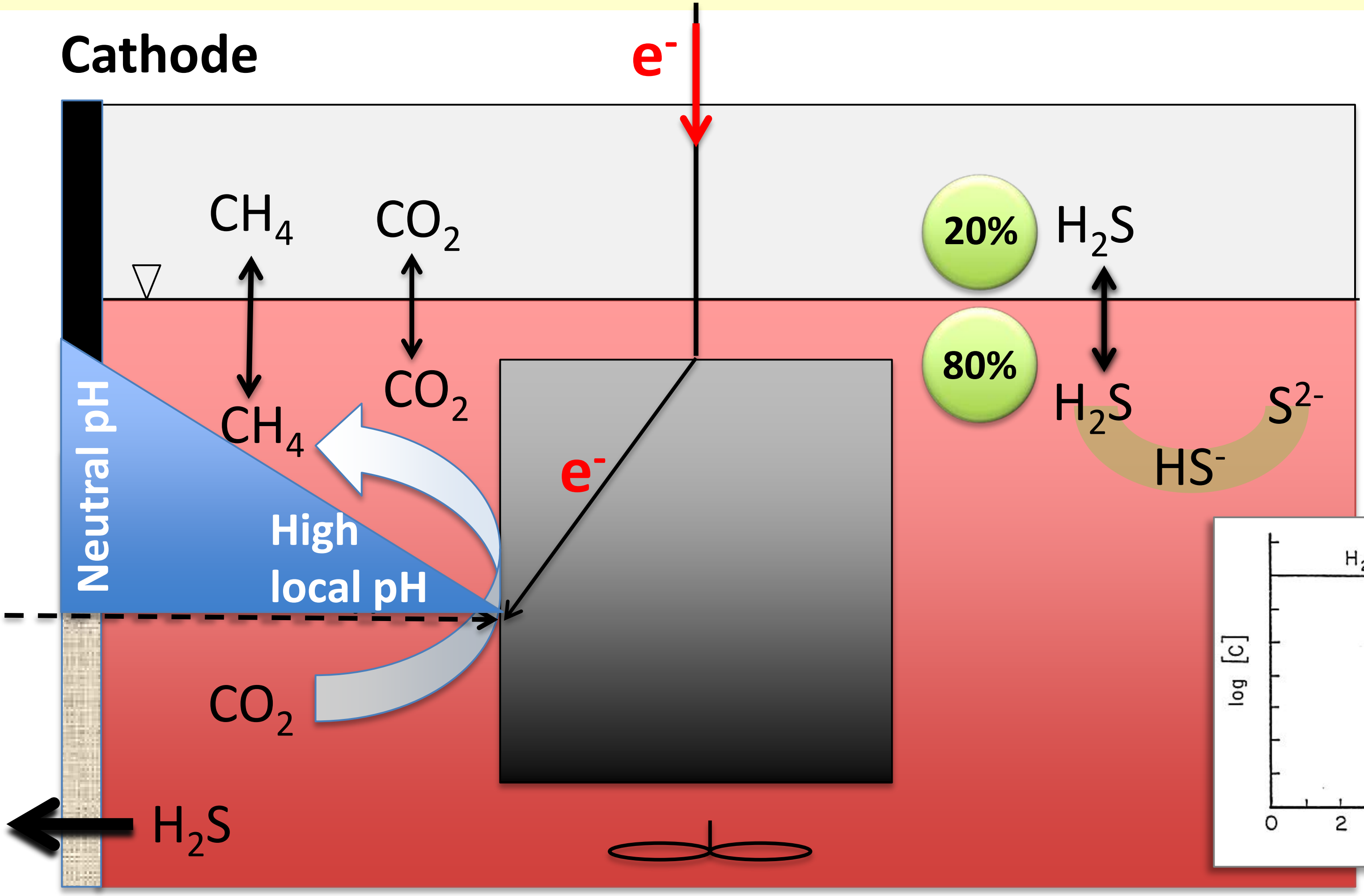
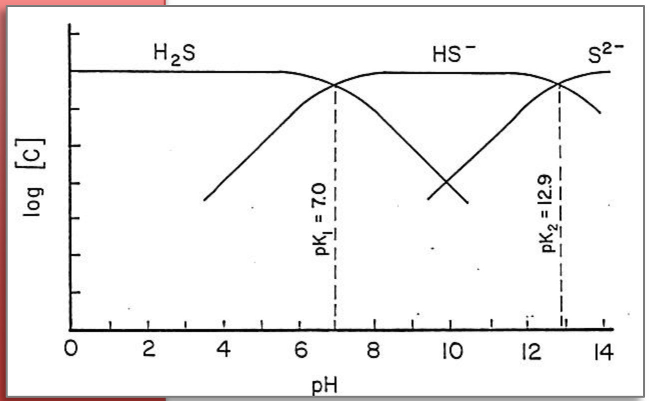
Biocathode Performance – Effect of H_2S



H$_2$S is the most toxic of the sulfide species



The methanogenic biocathode is protected from sulfide inhibition by **biofilm formation** and a **local higher pH** at the cathode electrode surface.

Dykstra and Pavlostathis, *Water Research*, 2021

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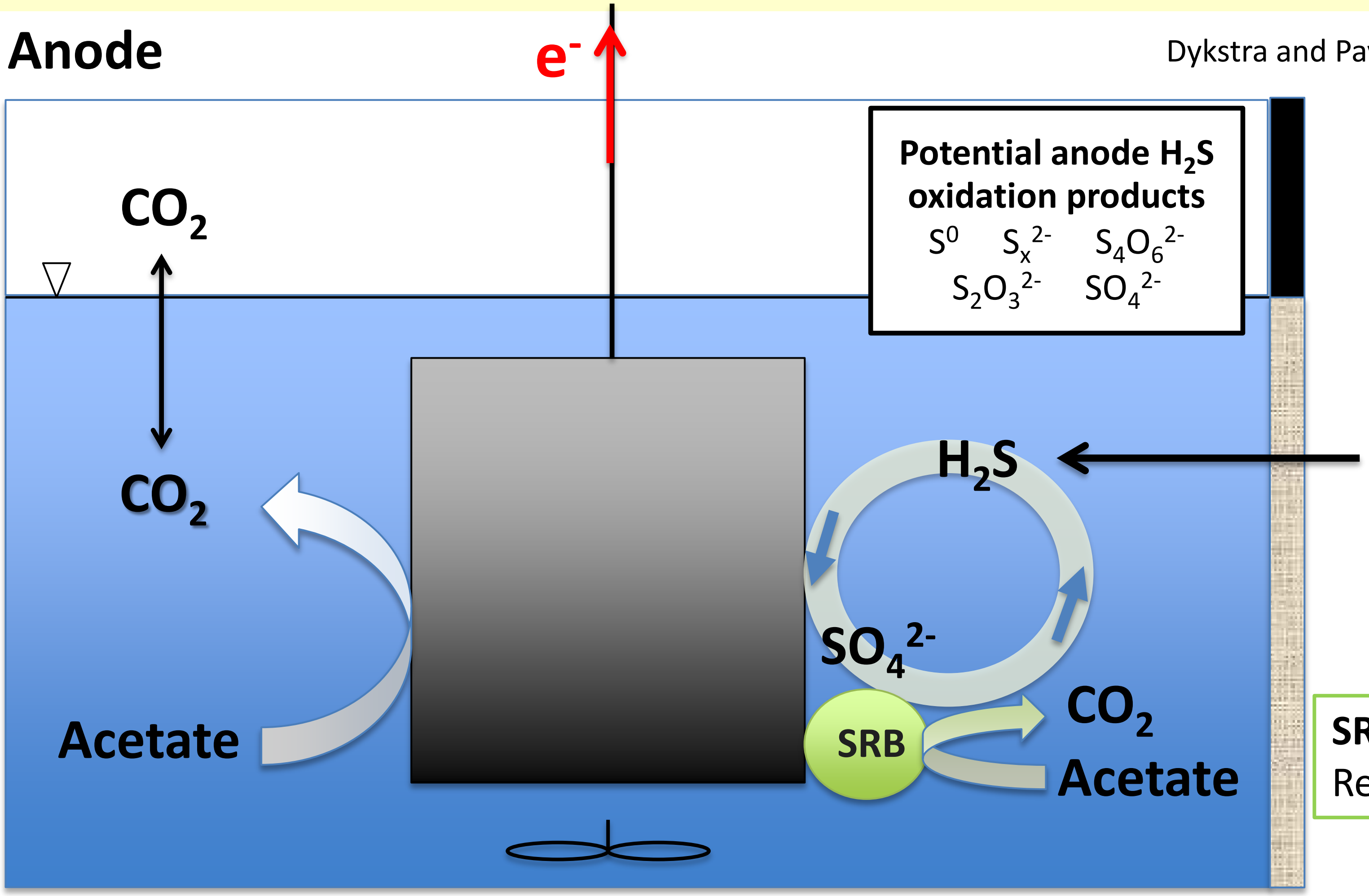
Biocathode Performance – Effect of H_2S

Dykstra and Pavlostathis, *Water Research*, 2021



SRB: Sulfate Reducing Bacteria

- **Low H_2S** → more electrons donated to the anode → higher biocathode CH_4 production
- **High H_2S** → stimulate sulfur cycling → divert acetate electron equivalents from the anode → lower biocathode CH_4 production

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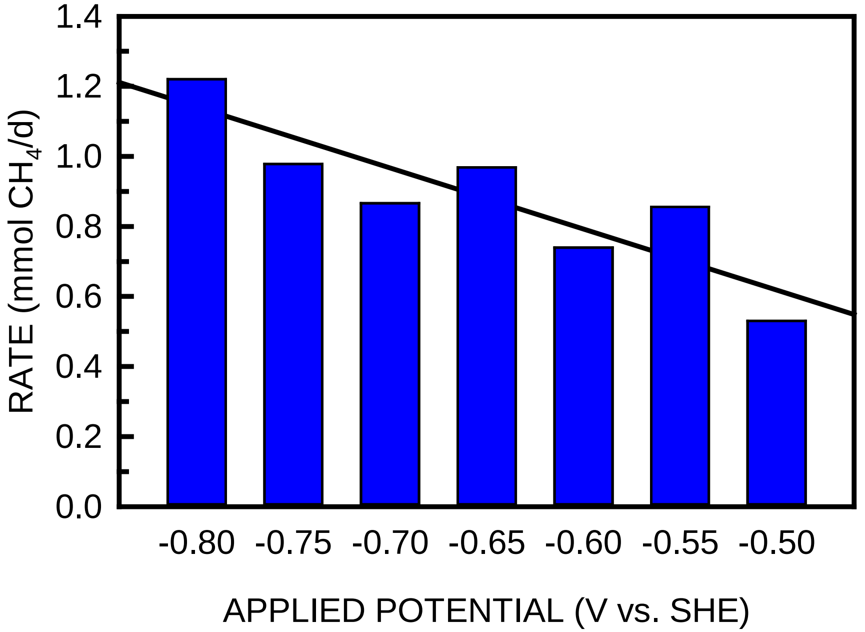
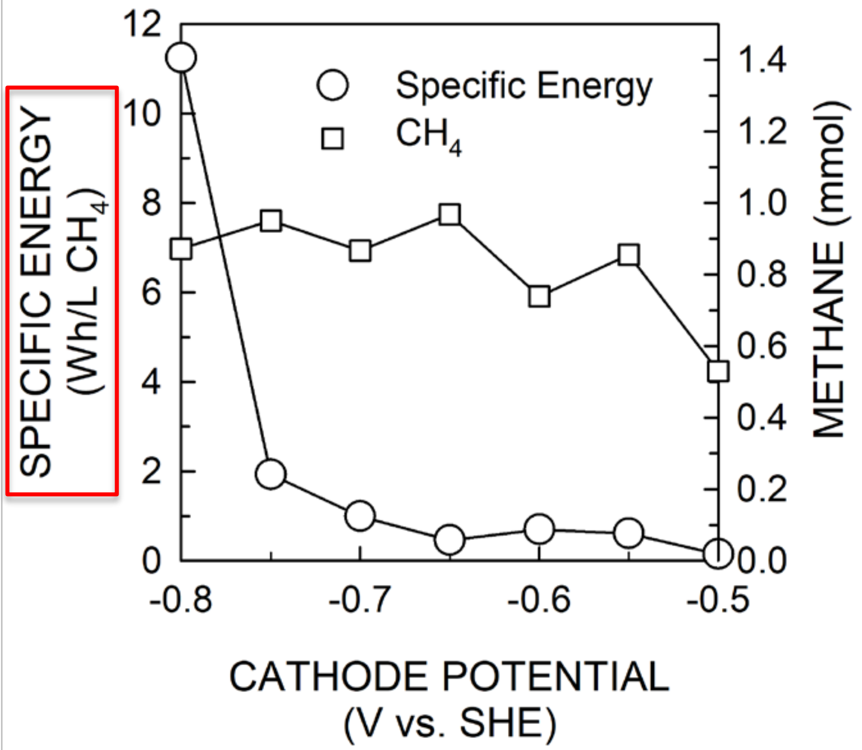
BES Performance – Cathode Potential



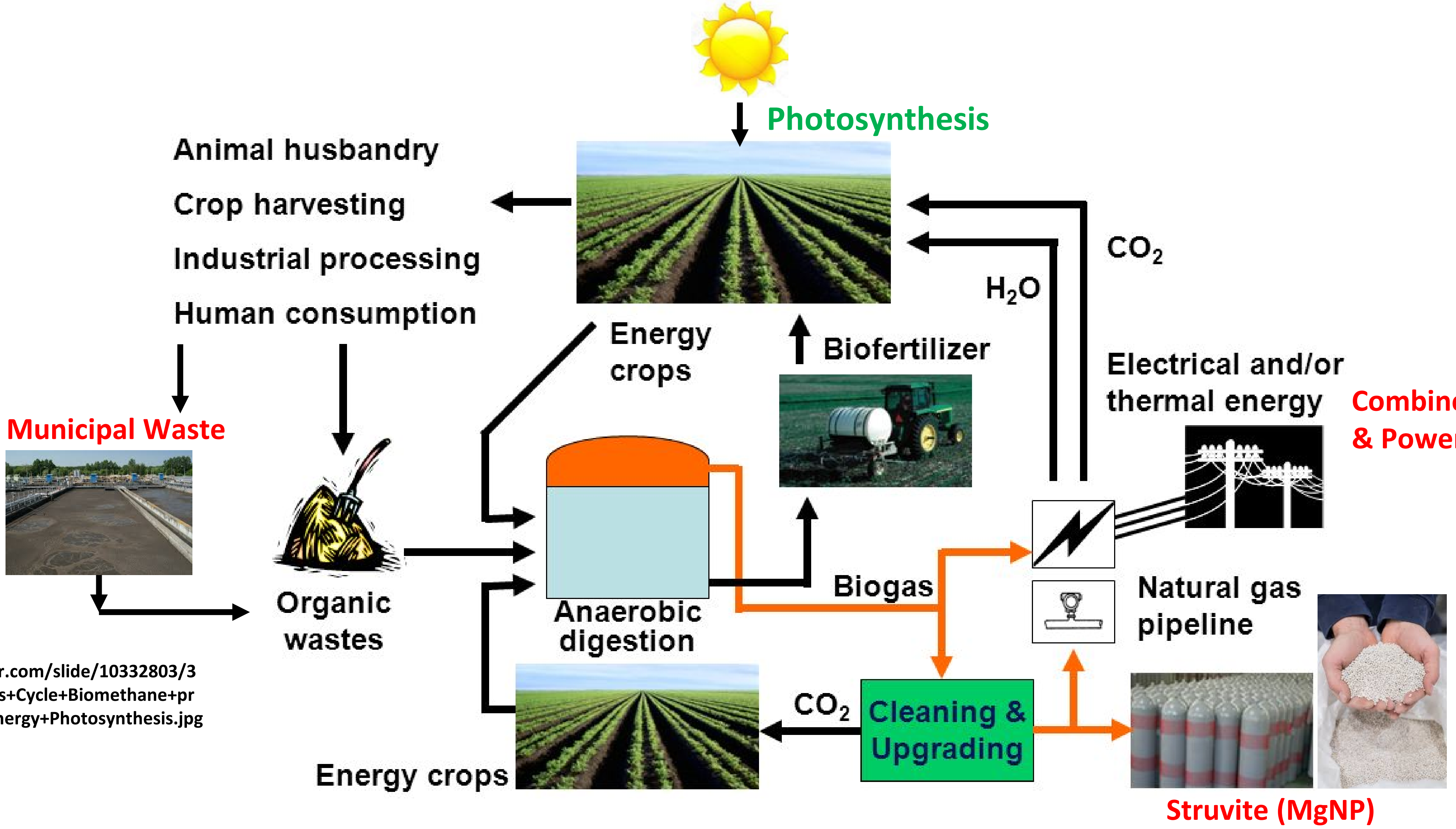
Cathode Potential (V vs. SHE)	CH_4 Production Rate (mmol/d)	Final Biocathode Biogas (%)	
		CH_4	CO_2
-0.80	1.22	96	4
-0.75	0.98	95	5
-0.70	0.87	94	6
-0.65	0.97	94	6
-0.60	0.74	92	8
-0.55	0.86	92	8
-0.50	0.53	90	10

Dykstra and Pavlostathis, *Water Research*, 2021

- At a more positive applied cathode potential, the cell potential (driving force for electron transport) decreased and the anode potential decreased.
- At lower anode potentials, the transfer of electrons from a substrate to the anode is less energetically favorable.
- However, anode acetate removal did not reflect the biocathode CH_4 production rate, likely due to microbial acetate uptake and storage.



Biogas Utilization – CO_2 Recycle/Zero-net Carbon Products



https://slideplayer.com/slide/10332803/35/images/5/Biogas+Cycle+Biomethane+production+Solar+energy+Photosynthesis.jpg

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Acknowledgements

- **The MEC H_2 production study** was supported by the U.S. Department of Energy, BioEnergy Technologies Office, under Contract No. DE-AC05-00OR22725.
  Contributors: Dr. Xiaofei Zeng (Georgia Tech PhD student), Microsoft Corporation, Redmond, WA, USA

  Dr. Abhijeet P. Borole, Oak Ridge National Laboratory, Oak Ridge, TN, USA

- **The BES CO_2 conversion to CH_4 study** was in part supported by the U.S. National Science Foundation Graduate Research Fellowship awarded to Christy M. Dykstra under Grant No. DGE-1148903.
  Contributors: Dr. Christy M. Dykstra (Georgia Tech PhD student), San Diego State University, San Diego, CA, USA

  Dr. Cheng Cheng (Georgia Tech visiting Ph.D. student), supported by the China Scholarship Council, Shandong University, Jinan, P.R. China

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