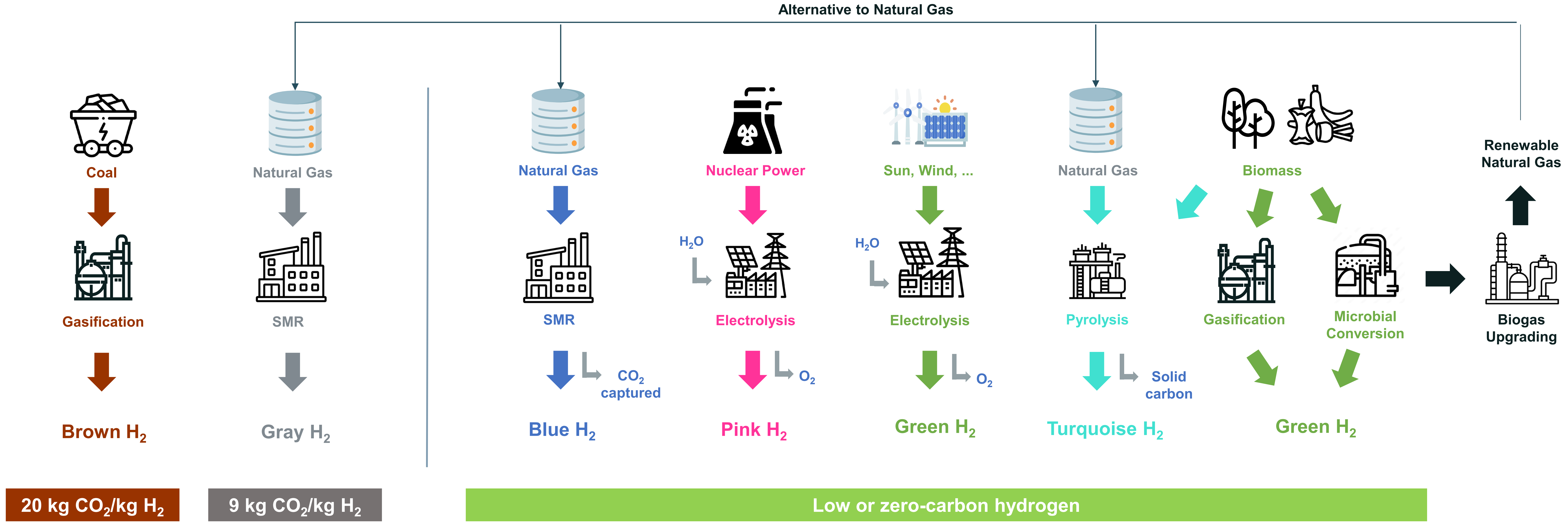
Waste to Hydrogen (Biological Pathways)

February 16, 2023

LA County
Integrated Waste Management Task Force
Alternative Technology Advisory Subcommittee (ATAS)

Hydrogen Production Pathways

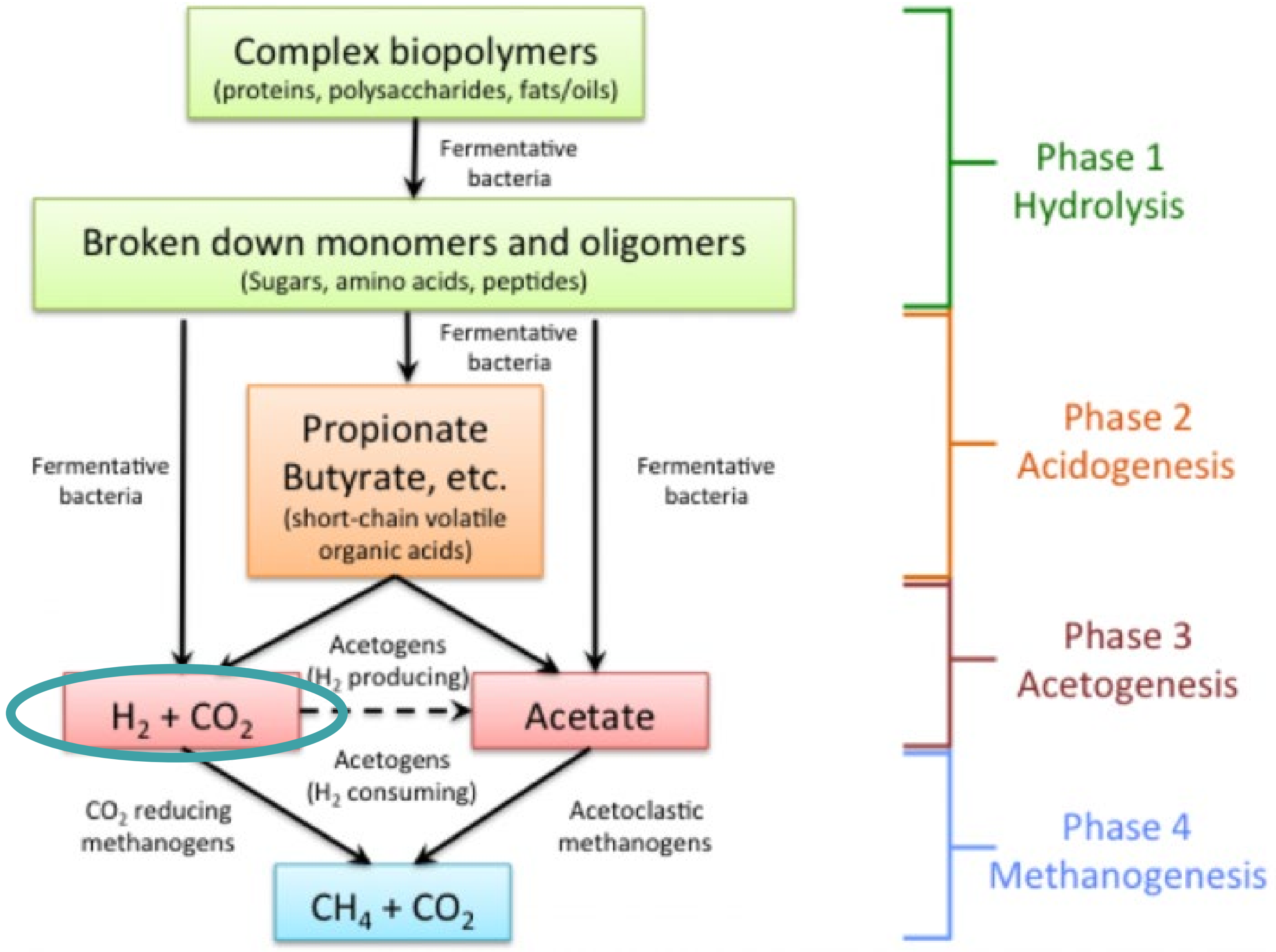


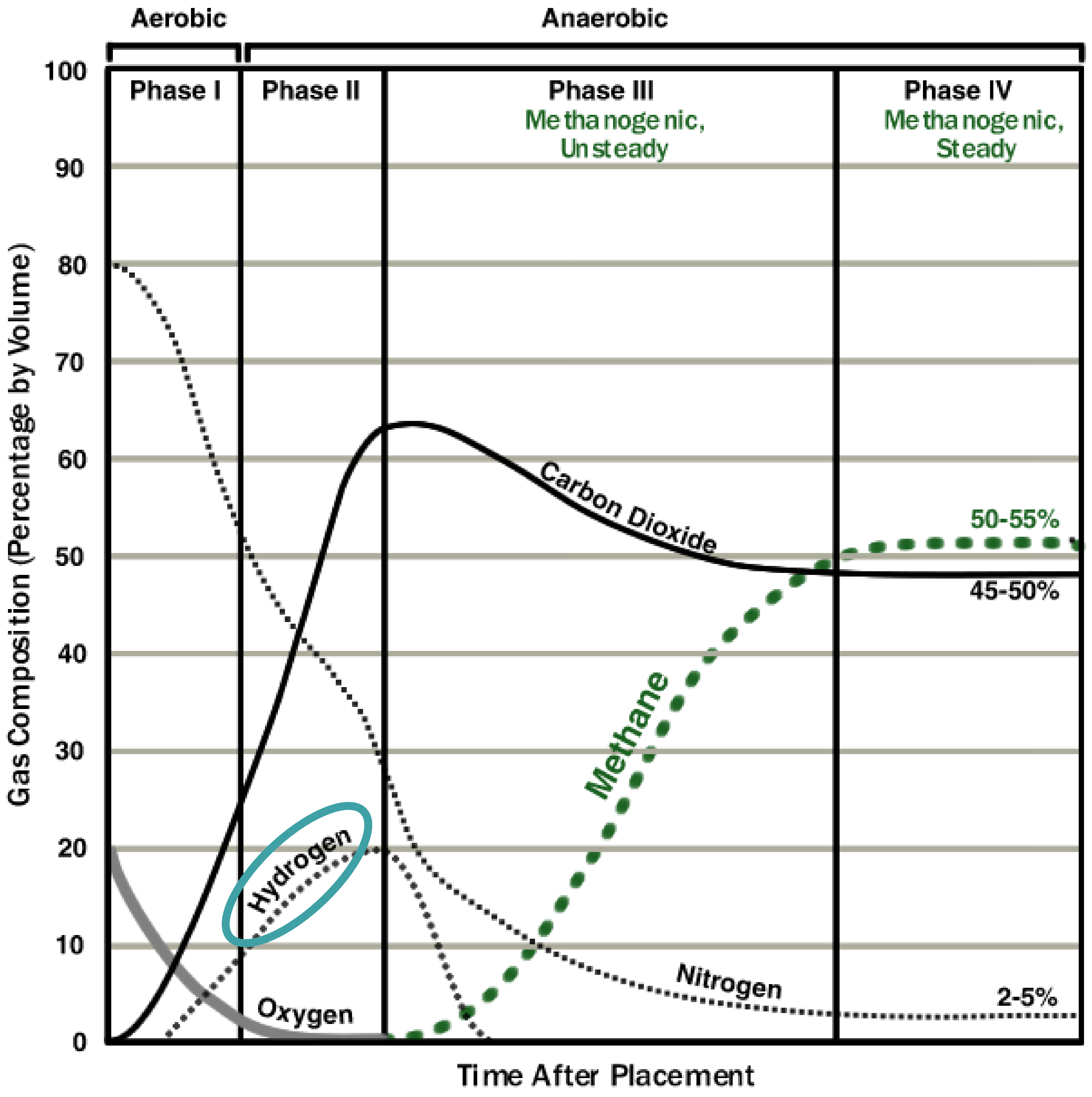
GHD

Waste to Hydrogen Pathways Overview

1	**Via Biogas (Digester Gas or Landfill Gas)**	• RNG SMR	→ Mature	
		• Methane Pyrolysis	→ One commercial facility	monolith
		• Biogas Reforming	→ Research	
2	**Thermal Treatment**	• Pyrolysis	→ Various types. Proven (depending on feedstock)	Kore, CHAR technologies
		• Gasification	→ Various types. Proven (depending on feedstock)	SG H2 ENERGY (FUELING A CLEAN ENERGY FUTURE, TODAY), RAVEN, SIERRA ENERGY
3	**Biological Production**	• Fermentation	→ Research	
		• Microbial Electrolysis	→ Research	electro-active technologies

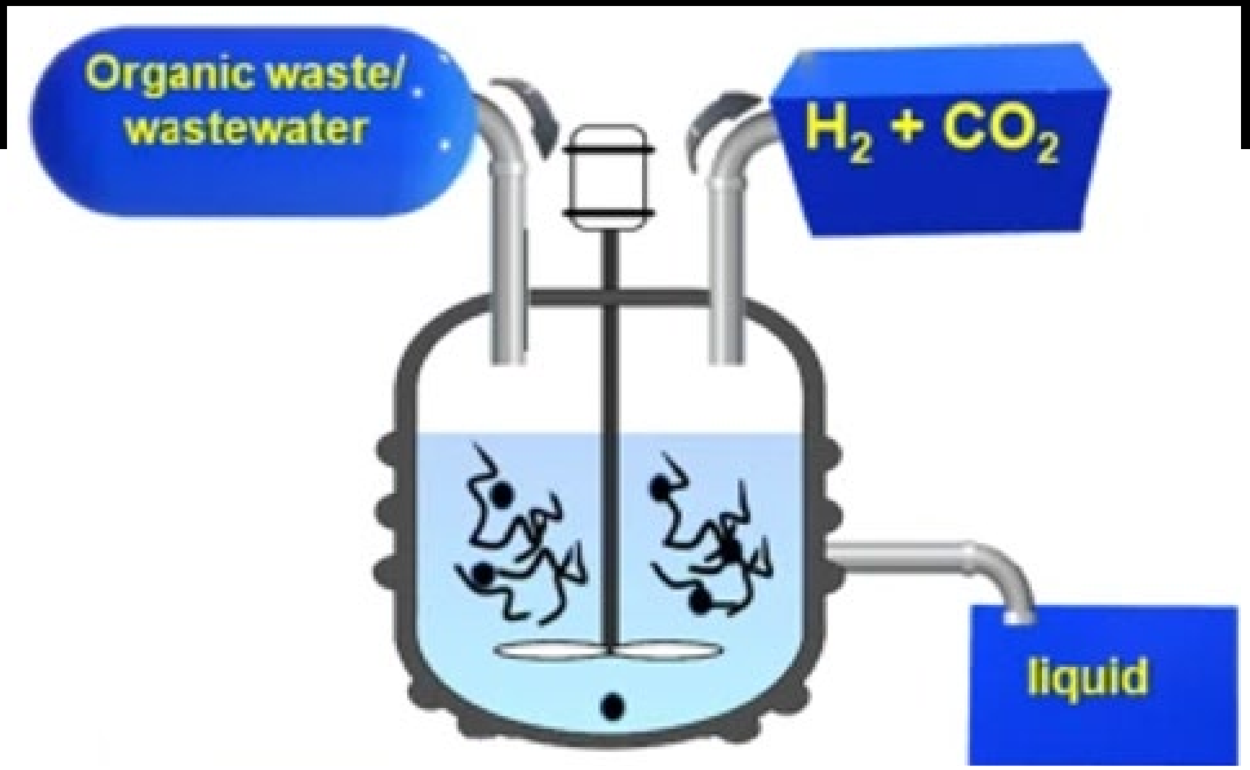
The Four Phases of Biogas Production





Source:
Penn State, https://www.e-education.psu.edu/egee439/node/727
USEPA, https://www.epa.gov/lmop/basic-information-about-landfill-gas

Dark Fermentation



PROCESS

- Anaerobic microorganisms break down organic matter and produce H_2
- Goal is to inhibit production of H_2-consuming microorganisms
  - ✓ Pre-treat inoculum
  - ✓ Keep pH outside of methanogen optimal pH range of 7-8
- No light required ("dark fermentation")
- HRT – 16 to 24 hours

FEEDSTOCK

- Variety of wastes have been tested (Ag, WW, FW, sewage sludge)
- Pre-treatment of lignocellulosic materials to improve yield

CHALLENGES / NEXT STEPS

- Improve rate & yield
- Required separation of H_2 and CO_2 after production
- Only lab scale currently
- Limited COD conversion (effluent contains organic acids)
  → Combine with downstream process to make industrially viable.

$$2H^+ + 2e^- \leftrightarrow H_2$$

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 12H_2$$

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

(Acetic acid pathway)

$$C_6H_{12}O_6 \rightarrow CH_3COOH + CH_3CH_2COOH + CO_2 + H_2$$

(Propionic acid pathway)

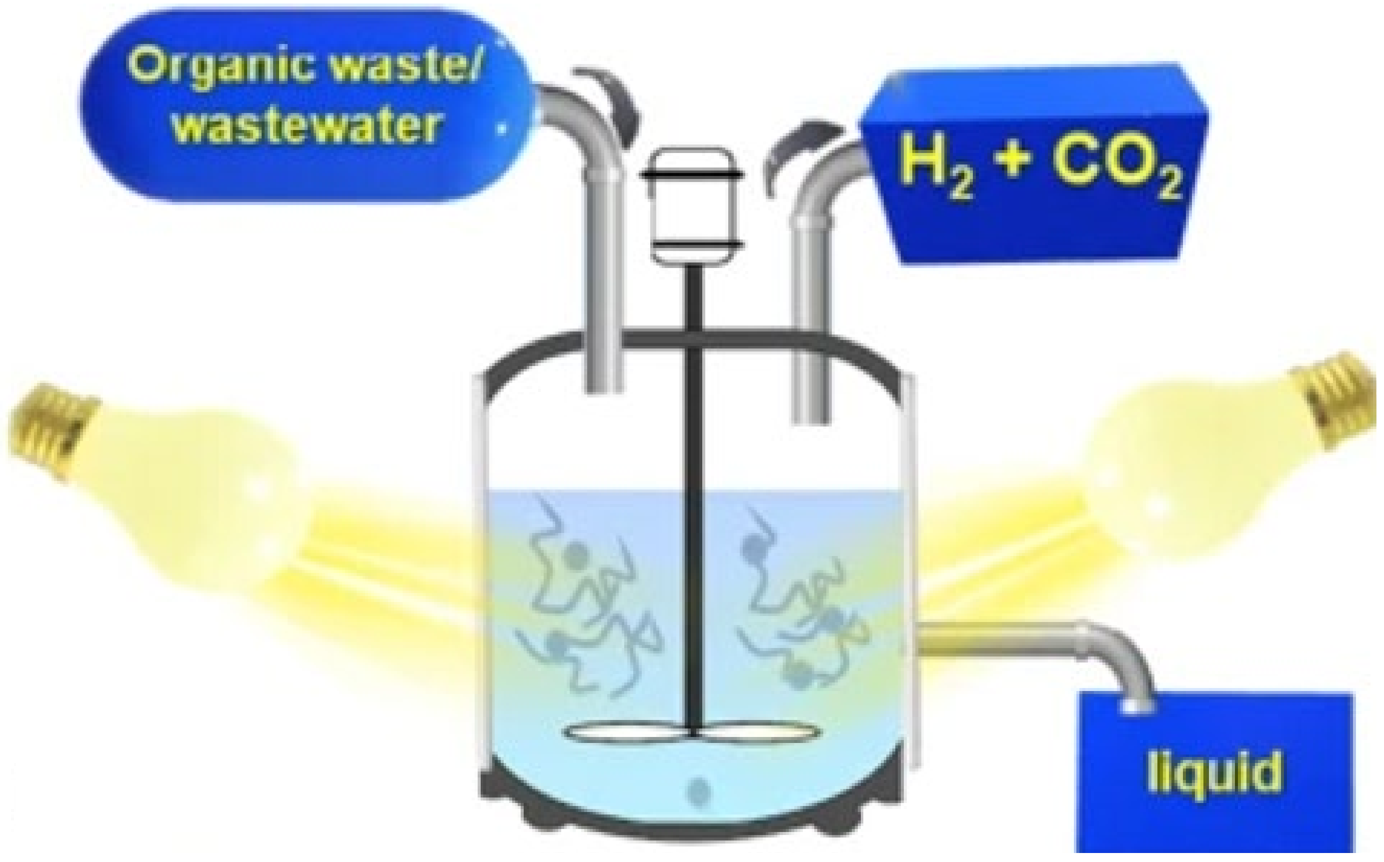
$$C_6H_{12}O_6 + 6H_2O \rightarrow 2CH_3CH_2CH_2COOH + 2CO_2 + 2H_2$$

(Butyric acid pathway)

Osman, A.I., Deka, T.J., Baruah, D.C. et al. Critical challenges in biohydrogen production processes from the organic feedstocks. Biomass Conv. Bioref. (2020)

Photo Fermentation

- Use purple non-sulfur (PNS) microbes.
  Bacteria selection factors include:
  - Ability to utilize available light from light source
  - Substrate degradation efficiency
- Major hurdle is light penetration – efficient photobioreactor with high light utilization efficiency is essential to commercialization
- Key considerations: temperature, pH, substrate concentration, source of light, illumination intensity
- PNS bacteria are anaerobic, have high nutrient uptake



$$C_6H_{12}O_6 + 6\,H_2O \xrightarrow{h\nu} 6\,CO_2 + 12\,H_2$$

Osman, A.I., Deka, T.J., Baruah, D.C. et al. Critical challenges in biohydrogen production processes from the organic feedstocks. Biomass Conv. Bioref. (2020)

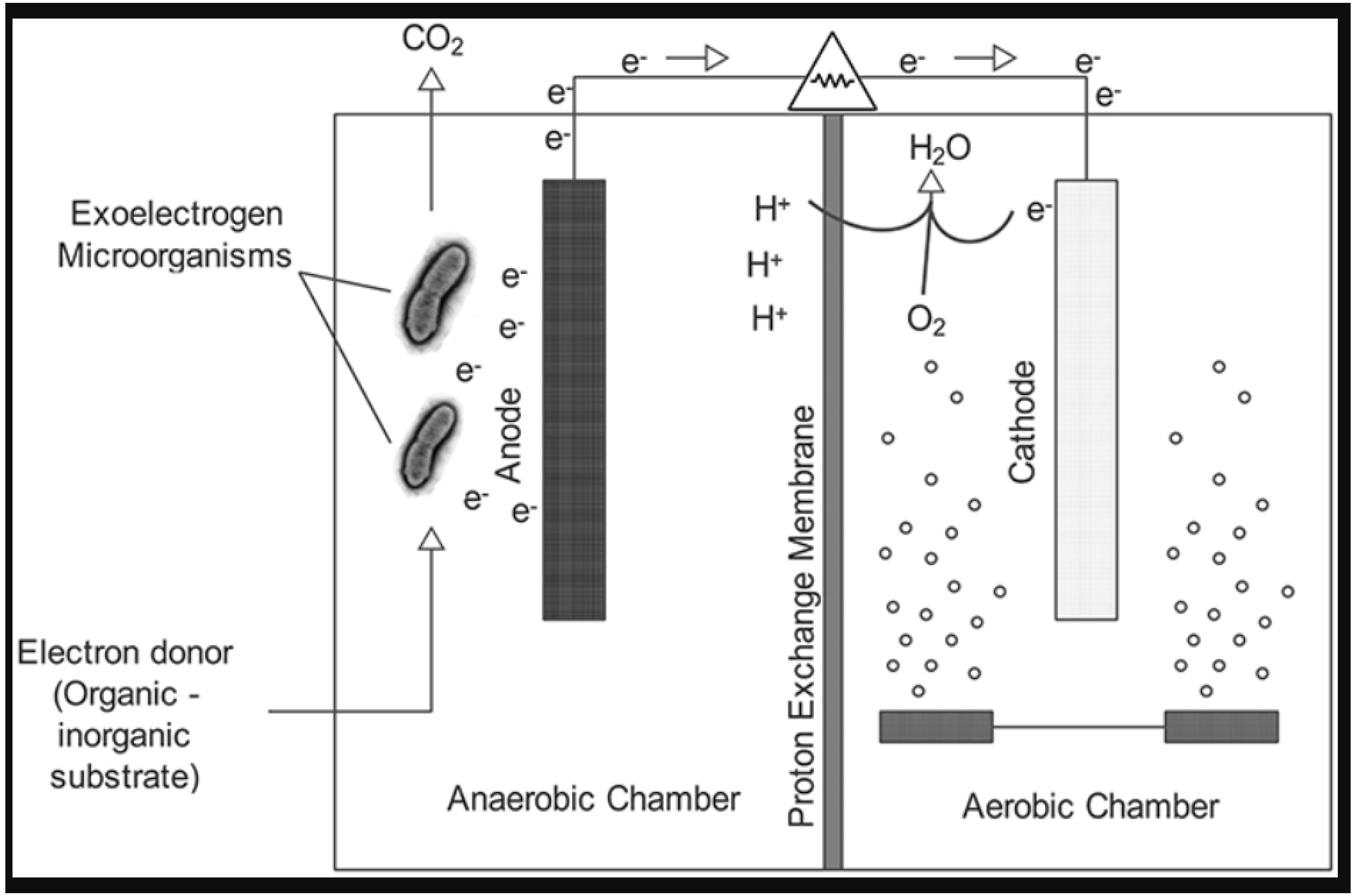
Microbial Fuel Cell (MFC) – Electricity Production

OVERVIEW & CHALLENGES

- Electrons flow from the anode to the cathode
- O_2 has high redox potential (good cathodic receiver)
  - Poor contact of O_2 with electrode leading to slow reaction rate
- Slow rate of reduction on normal carbon cathode
  - Catalytic-coated electrodes are expensive rare metals

RESEARCH

- Electron acceptors
  - ✓ Consider aquatic system pollutants
  - ✓ Increase voltage potential
- Electrode material
- Type of substrate and microorganisms



$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad (E^0 = 1.23\ V)$$

Denix, U., Yifeng, Z., Irini, A. An Overview of Electron Acceptors in Microbial Fuel Cells. Frontiers in Microbiology Vol. 8 (2017)

Microbial Electrolysis (MEC) – Hydrogen Production

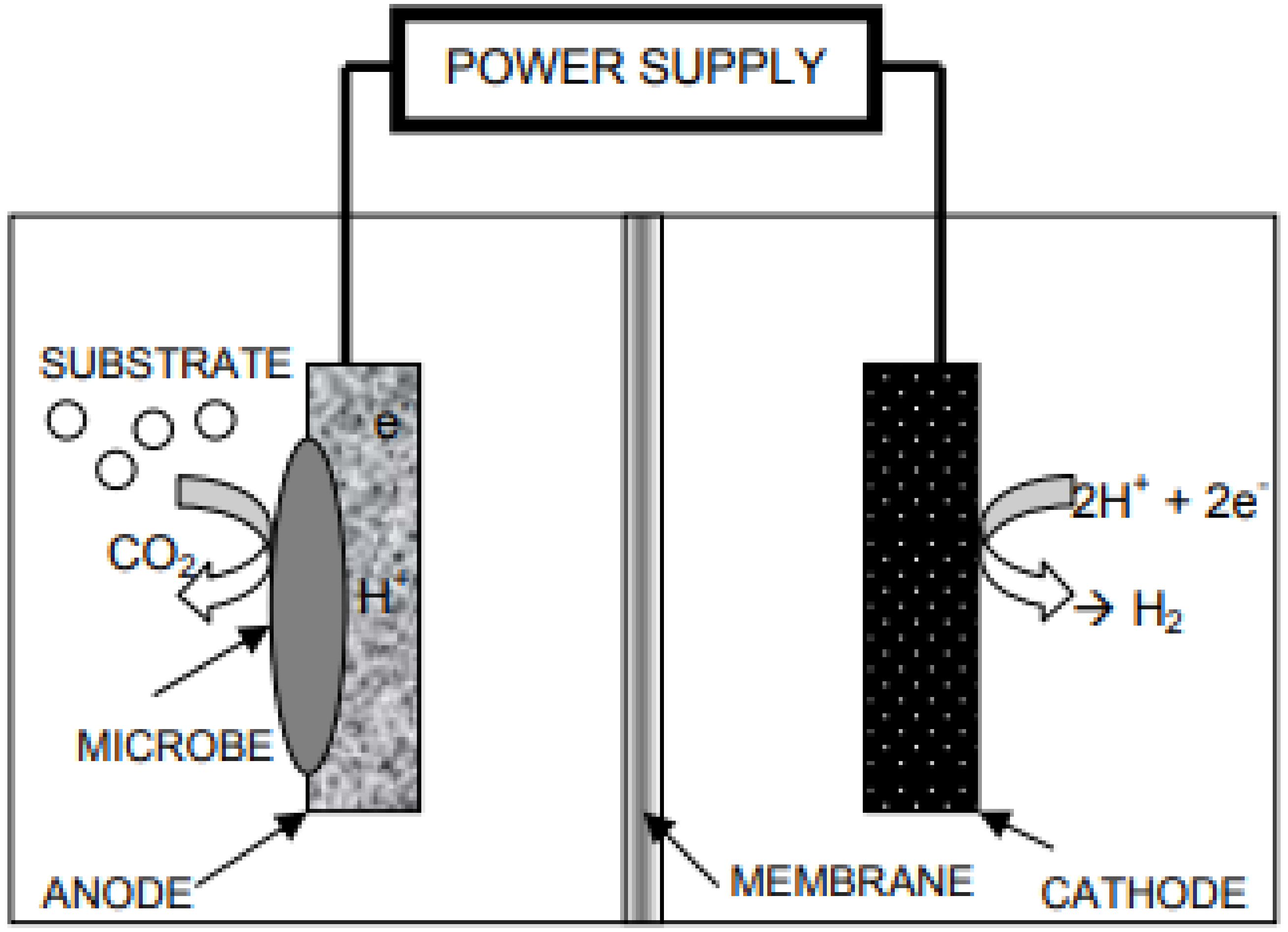
OVERVIEW

- Electrons flow from the anode to the cathode - requires power supply to make reaction thermodynamically feasible
- Theoretically half the electricity required for water electrolysis

CHALLENGES / RESEARCH

- High capital cost (high electrode and membrane or separator costs).
  - Lower cost cathode – stainless steel vs. platinum (Penn State U)
  - Reactor design – separation distance

- Improve rate & yield
  - Bacterial cultures
  - Hybrid systems integrating dark fermentation and MEC processes
  - MFC as power supply for MEC



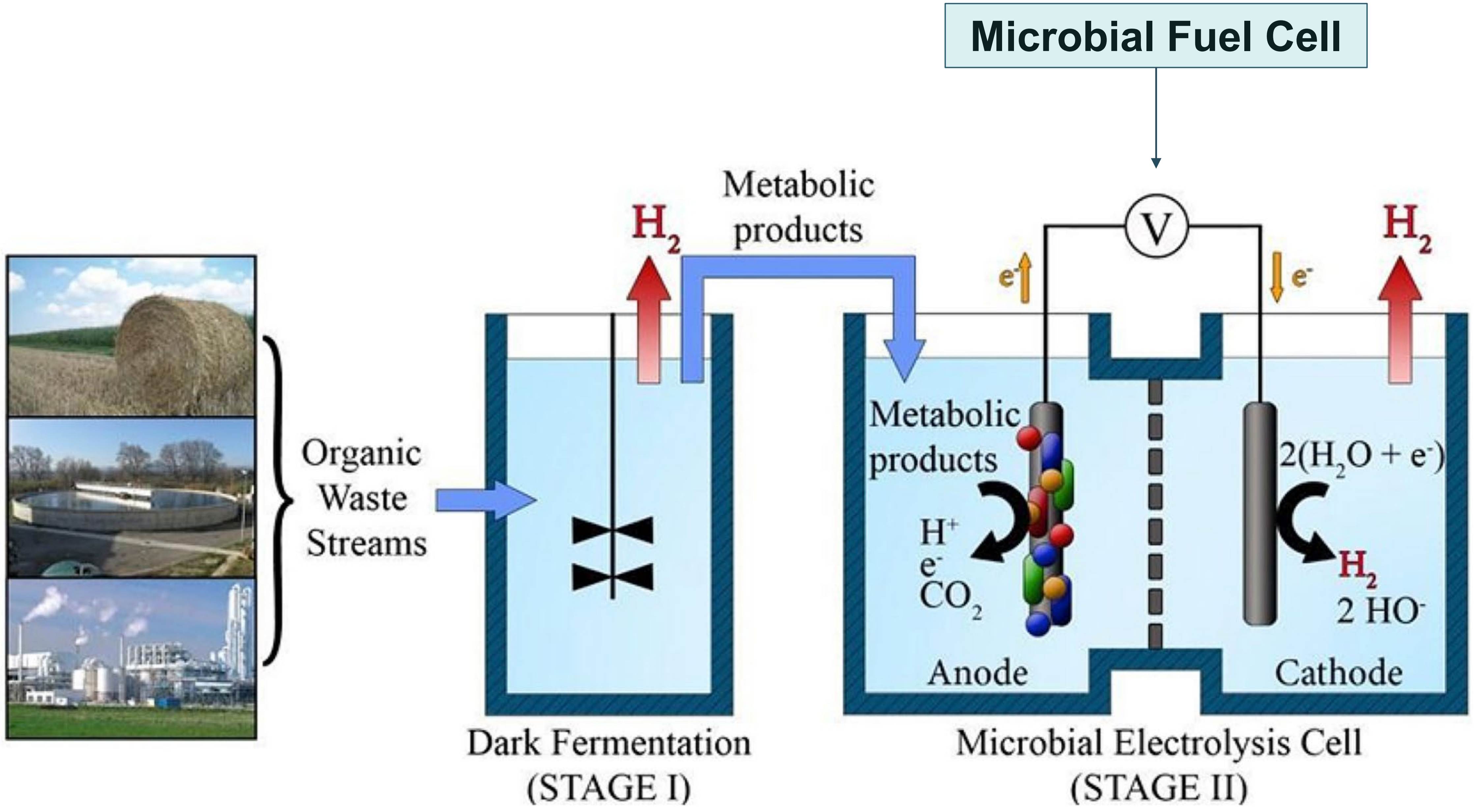
$$\text{Anode}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 8e^- + 8H^+$$

$$\text{Cathode}: 8e^- + 8H^+ \rightarrow 4H_2$$

$$\text{Overall}: CH_3COOH + 2H_2O \rightarrow 2CO_2 + 4H_2$$

Chorbadzhiyska, E., Hubenova, Y., Hristov, G., Mitov, M. Microbial Electrolysis Cells as Innovative Technology for Hydrogen Production. South-West University & Plovdiv University (2011)

Optimization Considerations – System Coupling



Marone, A., Ayala-Campos, A., Trably, E., Carmona-Martinez, A., Moscoviz, R., Latrille, E., Steyer, J., Alcaraz-Gonzalez, V., Bernet, N. Coupling Dark Fermentation and Microbial Electrolysis to Enhance Bio-Hydrogen Production from Agro-Industrial Wastewaters and By-Products in a Biorefinery Framework. International Journal of Hydrogen Energy, Volume 42, Issue 3, (2017)

What's Next?

Dark Fermentation & MEC

- Design improvements (bacterial cultures, electrode materials, system coupling…) to increase rate & yield and lower costs

Case Study	Optimistic Value (2007$/kg H_2)	Baseline (2007$/kg H_2)	Conservative Value (2007$/kg H_2)
Current Case (2015)	$59.76	**$67.71**	$75.67
Current Case (2015) with byproduct credit	$40.88	**$51.02**	$61.16
Future Case (2025)	$7.68	**$8.56**	$9.43
Future Case[6] (2025) with byproduct credit	$3.40	**$5.65**	$7.91

Randolph, K., Studer, S., Hydrogen Production Cost from Fermentation, Department of Energy (2017)

Other Emerging Biological Waste Conversion Pathways

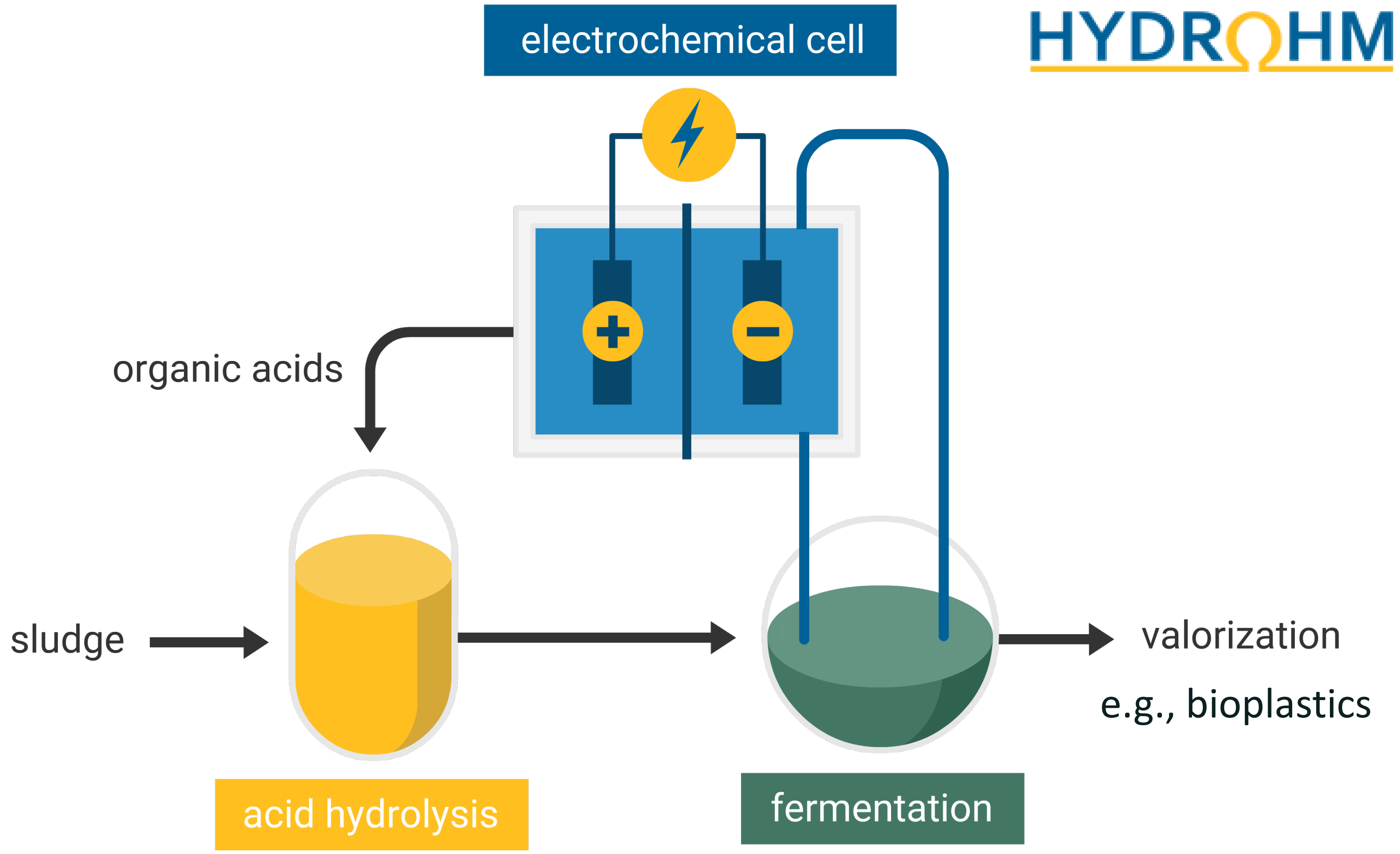
- Production of bioplastics
- Production of animal feed

mill

PAQUES biomaterials

Producing a natural alternative for plastic from waste(water) streams!

HYDROHM



*Thank You

→ The Power of Commitment