Hydrogen and electricity production using microbial fuel cell-based technologies

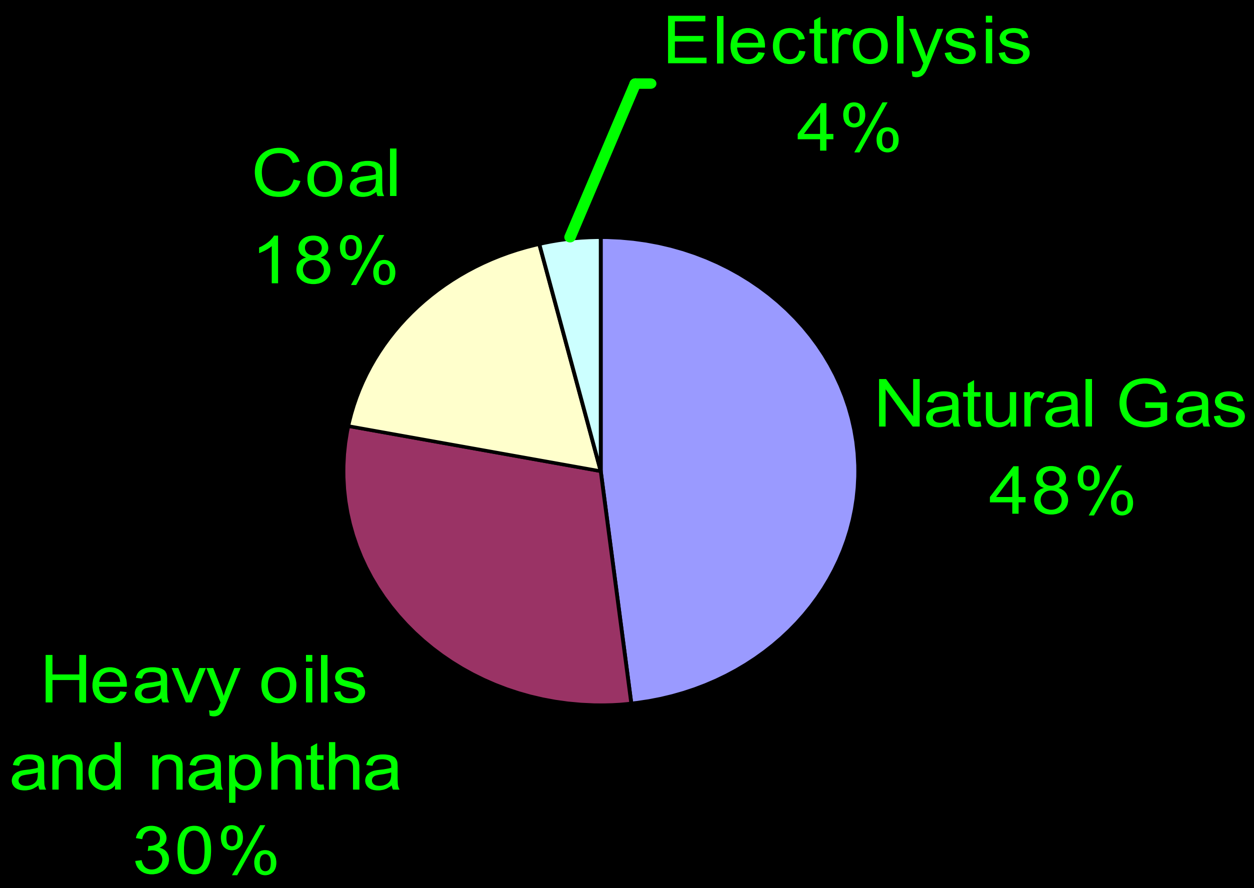
Bruce E. Logan and John M. Regan
Penn State University

Engineering
Environmental
Institute

Ethanol versus H_2 from Glucose

- Glucose: ΔH_c= 2808 kJ/mol
- Ethanol
  - Produce 2 ethanol per glucose by fermentation
  - 2×ΔH_c= 2× 1367 kJ/mol => ΔH_c= 2734 kJ/mol
- Hydrogen
  - Produce up to 12 H_2 per glucose
  - 12×ΔH_c = 12× 286 kJ/mol => ΔH_c = 3430 kJ/mol
- DOE
  - 10-12 mol-H_2/mol-glucose needed to make biological H_2 production feasible (9.6 mol H_2= ΔH_c for 2 ethanol from glucose)

Current sources of H_2 Production



Energy Utilization in the USA

US energy use: 97 quad

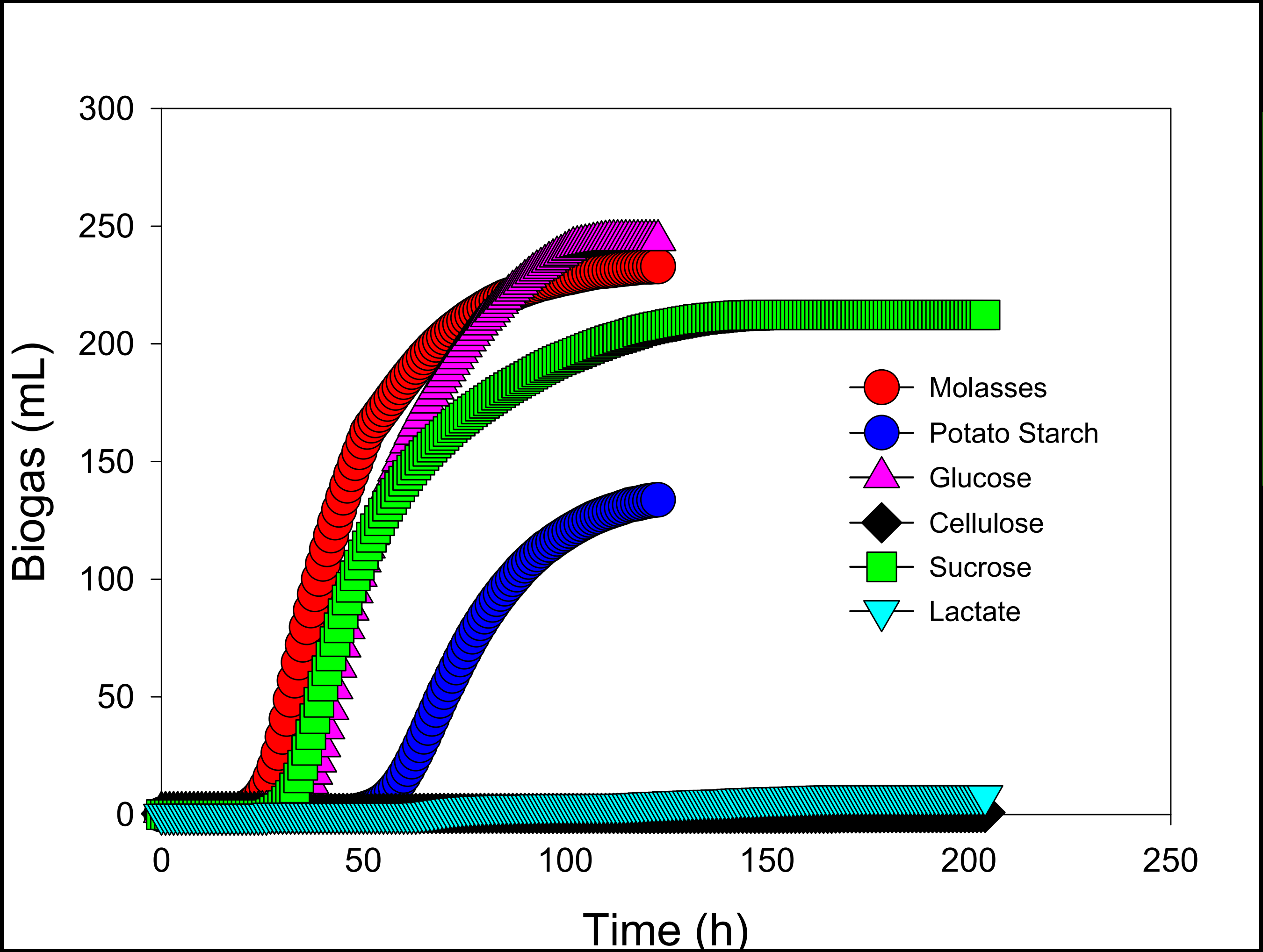
US electricity generation: 13 quad

Electricity needed for H_2 transportation:

Via water electrolysis: 12 quad
Using the BEAMR process: 1.2 quad

97 quad [quadrillion BTUs] = 28,400 TWh(terawatt hours)

H_2 results primarily from fermentation of sugars



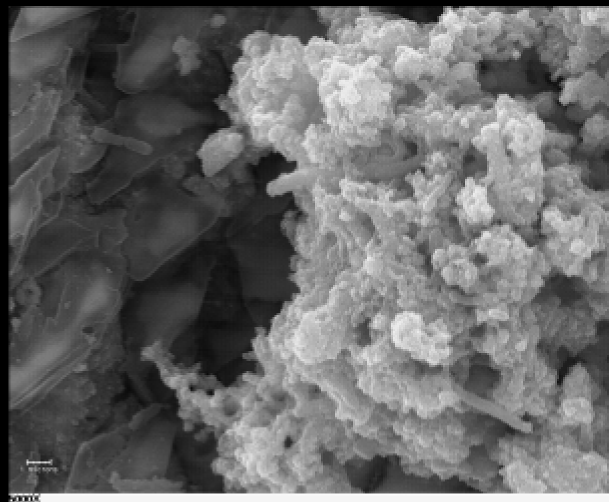
Biogas:

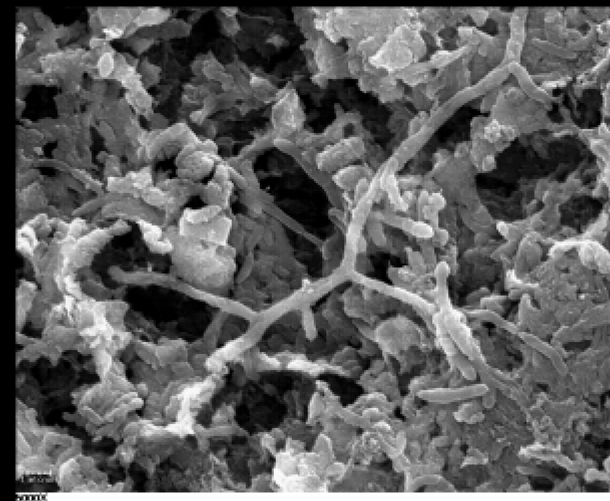
- 60% H_2

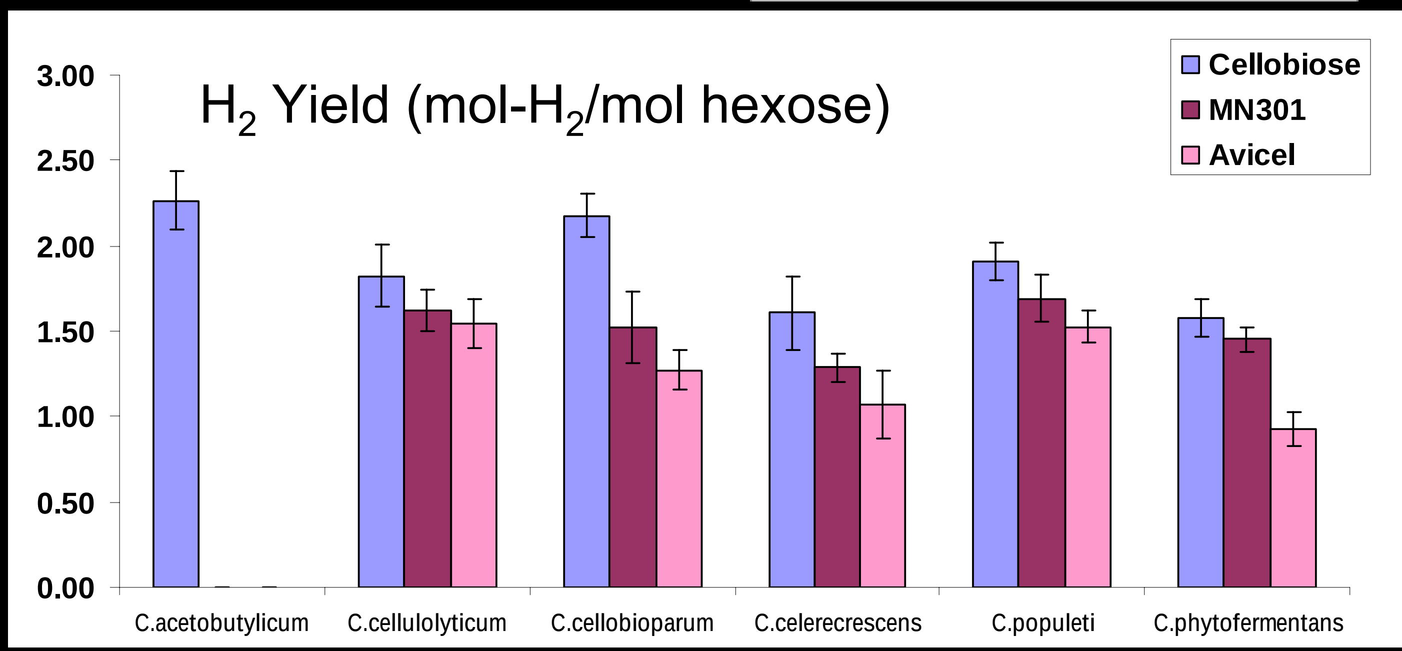
- 40% CO_2

Source: Logan, VanGinkel & Oh *Environ. Sci. Technol.* (2002)

H_2 can be produced by *cellulose fermentation*







Source: Ren and Regan (unpublished)

Observation: the "fermentation barrier"

Maximum: 12 mol-H_2/mol-hexose

$C_6H_{12}O_6 \rightarrow 2\ H_2 + C_4H_8O_2 + 2\ CO_2$

$C_6H_{12}O_6 + 2\ H_2O \rightarrow 4\ H_2 + 2\ C_2H_4O_2 + 2\ CO_2$

Maximum of 4 mol/mol
(2 mol/mol in practice)

Maximum of 4 mol/mol
(2 mol/mol in practice)

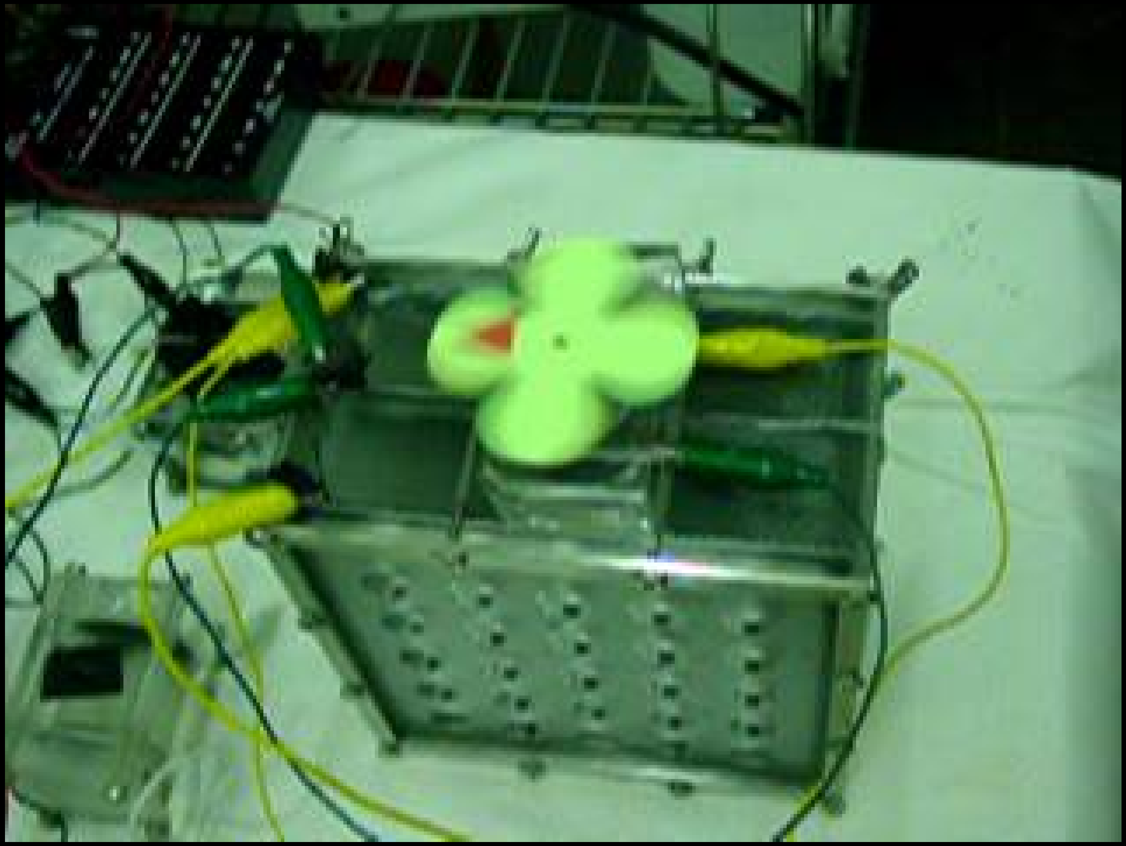
?

How can we recover the remaining 8 to 10 mol/mol?

Energy Production using MFC technologies

- Electricity production using microbial fuel cells
- H_2 Production from biomass using the BEAMR process: overcoming the “fermentation barrier”
- A path to renewable energy

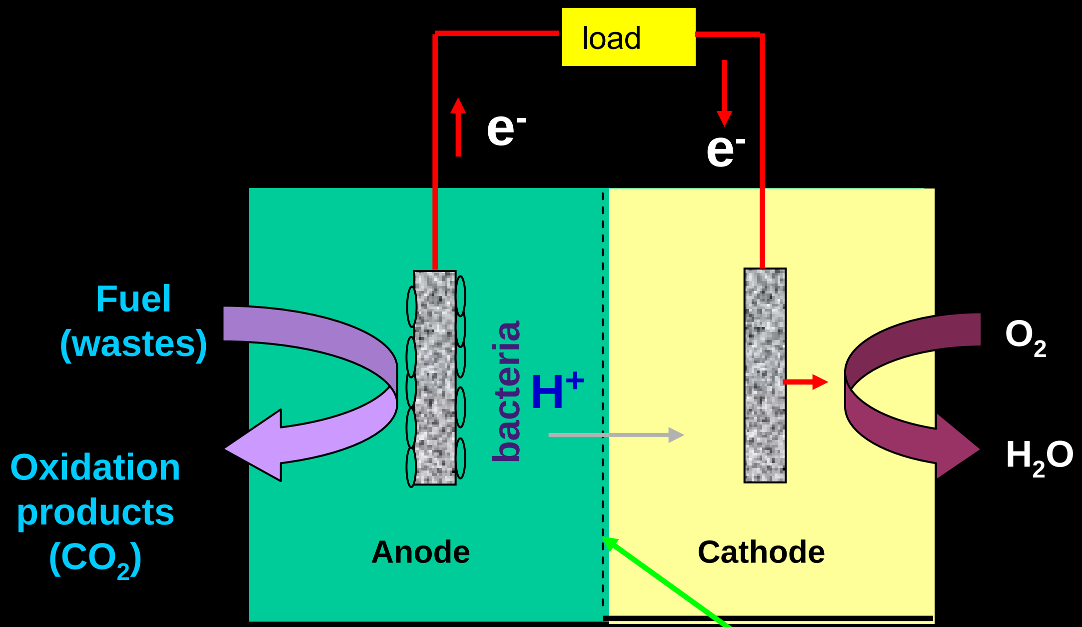
Demonstration of a Microbial Fuel Cell (MFC)

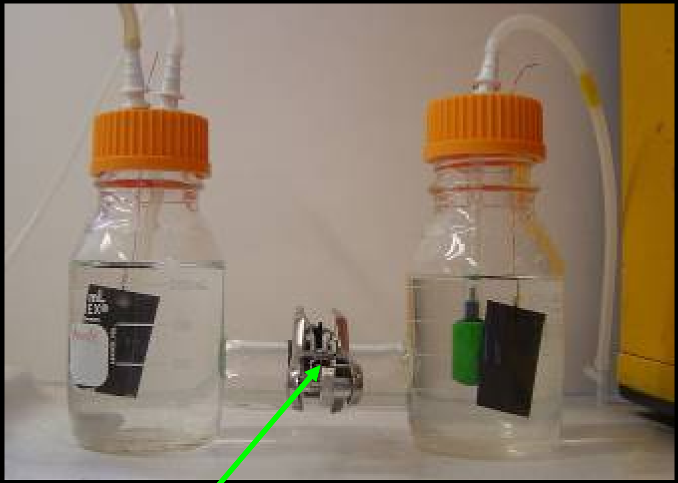


MFC webcam (live video of an MFC running a fan)

www.engr.psu.edu/mfccam

Microbial Fuel Cells: Aqueous cathode





Proton exchange membrane (PEM)

Source: Liu et al., *Environ. Sci. Technol.*, (2004)

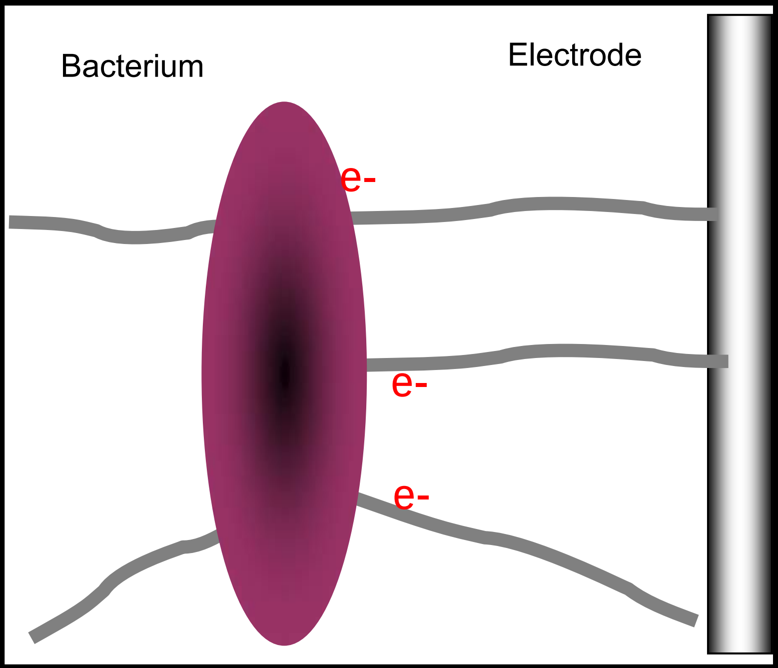
- *Methanogenesis*
  - Generation of methane
  - Methanogens
  - Anaerobic digesters

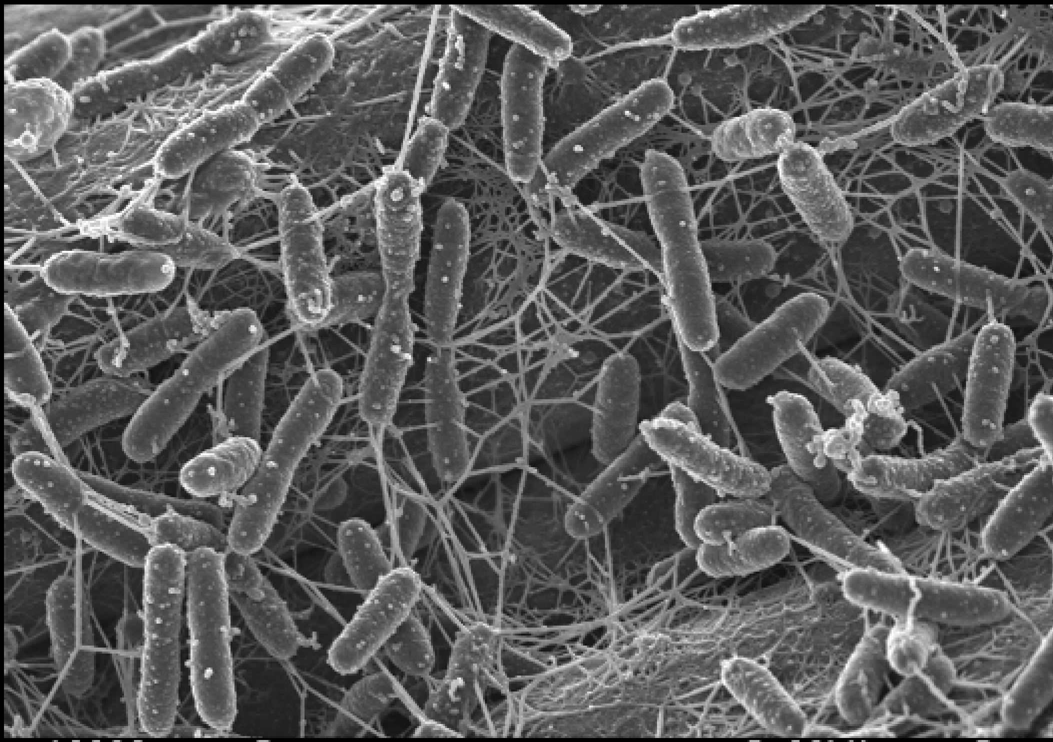
- *Electrogenesis*
  - Generation of electricity
  - Exoelectrogens
  - Microbial fuel cells (MFCs)
- *Electrohydrogenesis*
  - Generation of H_2 gas
  - Exoelectrogens
  - Bioelectrochemically assisted microbial reactors (BEAMRs)

Microbial community analysis

Inoculum (substrate)	Community	Reference
River sediment (glucose+glutamic acid)	α-*Proteobacteria* (mainly *Actinobacteria*)	Phung et al. (2004)
River sediment (river water)	β-*Proteobacteria* (related to *Leptothrix* spp.)	Phung et al. (2004)
Marine sediment (cysteine)	γ-*Proteobacteria*, 40% *Shewanella affinis* KMM, then *Vibrio* spp. and *Pseudoalteromonas* sp.	Logan et al. 2005
Wastewater (starch)	36%=unidentified, 25%=β- and 20%=α-*Proteobacteria*, and 19%= *Cytophaga+Flexibacter+Bacterioides*	Kim et al. (2004)
Wastewater (acetate)	24%=α-, 7%=β-, 21%=γ- , 21%= δ-*Proteobacteria;* 27%=others	Lee et al. (2003)

New finding: bacteria use “nanowires”



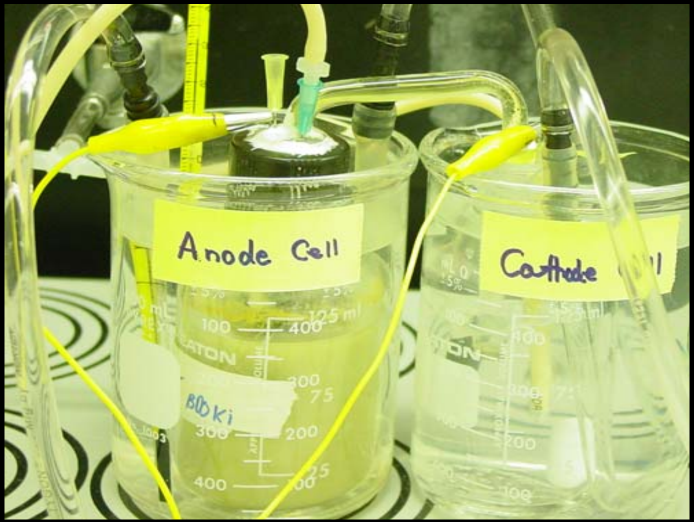


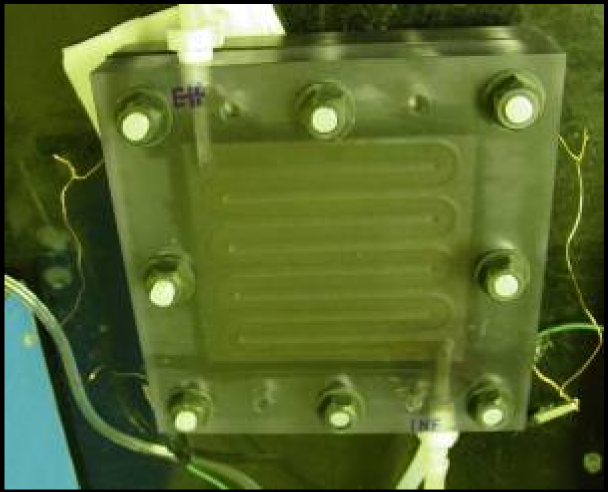
Bacteria that can transfer electrons directly to the electrode:

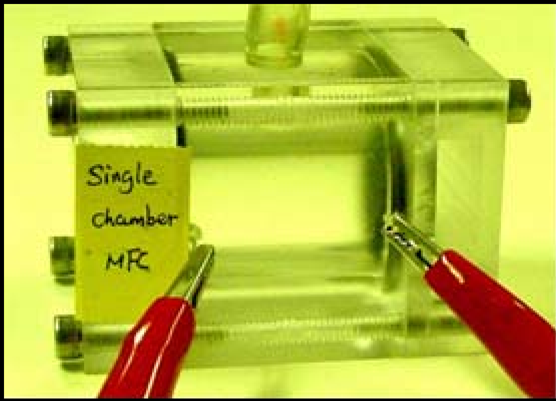
- *Geobacter sulfurreducens*
- *Alteromonas sp.*
- *Shewanella spp.*

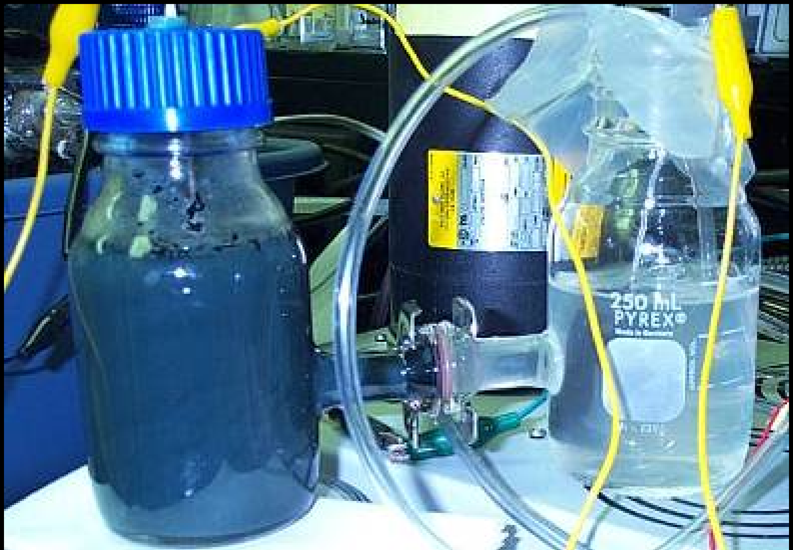
Gorby et al. (2006), *PNAS*.

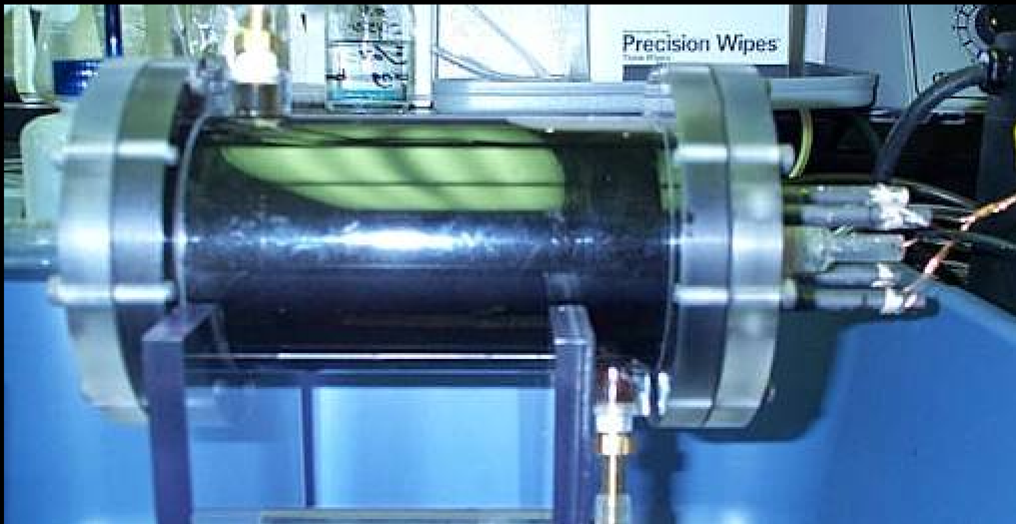
System architecture (not microbiology) limits power





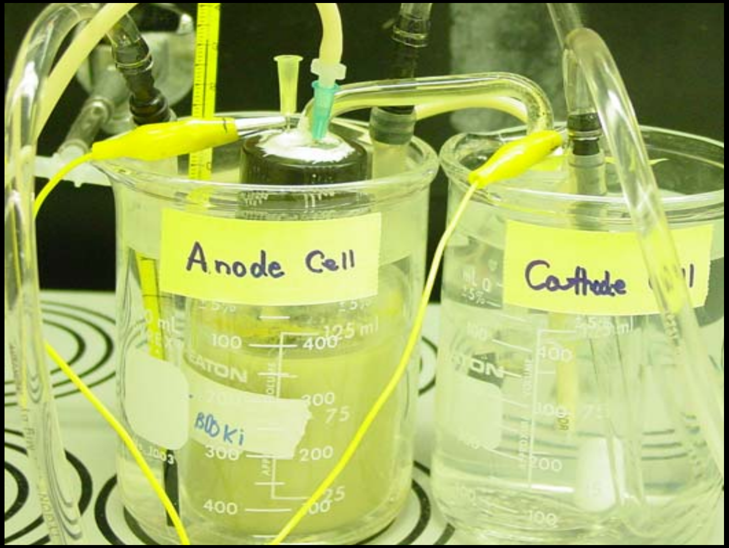






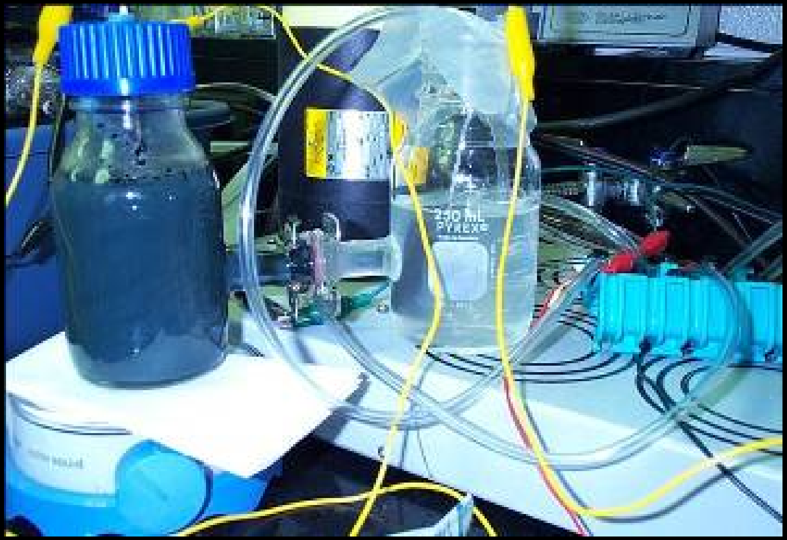
Power density is limited by internal (system) resistance

Power: 0.3-3 mW/m²



System resistance: 66,920 Ω

Power: 40 mW/m²



System resistance: 1,756 Ω

$$P = \frac{OCV^2 R_{ex}}{A(R_{\text{int}} + R_{ex})^2}$$

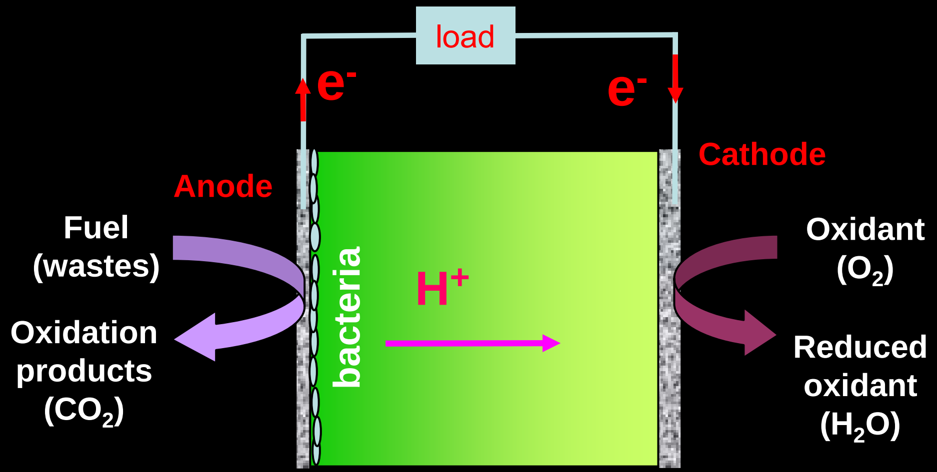
P=	Power normalized surface area
OCV=	Open circuit voltage
R_{ex}=	External resistance
R_{in}=	Internal resistance
A=	Electrode projected surface area

Source: Min et al., *Wat. Res (2005)*

Air Cathode MFC

- Bacteria oxidize organic matter

- Generate electricity from any form of biodegradable organic matter

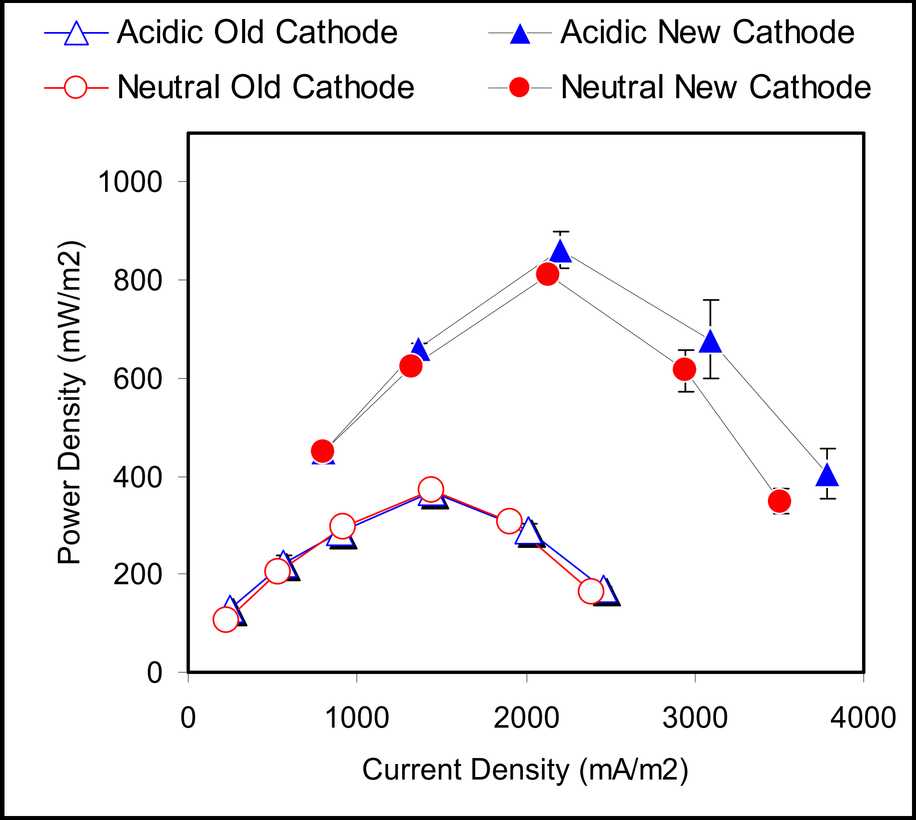


Power production (early studies)

Substrate	Power (mW/m^2)
Glucose	494
Acetate	506
Butryate	309
Protein	269
Domestic wastewater	146

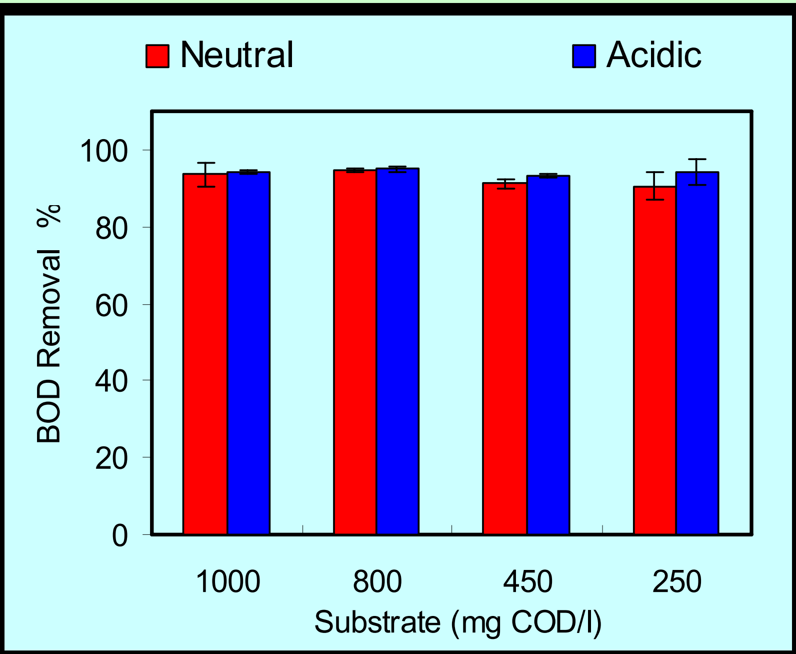
Electricity from corn stover hydrolysates

Corn stover: 90% of 250 million tons remains unused in fields (largest source of solid waste biomass in USA)



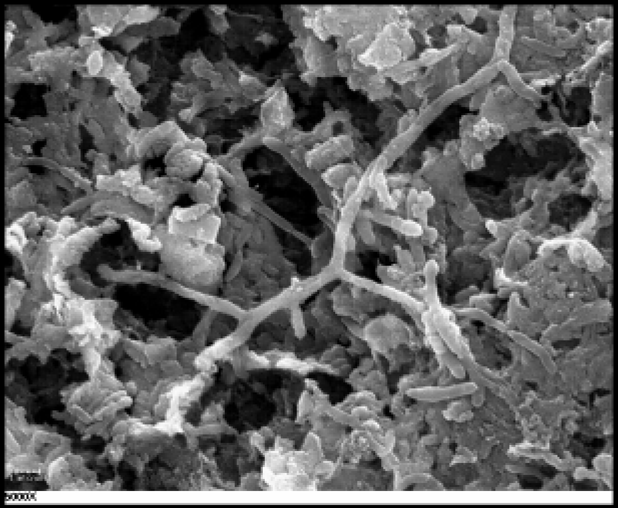
Maximum Power= 860 mW/m^2

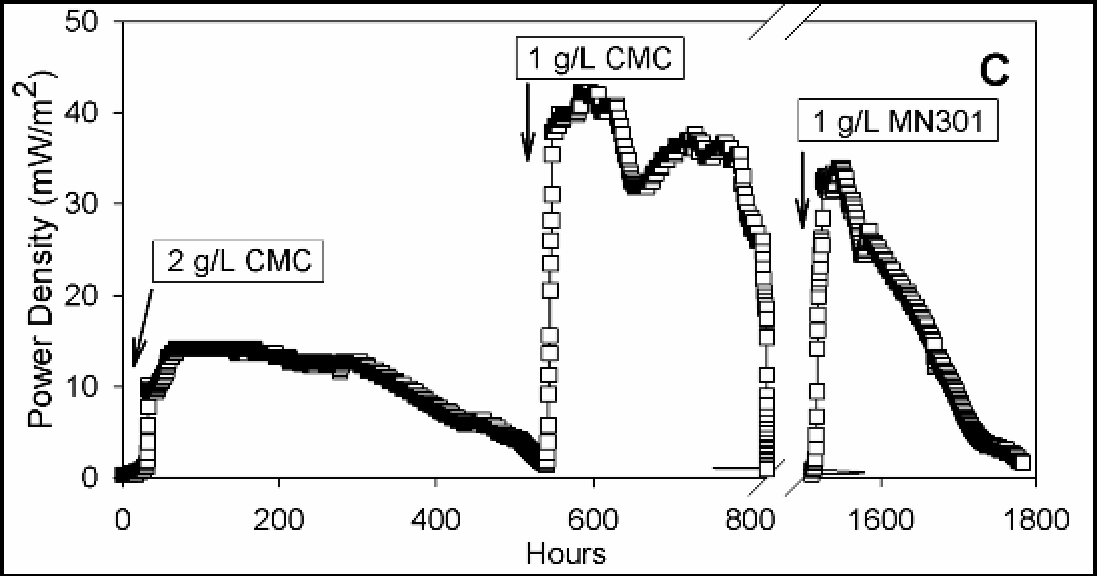
~93% removal of biodegradable organic matter



Source: Zuo et al. (2006) Energy & Fuels

Cellulose is directly used to make electricity





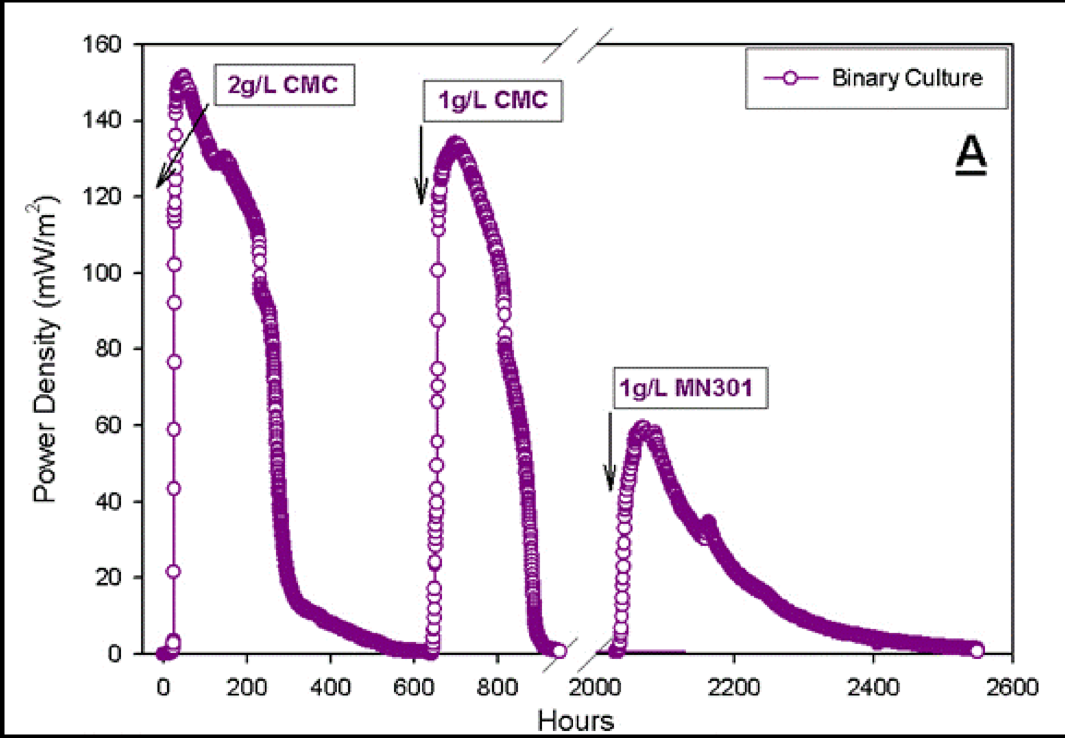
- Electricity produced with two different cellulosic materials

- Inoculum is wastewater (bacteria naturally present in the environment)

Ren, Ward,and Regan (Submitted)

Defined co-culture can also be used to make electricity from cellulose

- *Clostridium cellulolyticum*
  - Converts cellulose to H_2 and volatile acids
  - Can not produce electricity
- *Geobacter sulfurreducens*
  - Produces electricity from acetate
  - Can not degrade cellulose

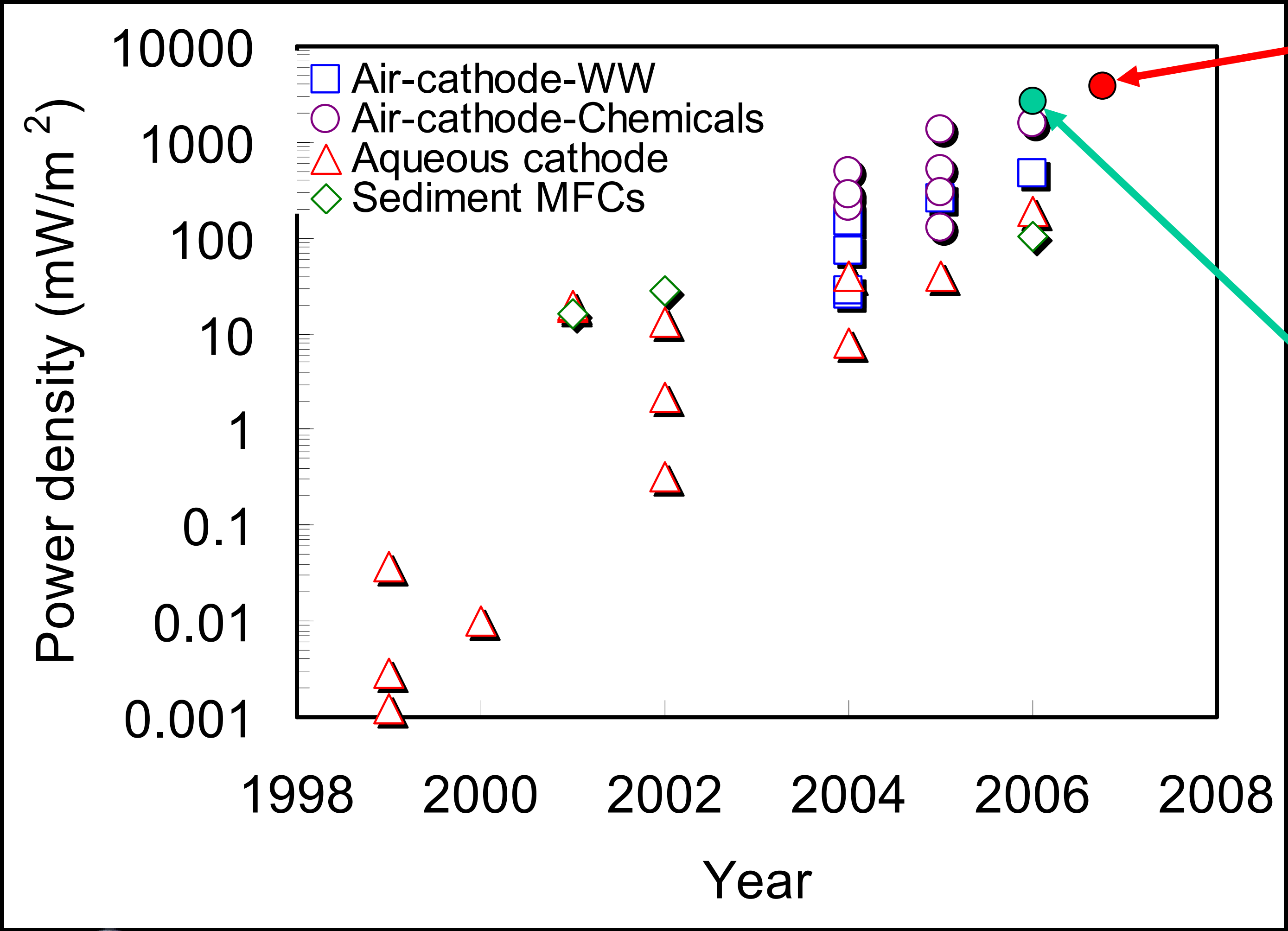


Ren, Ward,and Regan (Submitted)

Advances in operating conditions and materials selection

- Factors affecting performance
  - Solution conductivity
  - Electrode spacing
  - Continuous flow
- Cathode materials
  - Non-precious metal cathode catalyst
  - Diffusion layers for water control
- Anode materials
  - Treatment technique for rapid power generation (high-temperature ammonia gas)

Power production in MFCs is improving



Start of 2007:
2400 mW/m^2
76 W/m^3

End of 2006:
1970 mW/m^2
115 W/m^3

System Scale
(Wastewater Treatment)

What will a large scale MFC system of the future look like?

System Scale up

- Scale up covered by two Penn State patents
  - "Materials and configuration for scalable microbial fuel cells." Provisional patent.
  - "A bioelectrochemically assisted microbial reactor (BEAMR) that generates hydrogen gas." (60/588,022)

Energy Production using MFC technologies

- Electricity production using microbial fuel cells
- H_2 Production from biomass using the BEAMR process: overcoming the "fermentation barrier"
- A path to renewable energy

Overcoming the "Fermentation Barrier"

- Fermentation barrier:
  - Maximum H_2 yield of 4 mol/mol-glucose (average 2 mol/mol)
  - Only sugars (glucose) can be used
  - Acetic acid= "dead end"
- Bio-Electrochemically Assisted Microbial Reactor (*BEAMR*):
  - Acetic acid: Produce 2.9 to 3.9 mol-H_2/mol-acetate (versus a theoretical maximum of 4 mol/mol)
  - Couple fermentation + *BEAMR* process
  - Not limited to glucose– any biodegradable organic matter source (even wastewater) can be used

Essentials of the BEAMR Process

- Conventional MFC: oxygen at the cathode
  - Anode potential= -300 mV
  - Cathode Potential= +200 mV (+804 mV theory)
  - Circuit working voltage= 200 - (-300) = 500 mV

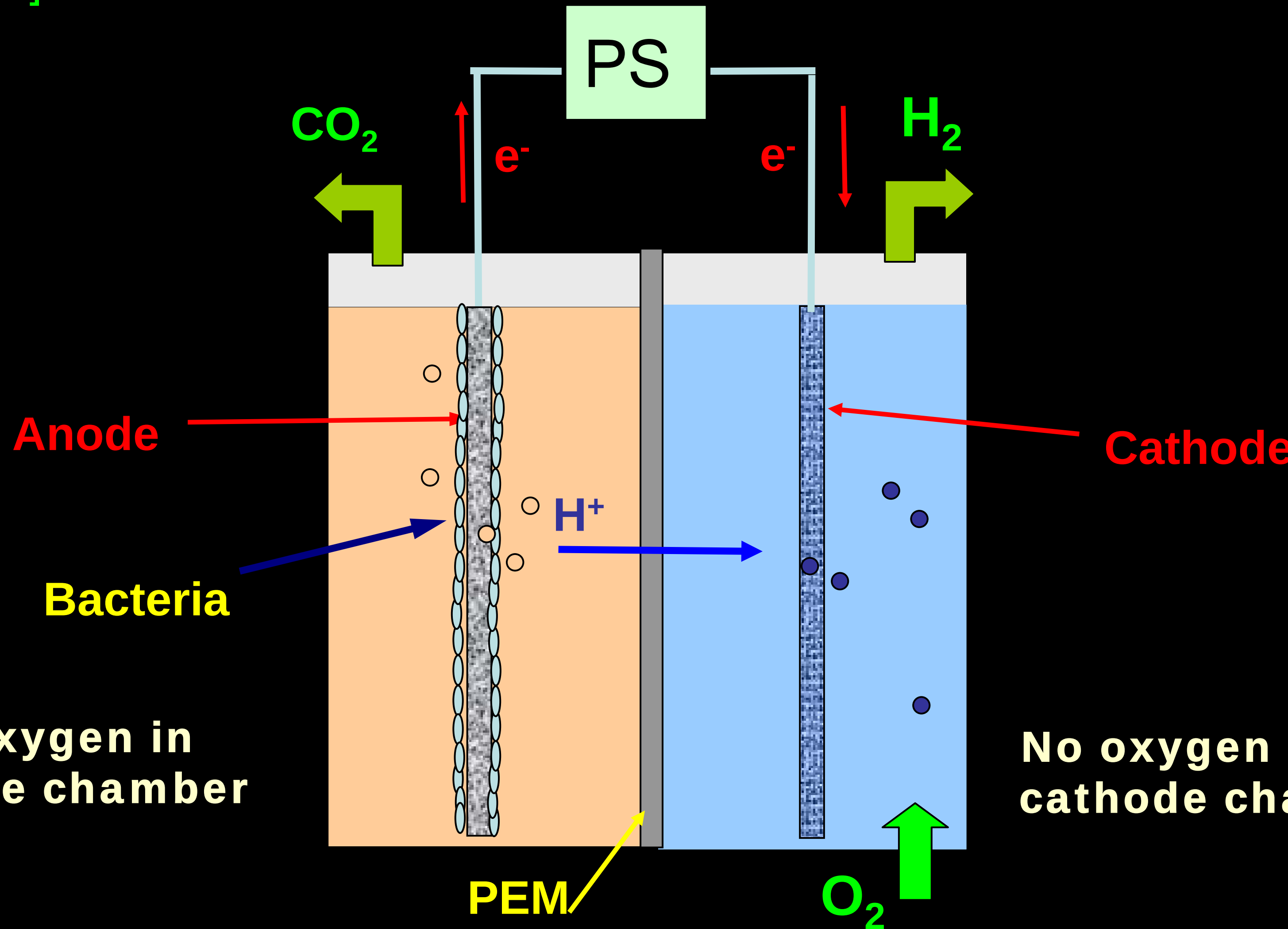
Anode: $C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+$
Cathode: $O_2 + 4\ H^+ + 4\ e- \rightarrow 2\ H_2O$

- *BEAMR Process: (no oxygen)*
  - Anode potential= -300 mV
  - Cathode potential: 0 mV
  - Needed to make H_2= 410 mV (theory)
  - Circuit (~300 mV) augmented with >110 mV= >410 mV

Anode: $C_2H_4O_2 + 2\ H_2O \rightarrow 2\ CO_2 + 8\ e^- + 8\ H^+$
Cathode: $8\ H^+ + 8\ e- \rightarrow 4\ H_2$

Biomass H_2- from any biomass using “BEAMR”

[Logan lab]



No oxygen in anode chamber

No oxygen in cathode chamber

0.25 V needed (vs 1.8 V for water electrolysis)

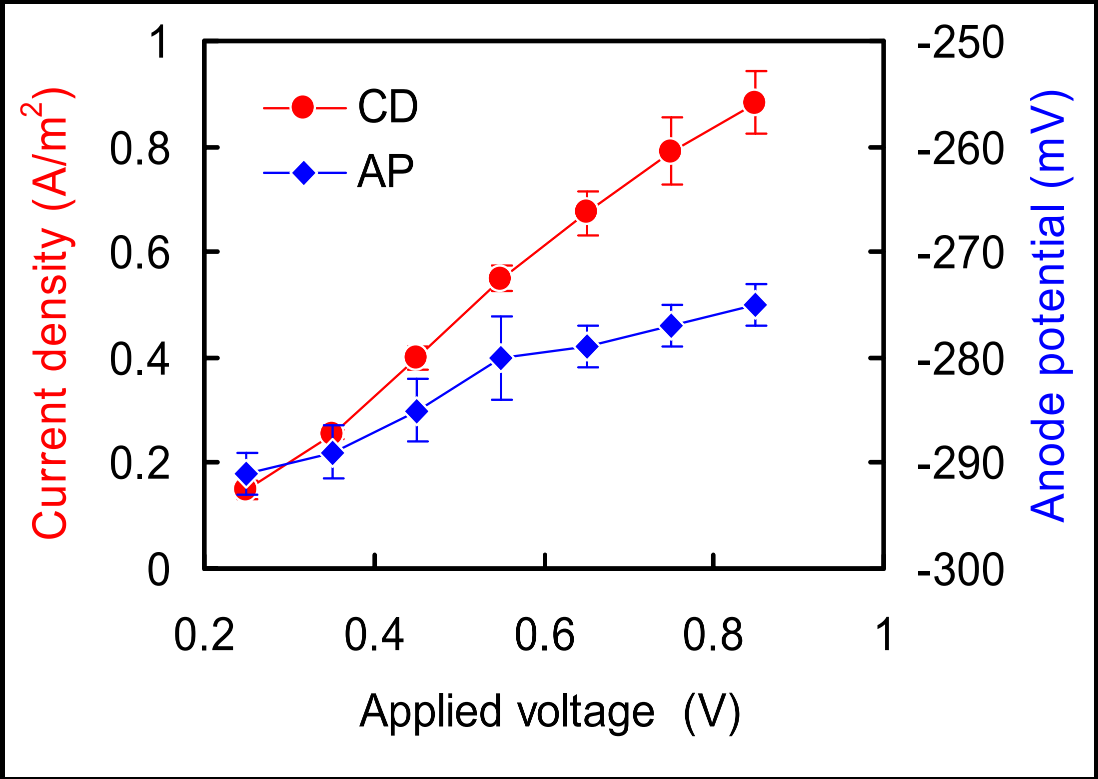
Ref: Liu, Grot and Logan, *Environ. Sci. Technol.* (2005)

Low applied voltages used for H_2 production

Minimum voltage needed is >0.25 V

(=0.11 V theory)

BEAMR voltage much less than that needed for water electrolysis (1.8 V)



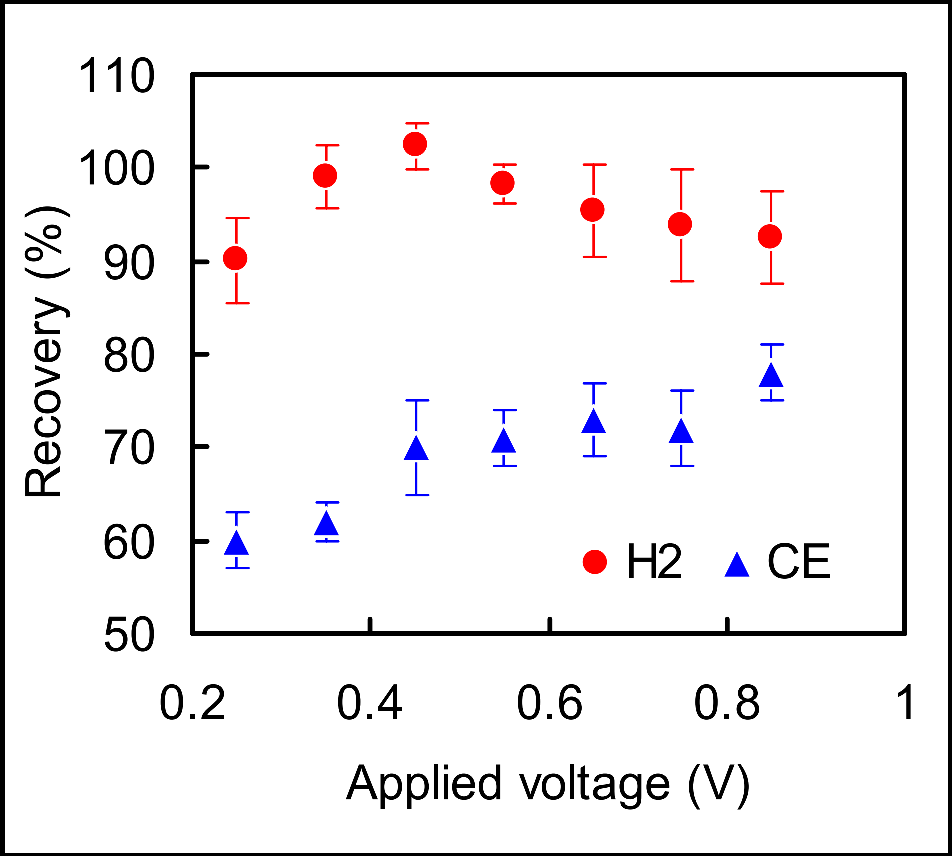
Source: Liu, Grot and Logan, *Environ. Sci. Technol.* (2005)

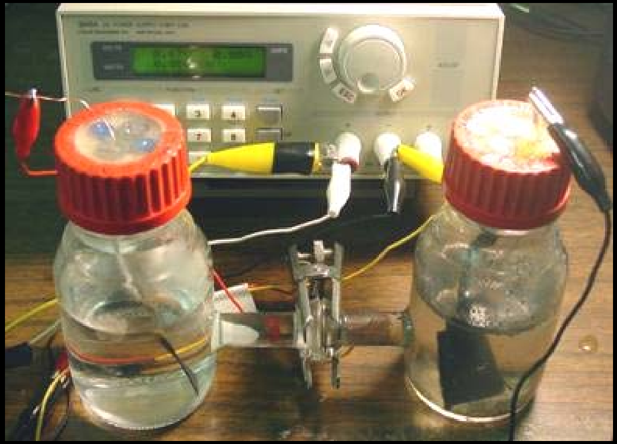
H2 Recovery

R_{CE}= 60%-78%
(electrons from substrate)

R_{Cat}=90-100%
(H_2 from electrons)

-Overall:
R_{H2}= >70% (>0.5 V)
(=2.9 mol-H_2/mol-acetate
vs maximum of 4 mol/mol)





Source: Liu, Grot and Logan, *Environ. Sci. Technol.* (2005)

Energy Production using MFC technologies

- Electricity production using microbial fuel cells
- H_2 Production from biomass using the BEAMR process: overcoming the “fermentation barrier”
- A path to renewable energy

Energy Utilization in the USA

US energy use:	97 quad
US electricity generation:	13 quad
Energy used for water infrastructure (water and wastewater)	0.6 quad (5%)

97 quad [quadrillion BTUs] = 28,400 TWh (terawatt hours)

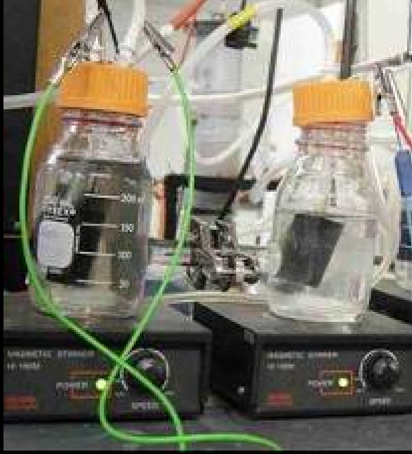
Energy value of wastewater

- Electricity used for water infrastructure= 0.6 quad (~5% of all electricity)
- Energy in wastewater= 0.5 quad
  - 0.1 quad of energy in domestic wastewater
  - 0.1 quad in food processing wastewater
  - 0.3 quad in animal wastes

Wastewater has 9.3× more energy than treatment consumes

(Toronto WWTP, Shizas & Bagley (2003)

CONCLUSIONS



- MFCs represent a viable technology for simultaneous electricity generation and wastewater treatment
- The BEAMR process can overcome the “fermentation barrier” and result in high yields of hydrogen from any source of biomass
- The technology now exists for system scaleup– pilot testing is needed.

Acknowledgements

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AFOSR: 2006-2009

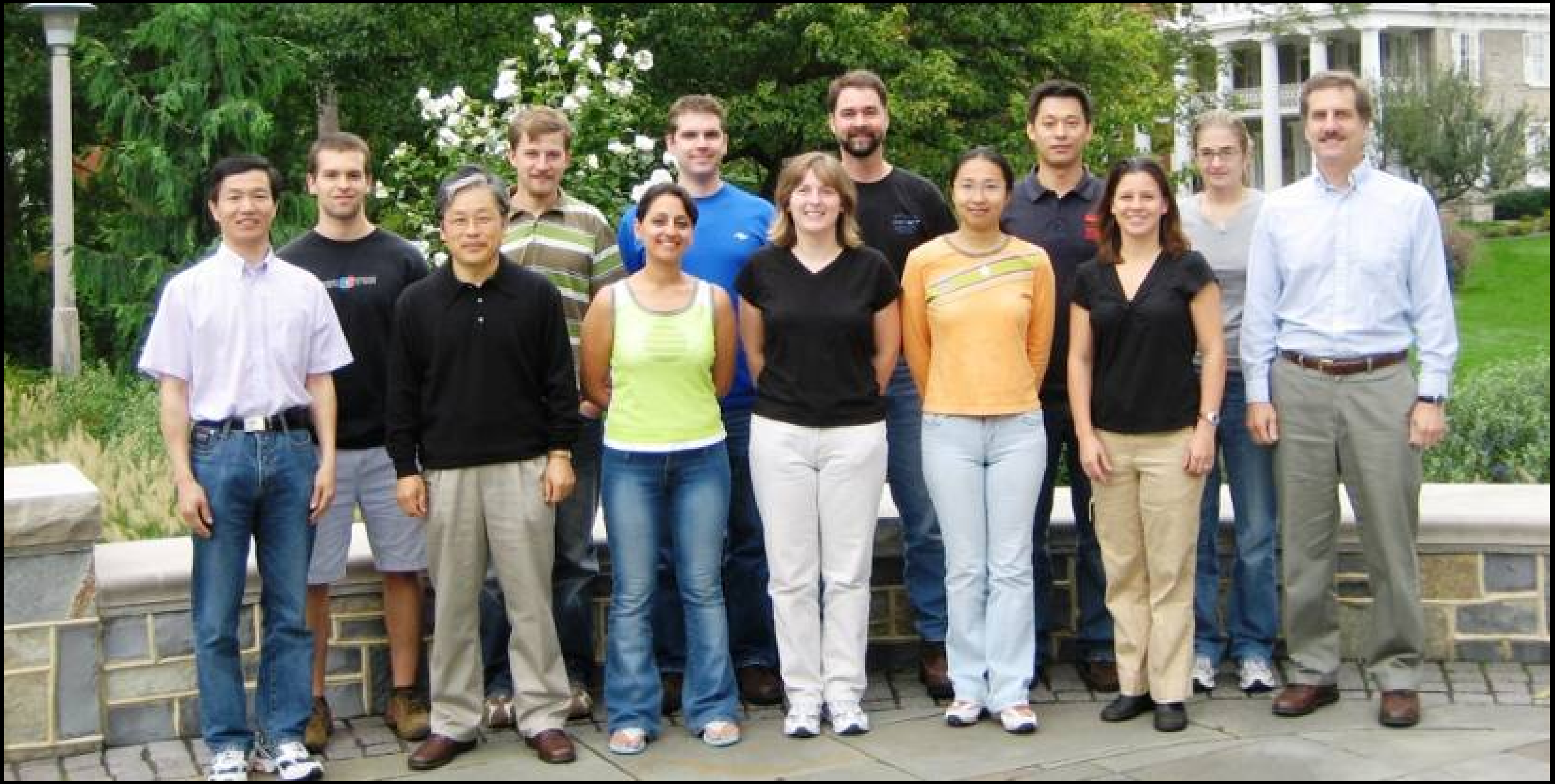
Air Products: 2006-2008

Previous sponsors:

NSF & EPA TSE (CTS Program)

USDA-DOE

Thanks to students and researchers in my laboratory at Penn State!



Left to right: Shaoan Cheng, Doug Call, KyeongHo Lim (visiting Prof), Markus Coenen (visitor), Farzaneh Rezai (PhD Ag&BioEng), Charles Winslow, Valerie Watson, David Jones (technician), Yi Zuo, Defeng Xing, Priscilla Selembo (PhD ChE), Rachel Wagner, [Bruce Logan]

Missing: Yujie Fang and YoungHo Ahn (visiting Profs), Jooyoun Nam (visiting student)

Questions ?

Email: blogan@psu.edu

Web page:
www.engr.psu.edu/ce/enve/logan.htm

Logan MFC webpage:
www.engr.psu.edu/ce/enve/mfc-Logan_files/mfc-Logan.htm

International MFC site:
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