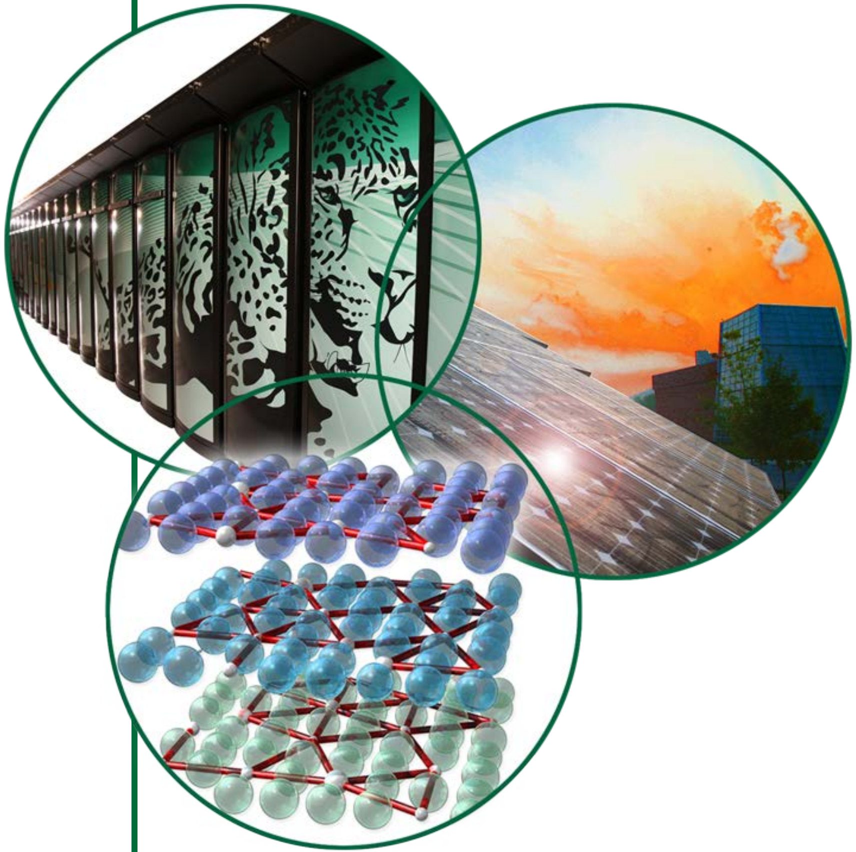
Renewable Hydrogen from Biomass Pyrolysis Aqueous Phase

Abhijeet P Borole (PI) [1]

Ramesh Bhave[1], Costas Tsouris[1,2], Spyros Pavlostathis[2], Sotira Yiacoumi[2], Philip Ye[3], Nikki Labbe[3], Pyongchung Kim[3], Jim Pollack[4], Dan Westerheim[5]

[1]Oak Ridge National Laboratory
[2]Georgia Institute of Technology
[3]University of Tennessee
[4]OmniTech international
[5]FuelCellEtc, Inc.
[6]Pall Corporation

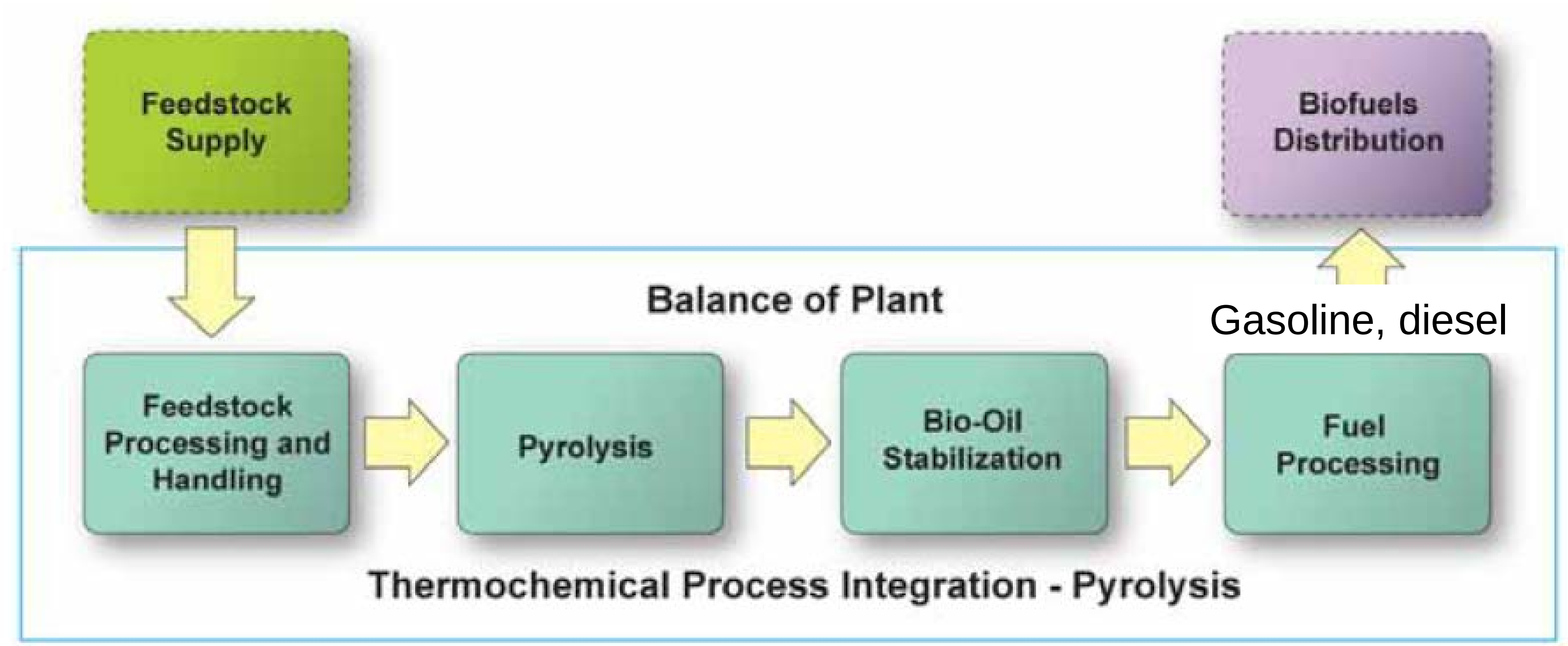
May 30, 2014
CHASE Project Webinar



Outline

- Background
  - Biomass pyrolysis process
  - Need for Hydrogen
  - Potential impact on efficiency of biofuel production
  - Potential impact on greenhouse gas emissions and sustainability
- Objectives
- Project tasks
- Team members
- Microbial Electrolysis
- Bio-oil production, oil-water separation, downstream membrane separations, LCA analysis.

Fast pyrolysis-based biofuel production


Feedstock Supply

Biofuels Distribution

Balance of Plant

Gasoline, diesel

Feedstock Processing and Handling

Pyrolysis

Bio-Oil Stabilization

Fuel Processing

Thermochemical Process Integration - Pyrolysis

Figure 2-16: Thermochemical Pyrolysis Route for Biomass to Biofuels

Ref: Biomass Multi-year Program Plan

Fast Pyrolysis Process Flow Diagram

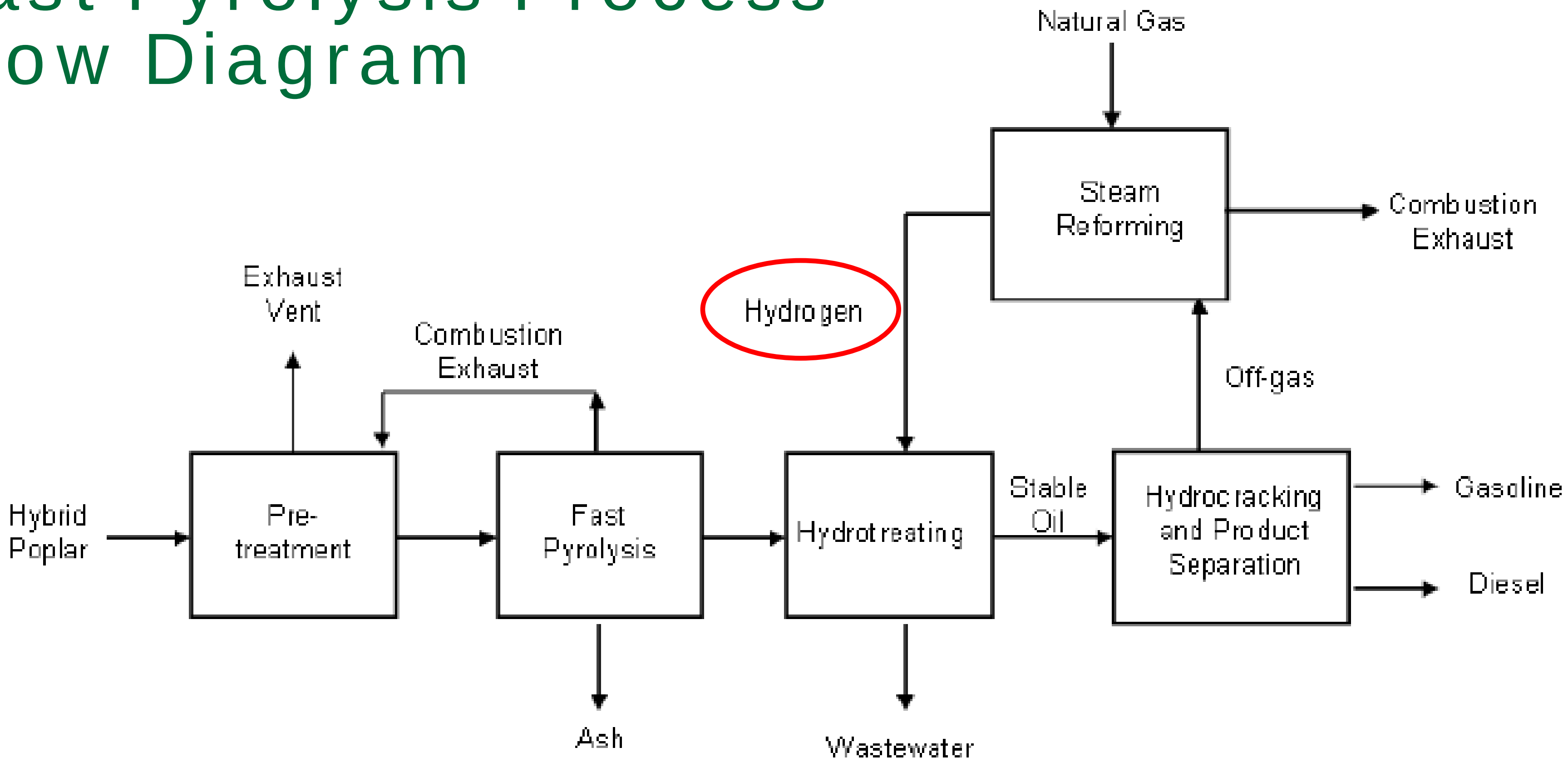


Figure 4.1. Block Diagram of Overall Design

Ref: Jones et al., *Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: A design case.*; PNNL-18284 Rev.1; Pacific Northwest National Laboratory: 2009

Biomass: $C_5H_7O_2N$ → gasoline (C_8H_{18}), diesel ($C_{12}H_{23}$)

Needs significant amount of hydrogen

Hydrogen production from natural gas

- Natural gas
  - *Steam-Reforming Reactions*
    Methane:
    $CH_4 + H_2O$ (+ heat) $\rightarrow CO + 3H_2$

T = 700-1000°C
P = 3-25 bar

- Producer gas from pyrolysis
  - *Water-Gas Shift Reaction*
    $CO + H_2O \rightarrow CO_2 + H_2$ (+ small amount of heat)

Hydrogen Efficiency and Process yields

Biooil characterization

	Model Results	Reference Data[a]	Reference Data[b]
Yields, lb/100 lb dry wood			
Oil	65	59.9	66
Water	10	10.8	12
Char & Ash	13	16.2	8
Gas	12	13.1	11
Loss			3
Oil Composition			
Water in oil, wt%	21	15-30	
Carbon, wt% dry	58	55-58	
Hydrogen, wt% dry	6	5.5-7.0	
Oxygen, wt% dry	36	35-40	

(a) Ringer et al. 2006
(b) Mohan et al. 2006

Fuel product characterization

	Model	Reference Data[a]	Reference Data[b]
Yields, lb /100 lb wet pyrolysis oil			
Stable Oil (Stream 304)	44		38
Water (Stream 230)	48		50
Gas (Streams 270 and 302)	13		12 by difference
Chemical H_2 Consumption, lb/100 lb dry oil	4.96	5.01	3.45
Stable Oil Composition (Stream 304)			
Water, ppm	0	50	0
Aromatics, wt%		10.0	Not reported
Carbon, wt% dry	88.1	86.8	86.8
Hydrogen, wt% dry	10.5	13.2	10.8
Oxygen, wt% dry	1.5	0.02	2.5
Specific Gravity	0.87	0.83	0.93
Btu/lb, gross	17,600	19,765	17,302
Btu/lb, net	16,600	18,525	16,276

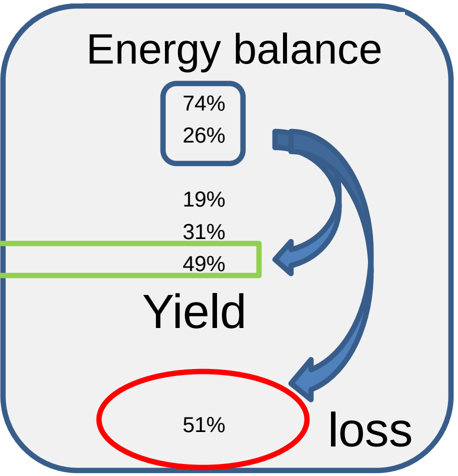
(a) Tables 15 & 16 in Elliot 2007
(b) Beckman et al. 1990, Chapter 5

Ref: Jones et al., *Production of gasoline and diesel from biomass via fast pyrolysis, hydrotreating and hydrocracking: A design case.*; PNNL-18284 Rev.1; Pacific Northwest National Laboratory: 2009

Carbon balance

Feeds	Biomass	88%
	Natural Gas	12%
	sum	100%
Fuel Products	Gasoline Pool	23%
	Diesel Pool	32%
	Fuels sum	55%
Waste Products	Pyrolysis Unit Exhaust	23%
	Upgrading Wastewater	0%
	Upgrading Heaters Exhaust	2%
	Reformer Exhaust	20%
	Waste sum	45%

Energy balance



The energy content of the fuel product depends significantly on natural gas input (26-40% of energy input)

ORNL preliminary energy balance

Note: The data on this slide should not be distributed, forwarded or cited.

Other issues

- Problems
  - Stability of biooil (polar-non-polar separation over time)
  - Corrosivity due to acids (biooil pH = 2.8)
  - Biooil and fuel yield (biomass basis)
  - Loss of carbon to aqueous phase

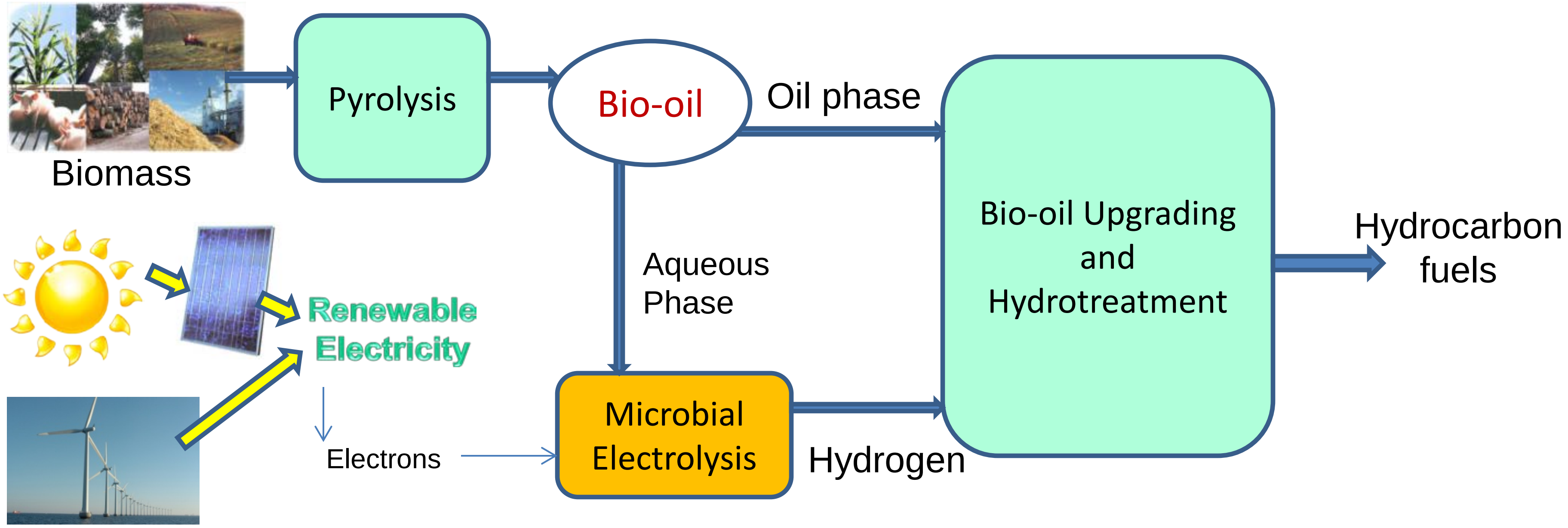
Phenolic acids

CH_3COOH

Acetic acid

CHASE program:
Carbon, hydrogen and separations efficiency improvement.

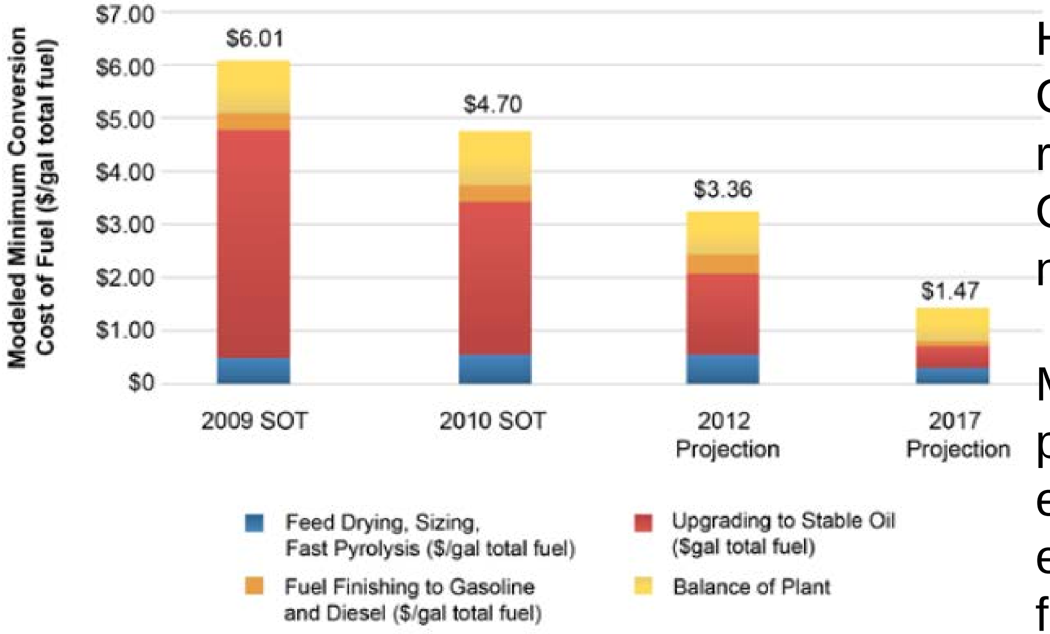
Project Outline



Schematic of the biomass to biofuel process with modifications to enable improvement in hydrogen efficiency

Note: The information on this slide should not be distributed, forwarded or cited.

Focus: Hydrogen



Ref: Biomass Multi-year Program Plan

Hydrogen production expenses:
Capital costs: 28% for natural gas reformer
Operating Expenses: 16% for natural gas

Minimizing natural gas use has potential to minimize operating expenses, while meeting GHG emission goals to meet Renewable fuel standard (RFS).

- Is there an alternate way to meet the objectives without using natural gas?
  - Oil stabilization
  - Upgrading to gasoline/diesel fuels
  - Reducing cost of hydrogen

Project objectives

- **Develop reforming process for efficient conversion of aqueous phase organics to hydrogen via microbial electrolysis.**
- Develop energy-efficient methods to separate bio-oil aqueous phase, extract acidic and polar compounds from bio-oil for production of hydrogen.
- Demonstrate improvement in hydrogen efficiency via mass and energy balance.
- Demonstrate potential for reduction in life cycle greenhouse gas emissions via life-cycle analysis.

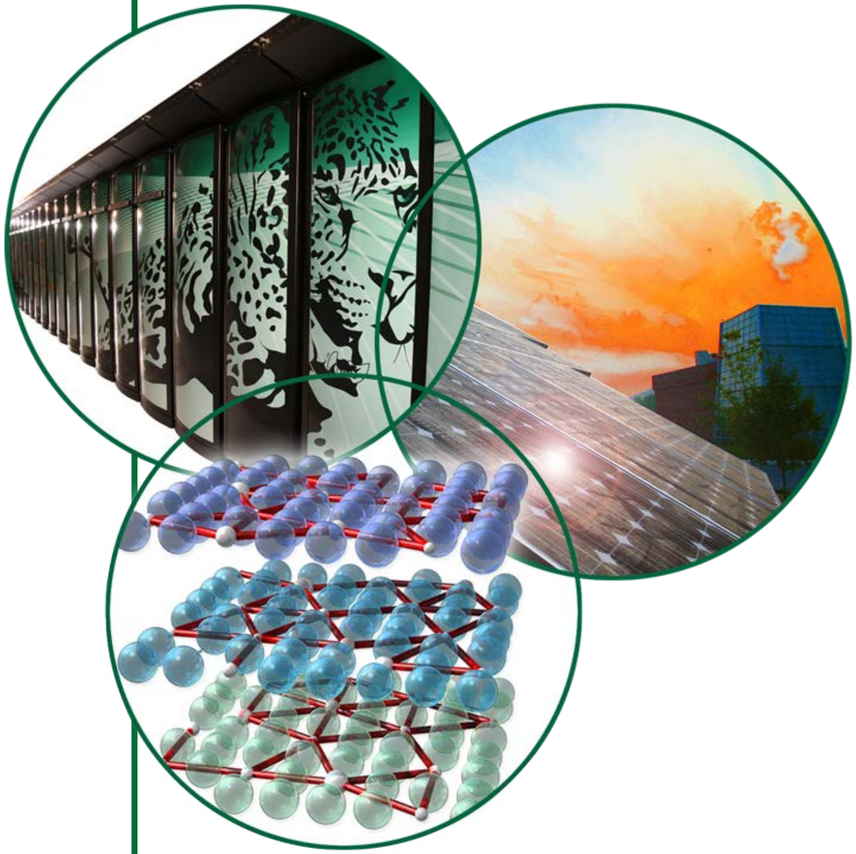
Address Technical Area 2: Hydrogen Efficiency,

Subtopic: *Reforming hydrogen from aqueous streams in biomass liquefaction*.

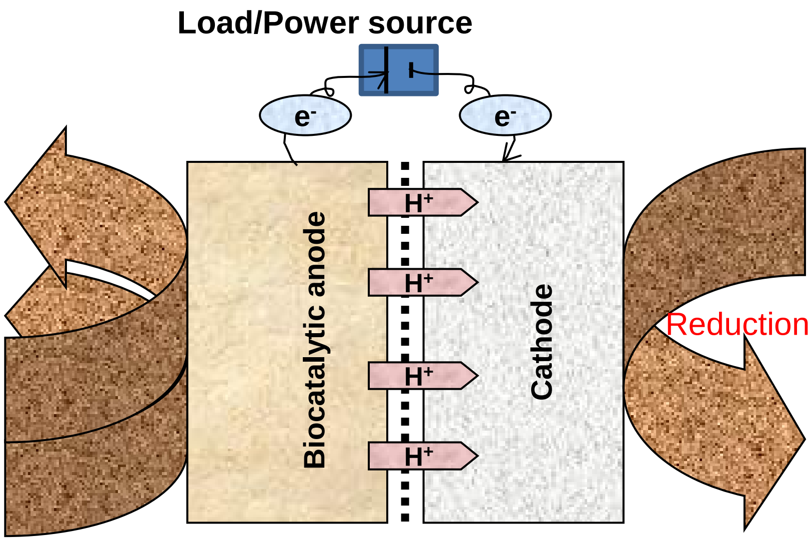
Potential Impacts

- The proposed work will enable efficient conversion of the corrosive and polar, carbon-containing compounds in bio-oil aqueous phase to hydrogen.
- Potential to improve the stability of the bio-oil and reduce corrosivity.
- The implementation of MEC reforming and separation unit operations being developed in this study will enable improvements in hydrogen production and overall biomass to biofuel conversion efficiency while minimizing use of natural gas and thus reducing life cycle greenhouse gas emissions.

Microbial Electrolysis



Bioelectrochemical Conversion Technology



Cell mass

$CO_2 + H_2O$

Nutrients

Organic Carbon/ Reduced substrate/ Waste

Substrate

Product / Fuel / Chemical

BioElectrochemical System (BES)

$C_xH_yO_z \rightarrow CO_2 + H^+ + e^-$

MEC: $H^+ + e^- \rightarrow H_2$

Type of BES	Cathode substrate	Product
MFC	Oxygen	Electricity
MEC	**Protons**	**Biohydrogen**
BES	Acetate	Ethanol/biofuel
BES	Oxygen	Hydrogen peroxide
BES	Carbon dioxide	Electrofuels
BES	other/sunlight	Photo/biofuels

[2] Borole, A. P., Reguera, G; Ringeisen, B.; Wang, Z-W; Feng, Y.; Kim, B H; I. (2011). "Electroactive biofilms: Current status and future research needs." Energy Environ. Sci. **4**: 4813-4834.

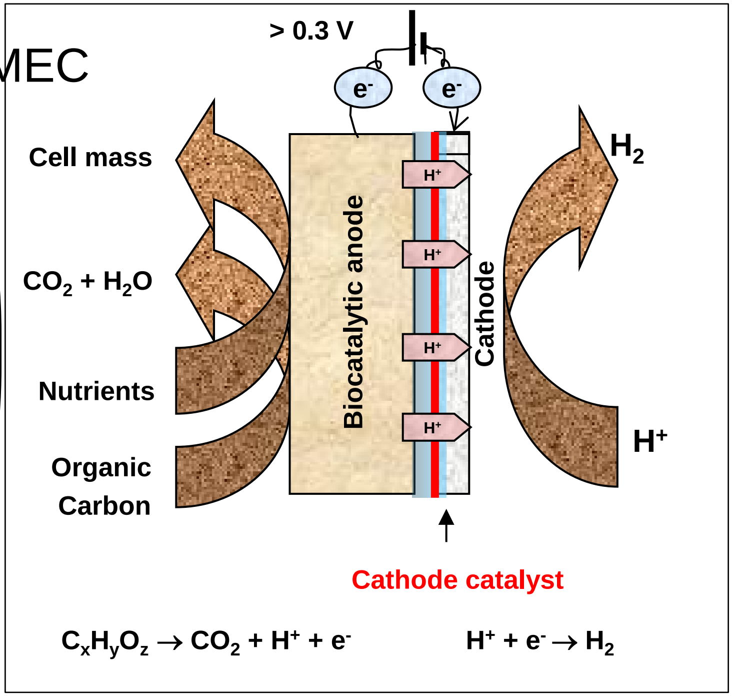
Proposed path: Bio-oil Aqueous Phase

→ electrons + protons in MEC (anode)

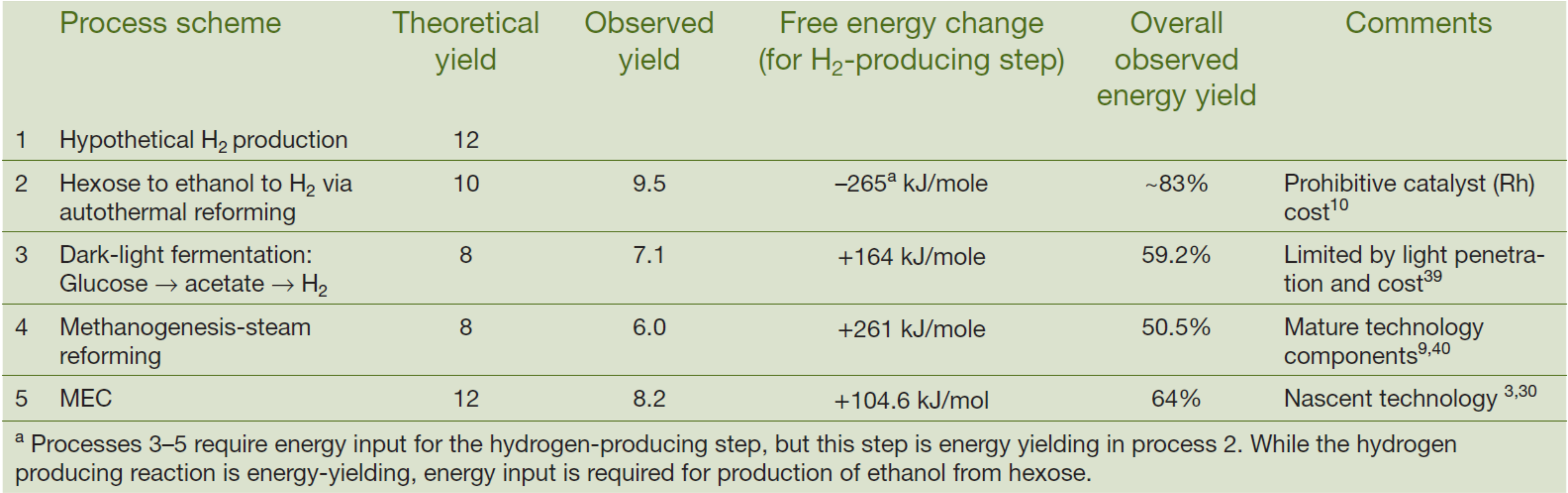
→ $BioH_2$ (cathode)

Microbial Electrolysis for converting aqueous phase generated during pyrolysis to hydrogen

- Pyrolysis derived aqueous phase
  - Potential for loss of carbon via aqueous phase
  - Emulsifies with oil phase
  - Makes bio-oil unstable (polar-non-polar separation over time)
  - Makes bio-oil corrosivity due to acids (bio-oil pH = 2.8)
- Microbial electrolysis
  - Conversion of biooil aqueous organics to hydrogen
  - Anode: Conversion of degradable organics to electrons, protons and CO_2
  - Cathode: Proton reduction to hydrogen at applied potential of 0.3-1V.
  - Develop electroactive biofilms with tolerance to inhibitory and toxic molecules in biooil aqueous phase (furfural, HMF, phenolics, etc.)



Biological hydrogen production MEC vs. Existing Technologies



	Process scheme	Theoretical yield	Observed yield	Free energy change (for H_2-producing step)	Overall observed energy yield	Comments
1	Hypothetical H_2 production	12				
2	Hexose to ethanol to H_2 via autothermal reforming	10	9.5	–265[a] kJ/mole	~83%	Prohibitive catalyst (Rh) cost[10]
3	Dark-light fermentation: Glucose → acetate → H_2	8	7.1	+164 kJ/mole	59.2%	Limited by light penetration and cost[39]
4	Methanogenesis-steam reforming	8	6.0	+261 kJ/mole	50.5%	Mature technology components[9,40]
5	MEC	12	8.2	+104.6 kJ/mol	64%	Nascent technology [3,30]

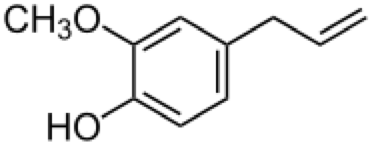
[a] Processes 3–5 require energy input for the hydrogen-producing step, but this step is energy yielding in process 2. While the hydrogen producing reaction is energy-yielding, energy input is required for production of ethanol from hexose.

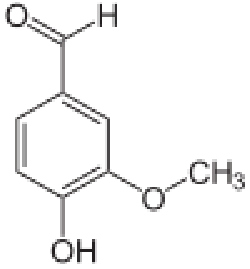
Borole, A. P. (2011). Biofuels, Bioproducts & Biorefining "Improving energy efficiency and enabling water recycle in biorefineries using bioelectrochemical cells." **5**(1): 28-36.

Pyrolysis-derived water-soluble compounds

- Furfural
- Acetic acid
- Phenolics
- Vanillin
- Eugenol
- Acetol
- unknowns

Convert in MEC:
e.g., Vanillin:
$C_8H_8O_3 + 13H_2O \rightarrow 17H_2 + 8CO_2$.





Many of these molecules have not been tested in MEC previously

Biomass to fuels conversion reaction (with MEC reforming included):

$30\ CH_2O$ (biomass) $+ 0\ CH_4 + 0\ H_2O + kW$

$\rightarrow C_8H_{18}$ (gasoline) $+ C_{12}H_{23} + 10\ CO_2 + 10\ H_2O$ (diesel)

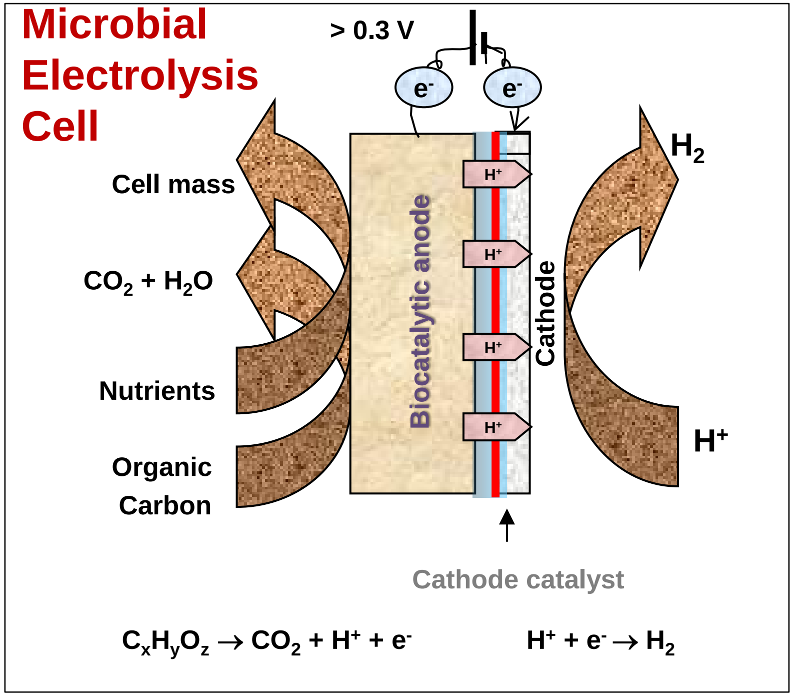
Note: The data on this slide should not be distributed, forwarded or cited.

Interdisciplinary Components

Analytical chemistry

Bio-oil and aqueous phase analysis

- *-Chromatography*
- *-Mass spectrometry*
- *-UV-Vis spectroscopy*



$C_xH_yO_z \rightarrow CO_2 + H^+ + e^-$

$H^+ + e^- \rightarrow H_2$

Biology

- *Microbiology*
- *Molecular Biology*
- *Biocatalysis*

Electrochemistry

- *Electrocatalysis*
- *Voltammetry*
- *Chronoamperometry*
- *Impedance spectroscopy*

Engineering

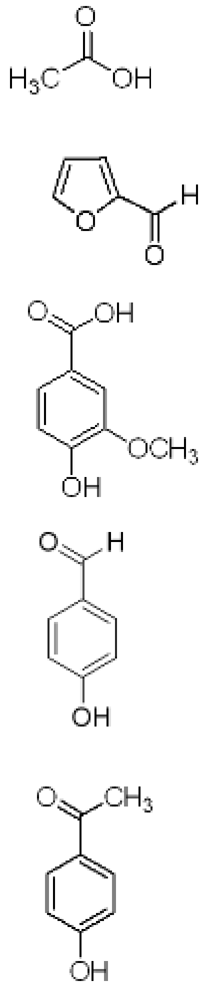
- *Chemical Engineering*
- *Electrochemical Engineering*
- *Environmental Engineering*
- *Life-cycle analysis*

Materials chemistry

- *Membrane materials*
- *Electrode materials*
- *Catalyst formulation*

Handling toxic molecules in MFC/MEC

- Typical substrates
  - Hemicellulose byproducts - acetic acid (deacetylation).
  - Sugar degradation products – furfural, hydroxymethylfurfural
  - Lignin degradation products – phenolic aldehydes and ketones and acids.
- Investigate energy recovery from acidic molecules while managing toxic compounds present in biooil aqueous phase (mechanisms).
  - Transformation of toxic molecules to non-toxic products without energy extraction
  - Mineralization of recalcitrant and inhibitory byproducts[1]
- Evaluate potential for water recycle
- Applicable to fermentation-derived biorefinery wastewater stream, enabling processing high biomass loading (> 20% solids) cellulosic biochemical conversion process with water recycle.



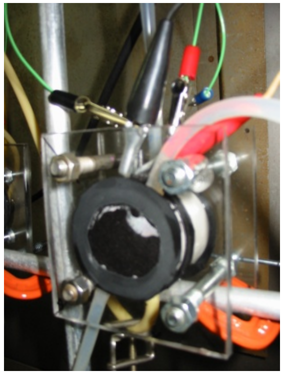
Borole, et.al., 2009, Biotechnol for Biofuels., *Controlling accumulation of fermentation inhibitors in biorefinery process water using Microbial Fuel Cells,* April 2009, 2, 1, 7.

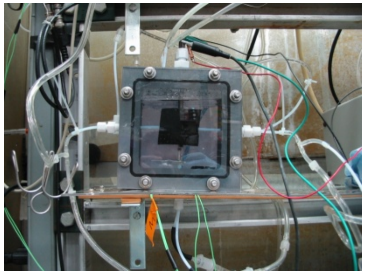
Approach to bioanode development

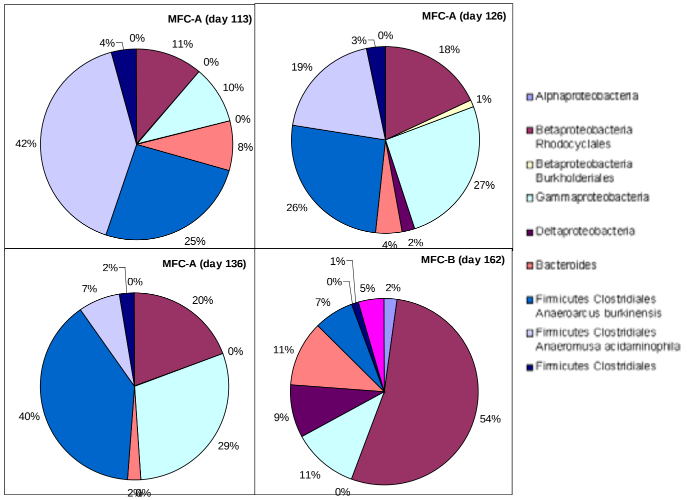
- Development of engineered bioanode systems for energy recovery – To increase current density.
- Designed novel BES systems to achieve high coulombic efficiency and current density – Engineering parameter optimization.
- Enrichment of electroactive microbial catalysts for conversion of organic acids, sugars, etc to bioenergy – Biocatalyst development.
- Assessment of limitations in bioanode performance – Electrochemical Impedance Spectroscopy.
- Characterization of the microbial communities to understand the diversity of novel electrogenic organisms.
    - Microbial diversity of exoelectrogens

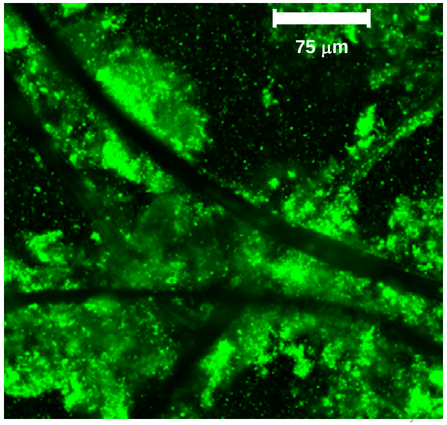
Borole, A. P. (2010). Microbial fuel cell with improved anode, US Patent 7,695,834. USA, UT-Battelle. US Patent 7,695,834.

Borole et.al., 2009, J. Power Sources, **191**(2): 520-527..



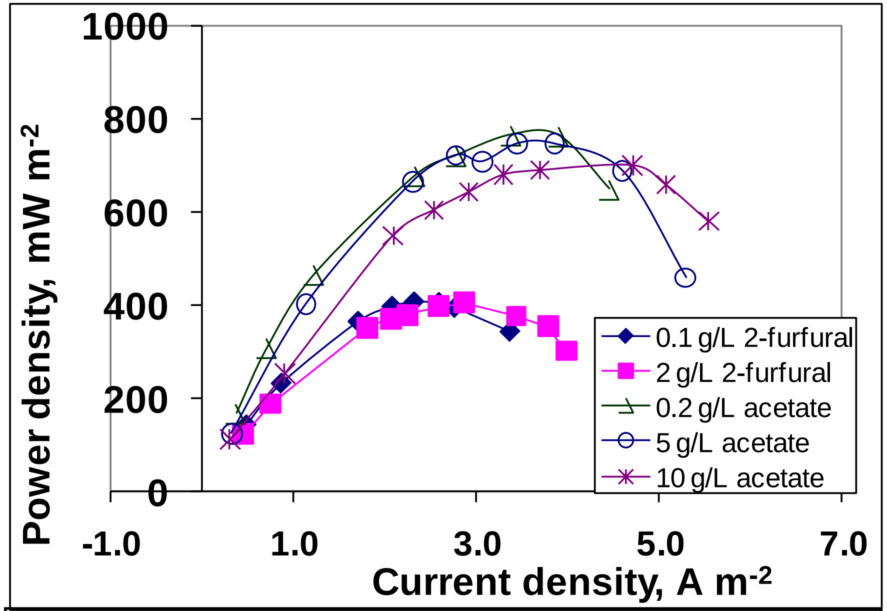


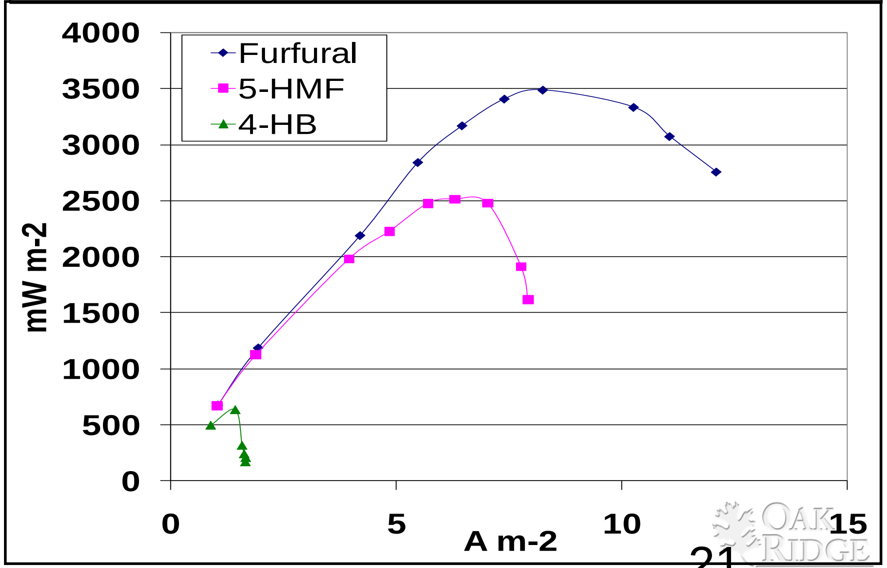




Conversion of furan aldehydes and phenolic molecules in bioanode

- Demonstrated potential of bioanode to remove furfurals, phenolics, organic acids, and sugar derivatives in model aqueous streams[3].
- Examine effect of concentration of toxic/ inhibitory molecules at representative concentrations (acetate 10 g/L, 2-furfural, HMF, phenolics: 1-4 g/L)
    - No detrimental effect on current production
- Near complete removal of the substrates
- Coulombic efficiency up to 64%
- Current density : up to 10 A/m2 (3700 mW/m2 power density)

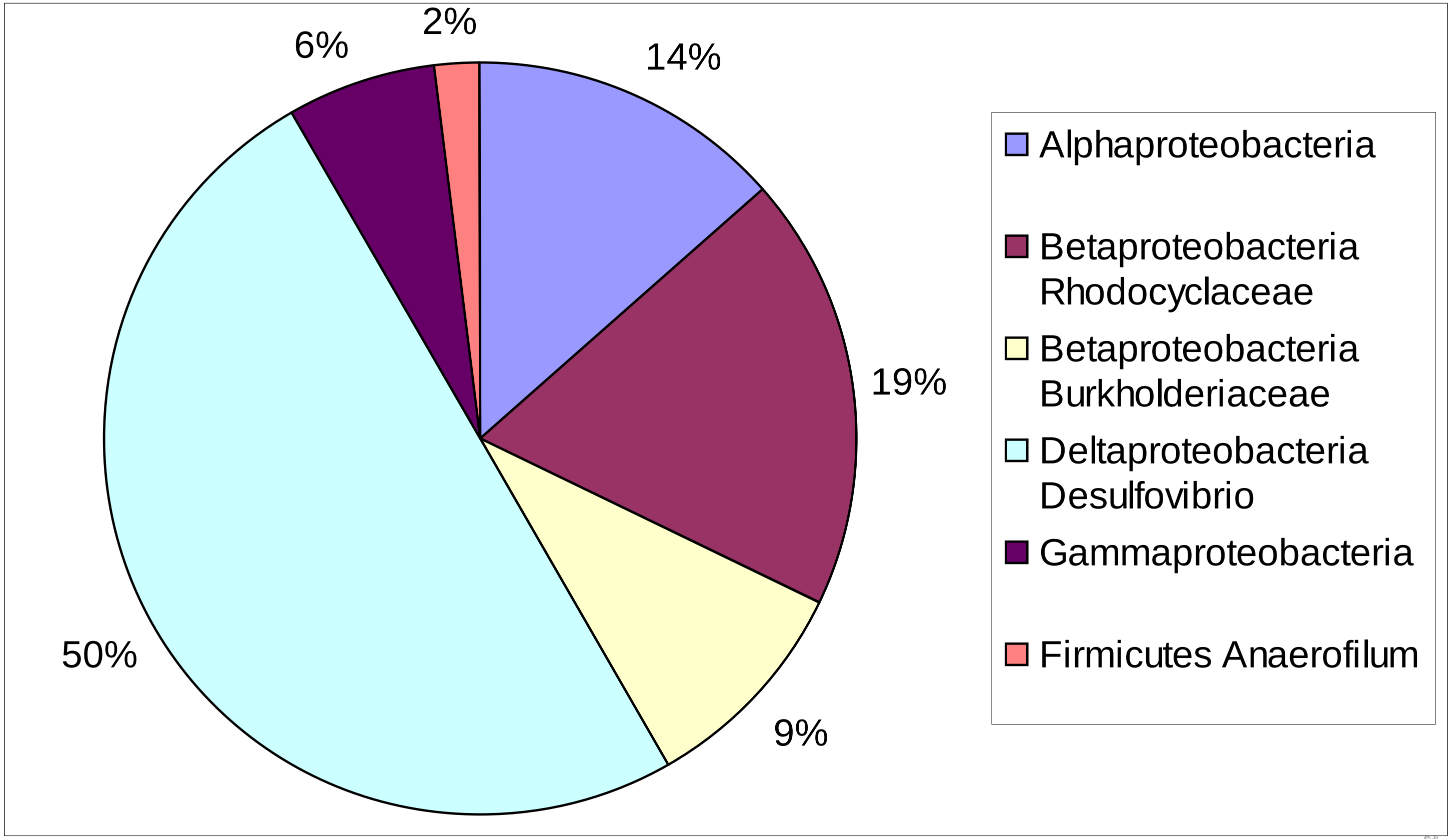


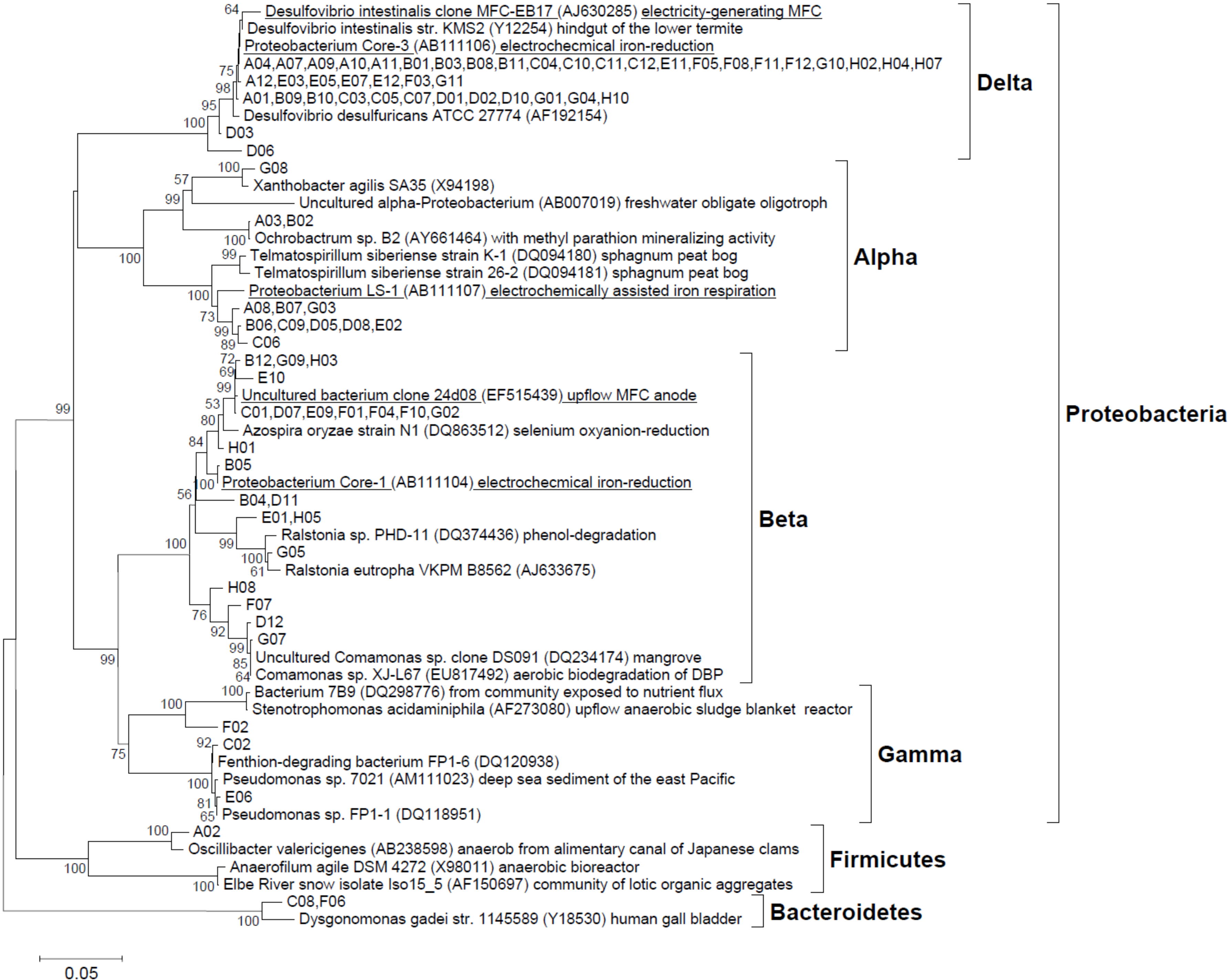


Borole, et.al., 2009, **Biotechnol for Biofuels.**, Controlling accumulation of fermentation inhibitors in biorefinery process water using Microbial Fuel Cells, April 2009, 2, 1, 7.

Electroactive Biocatalyst Characterization

- Biofilm sample from bioanode developed for model substrate mixtures (furfural, HMF, 3 phenolic compounds, acetic acid,)
- 16S rRNA analysis

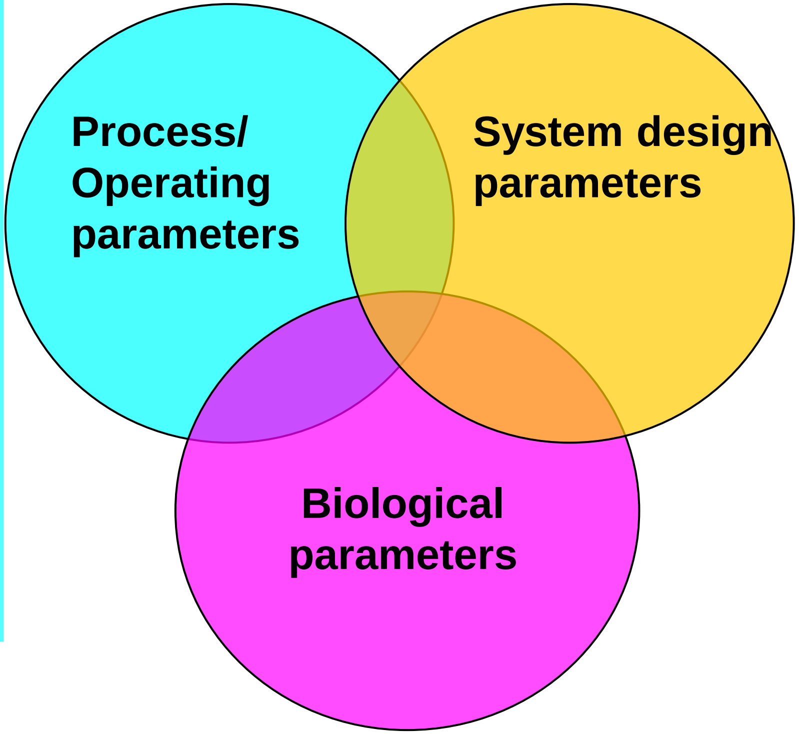



64
Desulfovibrio intestinalis clone MFC-EB17 (AJ630285) electricity-generating MFC
Desulfovibrio intestinalis str. KMS2 (Y12254) hindgut of the lower termite
Proteobacterium Core-3 (AB111106) electrochecmical iron-reduction
75
A04,A07,A09,A10,A11,B01,B03,B08,B11,C04,C10,C11,C12,E11,F05,F08,F11,F12,G10,H02,H04,H07
98
A12,E03,E05,E07,E12,F03,G11
95
A01,B09,B10,C03,C05,C07,D01,D02,D10,G01,G04,H10
100
Desulfovibrio desulfuricans ATCC 27774 (AF192154)
D03
D06
Delta
100
G08
57
Xanthobacter agilis SA35 (X94198)
99
Uncultured alpha-Proteobacterium (AB007019) freshwater obligate oligotroph
A03,B02
100
Ochrobactrum sp. B2 (AY661464) with methyl parathion mineralizing activity
100
99
Telmatospirillum siberiense strain K-1 (DQ094180) sphagnum peat bog
Telmatospirillum siberiense strain 26-2 (DQ094181) sphagnum peat bog
Alpha
100
Proteobacterium LS-1 (AB111107) electrochemically assisted iron respiration
73
A08,B07,G03
99
B06,C09,D05,D08,E02
89
C06
72
B12,G09,H03
69
E10
99
Uncultured bacterium clone 24d08 (EF515439) upflow MFC anode
53
C01,D07,E09,F01,F04,F10,G02
99
80
Azospira oryzae strain N1 (DQ863512) selenium oxyanion-reduction
84
H01
B05
100
Proteobacterium Core-1 (AB111104) electrochecmical iron-reduction
56
B04,D11
Beta
Proteobacteria
E01,H05
100
99
Ralstonia sp. PHD-11 (DQ374436) phenol-degradation
100
G05
61
Ralstonia eutropha VKPM B8562 (AJ633675)
H08
F07
76
D12
92
G07
99
Uncultured Comamonas sp. clone DS091 (DQ234174) mangrove
99
85
64
Comamonas sp. XJ-L67 (EU817492) aerobic biodegradation of DBP
100
Bacterium 7B9 (DQ298776) from community exposed to nutrient flux
100
Stenotrophomonas acidaminiphila (AF273080) upflow anaerobic sludge blanket reactor
F02
92
C02
Gamma
75
Fenthion-degrading bacterium FP1-6 (DQ120938)
100
Pseudomonas sp. 7021 (AM111023) deep sea sediment of the east Pacific
81
E06
65
Pseudomonas sp. FP1-1 (DQ118951)
100
A02
Oscillibacter valericigenes (AB238598) anaerob from alimentary canal of Japanese clams
Firmicutes
100
Anaerofilum agile DSM 4272 (X98011) anaerobic bioreactor
100
Elbe River snow isolate Iso15_5 (AF150697) community of lotic organic aggregates
C08,F06
Bacteroidetes
100
Dysgonomonas gadei str. 1145589 (Y18530) human gall bladder
0.05

Developing high performance MECs

Electroactive Biofilm Optimization

1. Batch vs. flow system
2. External resistance
3. Redox potential
4. Shear rate / liquid flow rate
5. pH
6. Substrate loading
7. Temperature
8. Aerobic vs. anaerobic
9. Ionic strength



1. Electrode spacing
2. Presence of membrane and type of membrane
3. Relative anode:cathode surface area
4. Electrode surface area to volume ratio
5. Electrode properties: conductivity, hydrophilicity, porosity, etc.
6. Type of cathode (oxygen diffusion)

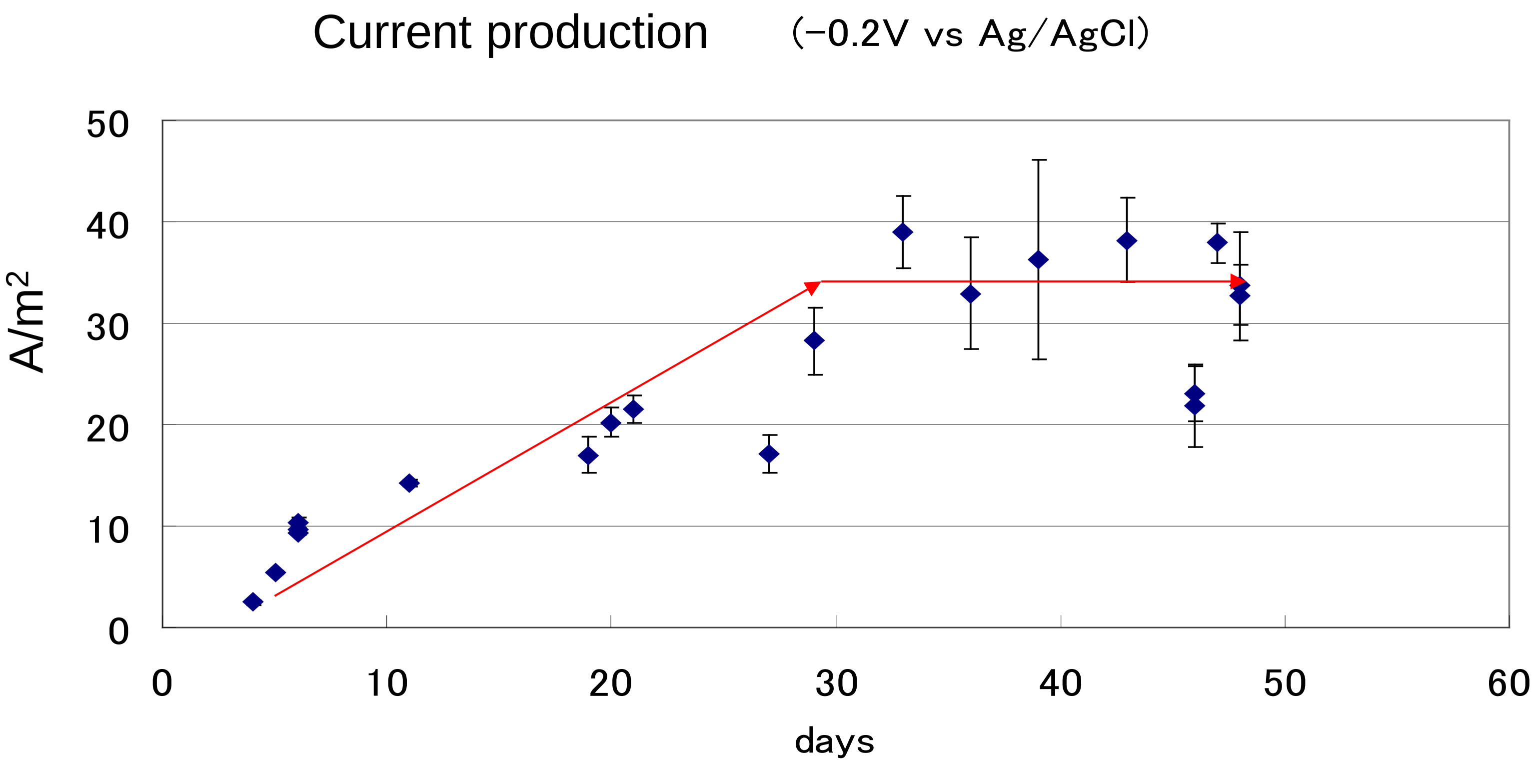
1. Source of inoculum
2. Pure culture vs. consortium
3. Gram-positive vs. Gram-negative

Biofilm parameters (Dependent variables)

1. Biofilm growth rate
2. Specific rate of electron transfer
3. Ability to synthesize redox-active mediators
4. Ability to grow nanowires and perform DET
5. Relative exoelectrogen population
6. Characteristics of EPS layer
7. Extent of substrate mineralization
8. Substrate specificity

Borole AP, Reguera G, Ringeisen B, Wang Z, Feng Y, Kim, BH, 2011, **Energy Environ. Sci**. (Review paper)
Electroactive Biofilms: Current Status and Future Research Needs, 4:4813-4834

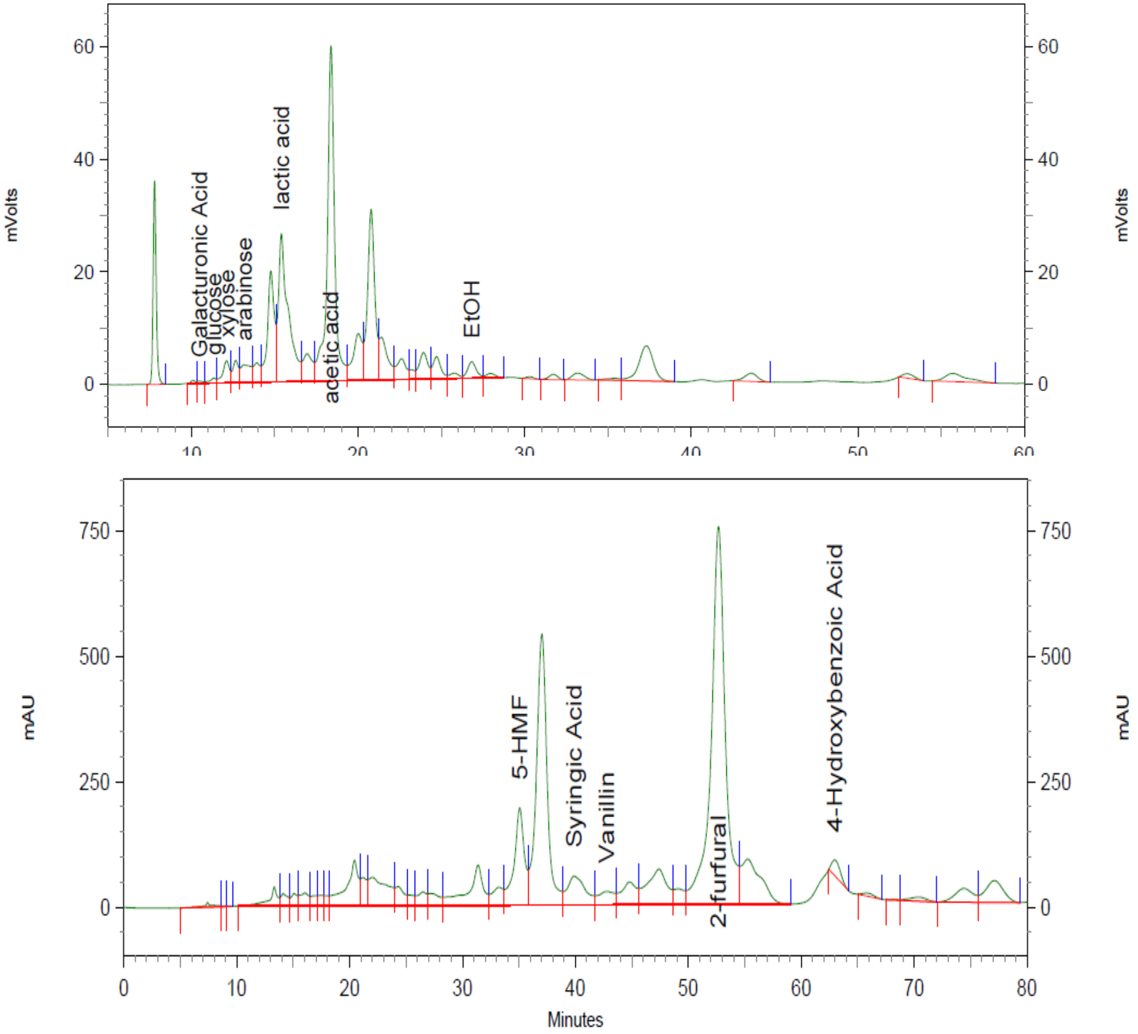
Stability of maximum current production



Current density increased first 30 days, thereafter, it remained ~ 35 A/m² for 20 days, but not without fluctuations.
Coulombic efficiency ranged from 50-80% (for fermentative substrates glucose + lactate)

Note: The data on this slide should not be distributed, forwarded or cited.

Biooil aqueous phase analysis

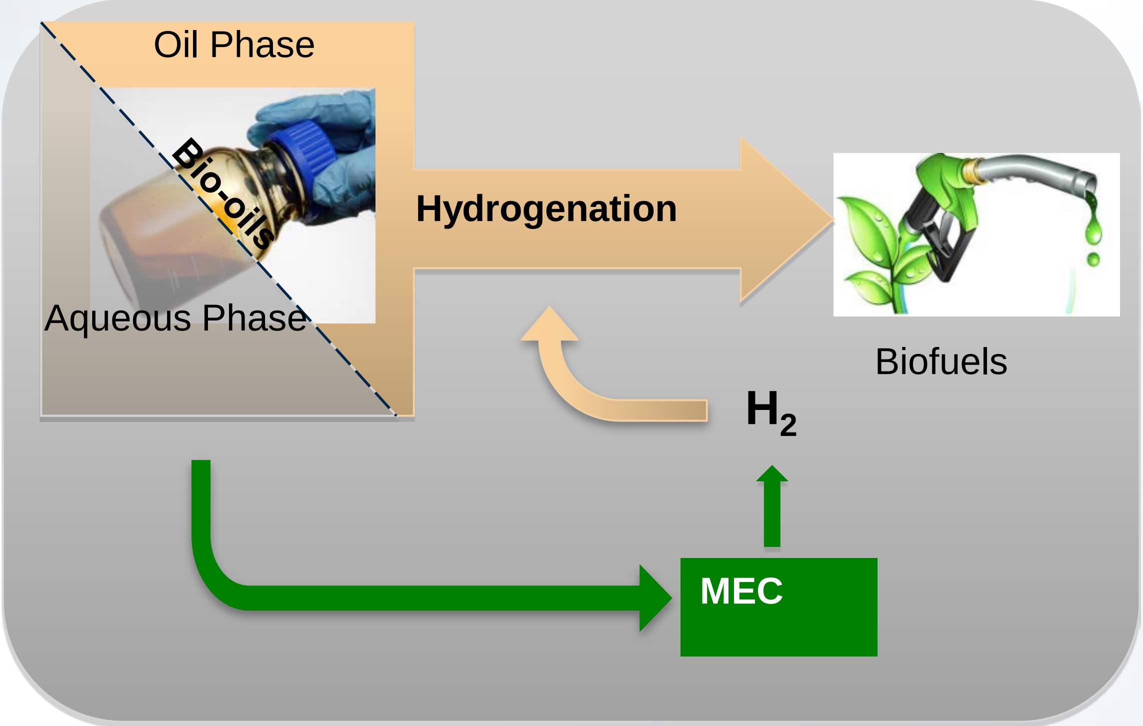


Bio-oil aqueous phase characterization via HPLC

Note: The data on this slide should not be distributed, forwarded or cited.

Renewable Hydrogen Production from Pyrolysis Aqueous Phase
Task II: Reforming of Aqueous Phase to Hydrogen using MEC

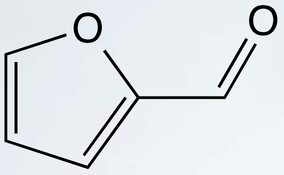
- Objective: Assess the biotransformation extent of specific model compounds in anodic biofilms and their contribution to hydrogen production



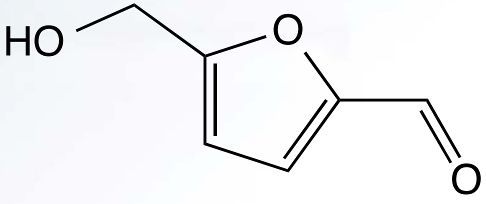
Renewable Hydrogen Production from Pyrolysis Aqueous Phase
Task II: Reforming of Aqueous Phase to Hydrogen using MEC

Model Compounds

Furan Compounds

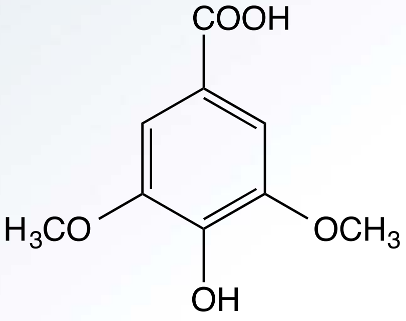


Furfural

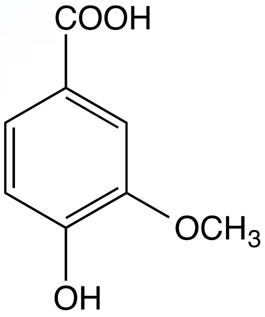


5-hydroxymethylfurfural

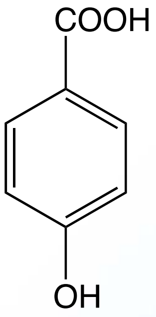
Phenolic Compounds



Syringic acid

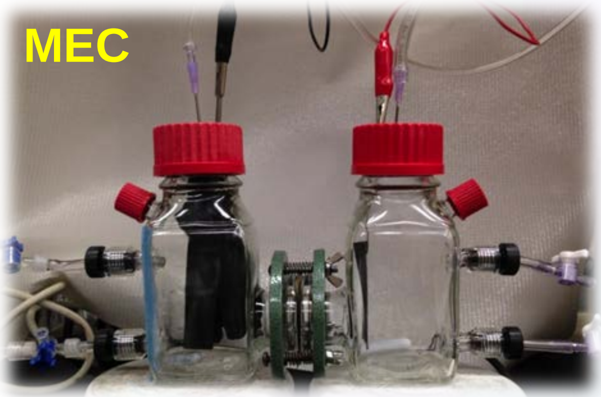


Vanillic acid



4-hydroxybenzoic acid

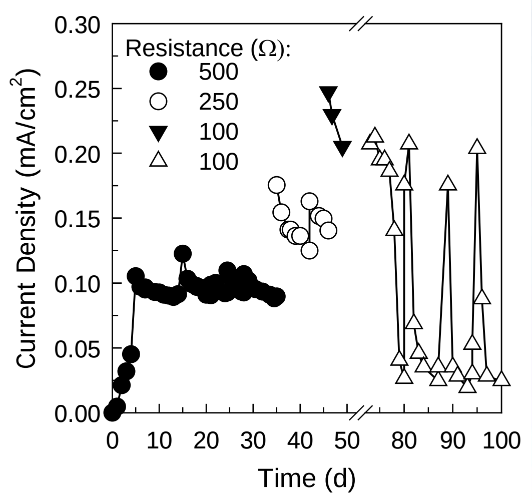
- **Experimental Setup**

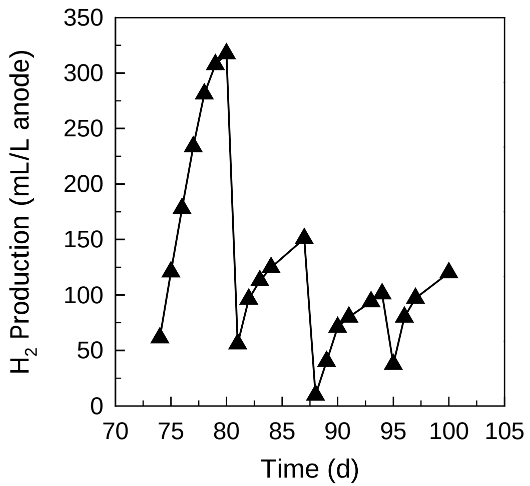


A MFC maintained as stock culture to provide inoculum for MECs

Renewable Hydrogen Production from Pyrolysis Aqueous Phase
Task II: Reforming of Aqueous Phase to Hydrogen using MEC

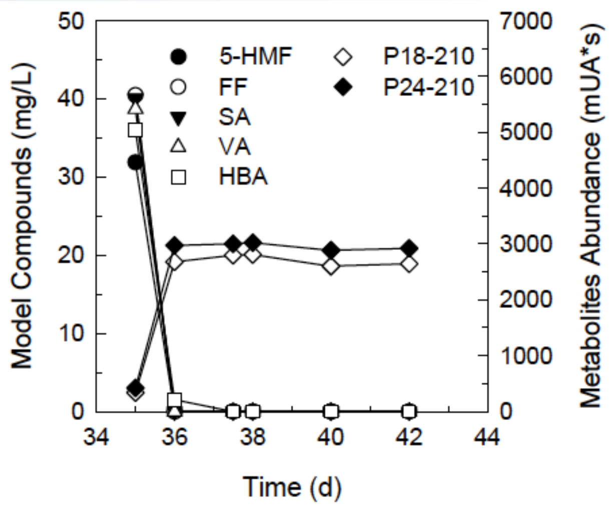
- **Results**

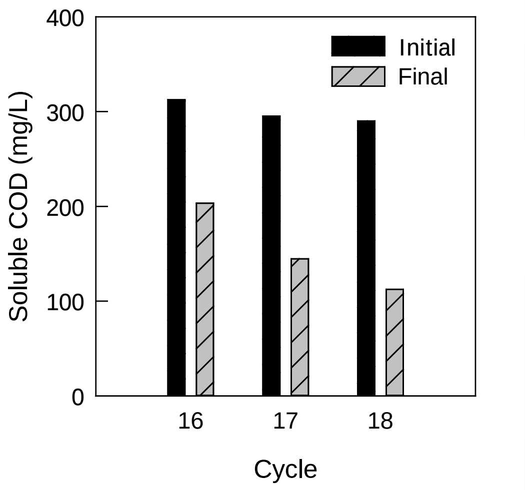


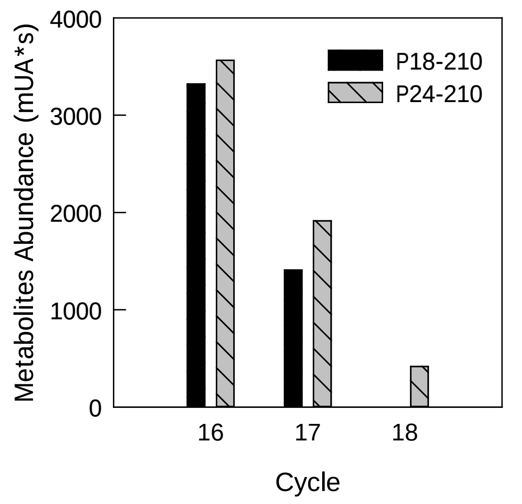


On-going Work

1. Startup of MEC
2. Bioconversion of furan and phenolic compounds in separate MFCs
3. Biotransformation pathways of model compounds

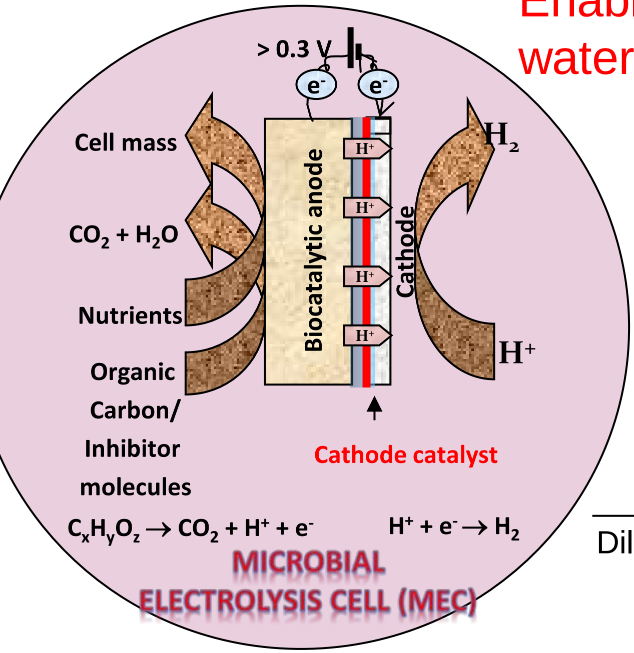


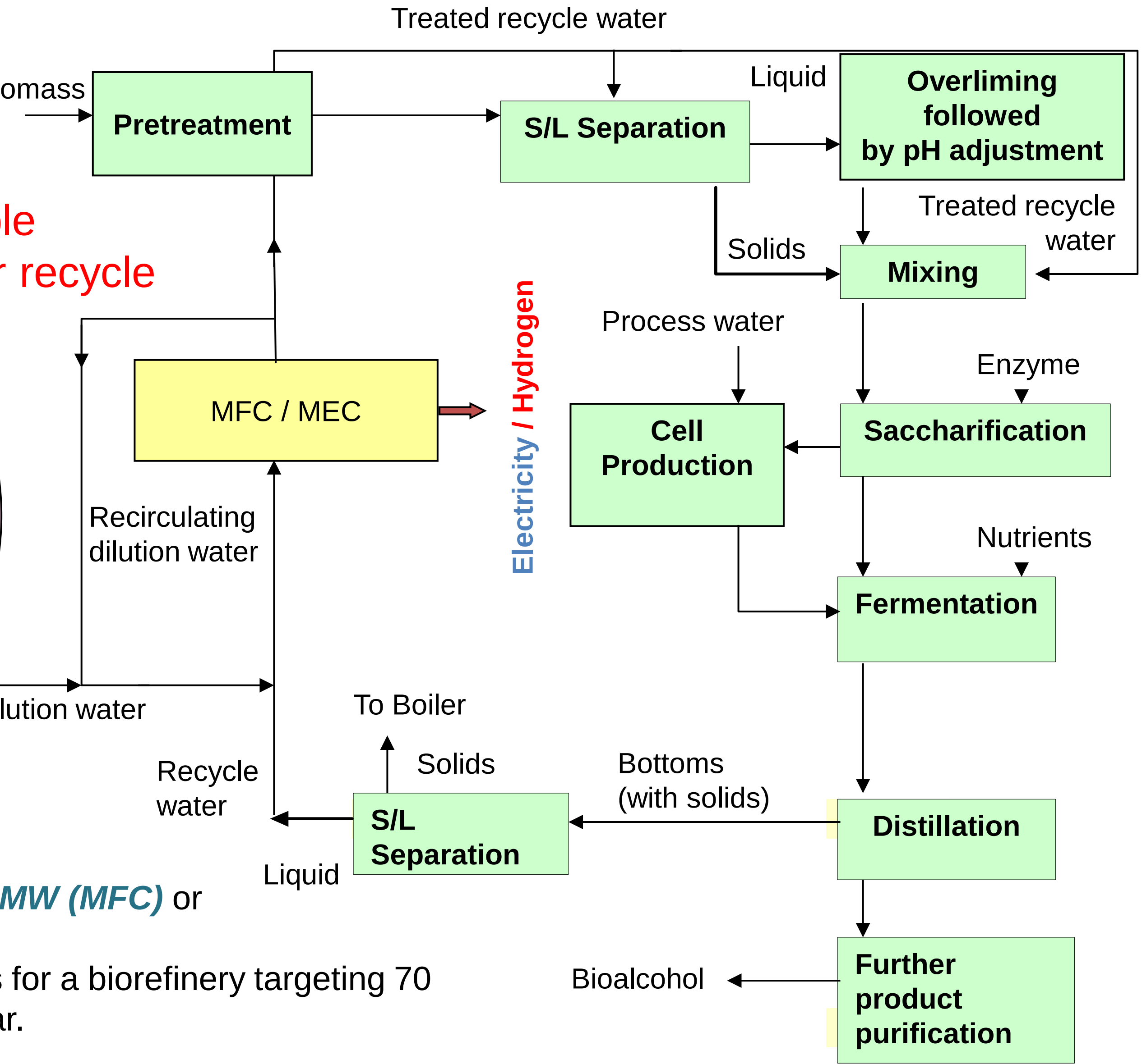




Note: The data on this slide should not be distributed, forwarded or cited.

Potential application in bioconversion-based biorefinery





Estimated Energy production

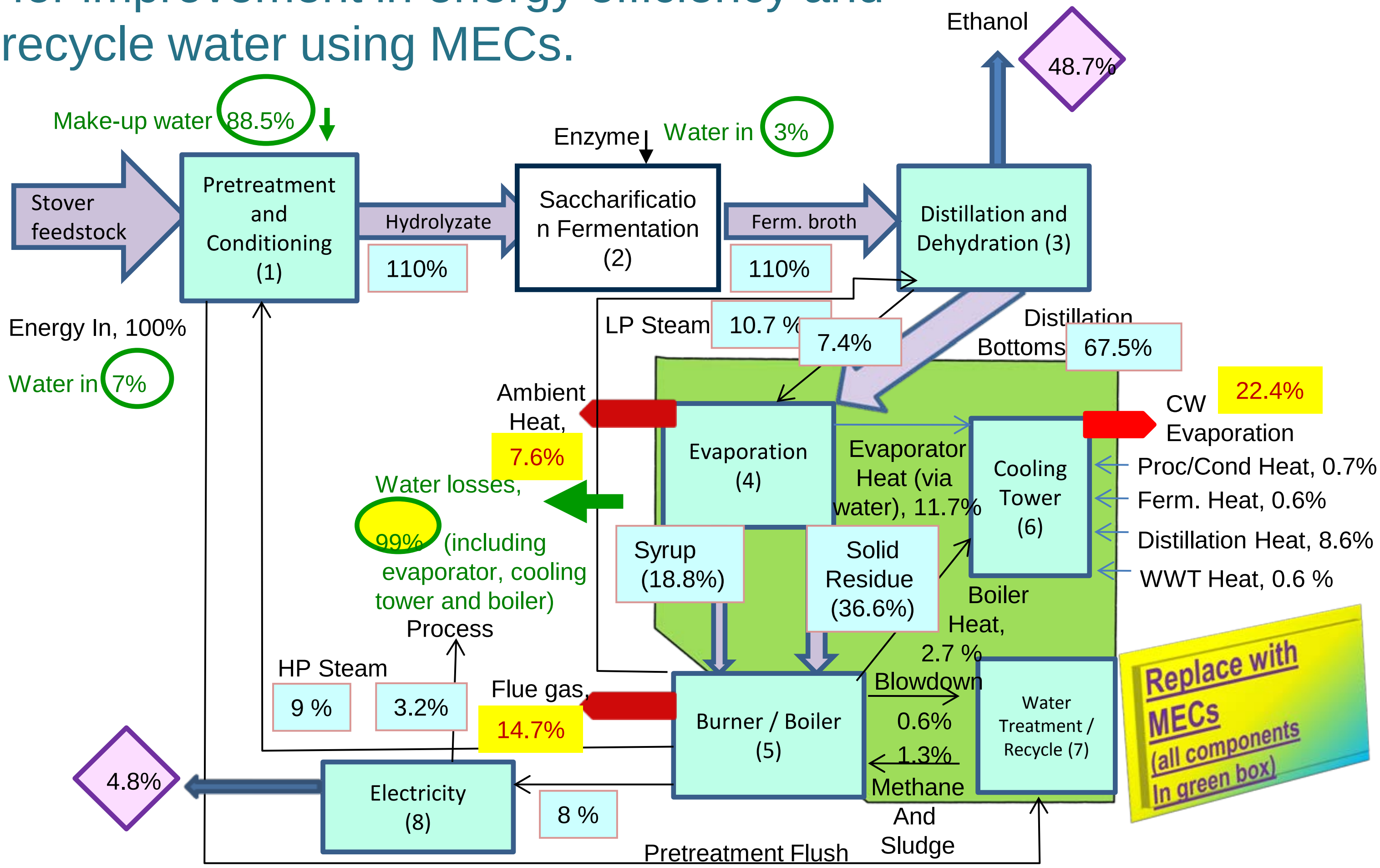
Electricity production = ***2.5 MW (MFC)*** or 7000 m^3/hr H2 (MEC)

~ 25% of total power needs for a biorefinery targeting 70 millions gallons ethanol/year.

Borole, A. P. US Patent, (2012). *Microbial fuel cell treatment of ethanol fermentation process water*, UT-Battelle, LLC.

Borole AP, Mielenz J, **Intl J Hydrogen Energy, 2011,** *Estimating Hydrogen Production Potential in Biorefineries Using Microbial Electrolysis Cell Technology*, 36, 14787–14795**.**

Potential for improvement in energy efficiency and ability to recycle water using MECs.

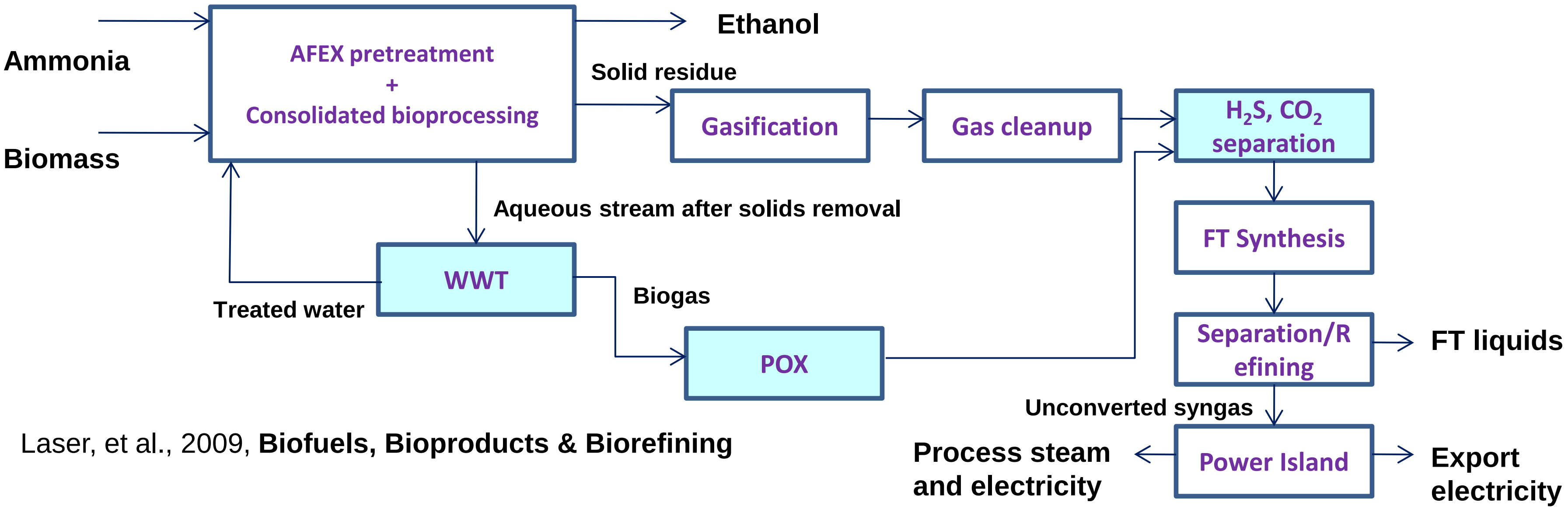


Legend

▭	Teal boxes show energy content of each stream as percent of total energy in (i.e., biomass) throughout the process
○	Green ovals indicate percent water content of the process stream in the flowsheet
◇	Product streams showing energy content as fraction of total energy in (Biomass) in the process reported by NREL
🟥	Heat loss paths in the process reported by NREL
🟨	Yellow shapes indicate energy/water loss from the existing process stream, which can be minimized using MECs.

Borole AP, **Biofuels, Bioproducts & Biorefining,** Improving Energy Efficiency and Enabling Water Recycle in Biorefineries Using Bioelectrochemical Cells. ***5(1):28-36 (2011).***

Projected mature biorefinery scenarios



Ammonia

Biomass

AFEX pretreatment
+
Consolidated bioprocessing

Ethanol

Solid residue

Gasification

Gas cleanup

H_2S, CO_2 separation

Aqueous stream after solids removal

WWT

Treated water

Biogas

POX

FT Synthesis

Separation/Refining

FT liquids

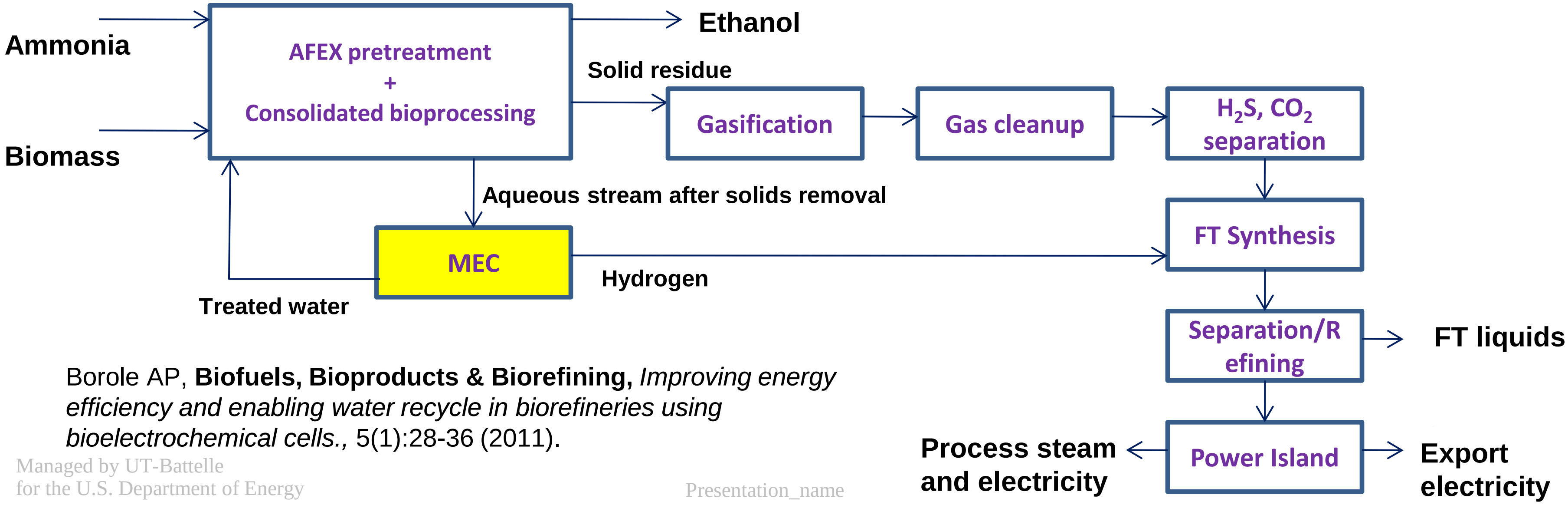
Unconverted syngas

Power Island

Process steam and electricity

Export electricity

Laser, et al., 2009, **Biofuels, Bioproducts & Biorefining**



Ammonia

Biomass

AFEX pretreatment
+
Consolidated bioprocessing

Ethanol

Solid residue

Gasification

Gas cleanup

H_2S, CO_2 separation

Aqueous stream after solids removal

MEC

Hydrogen

Treated water

FT Synthesis

Separation/Refining

FT liquids

Power Island

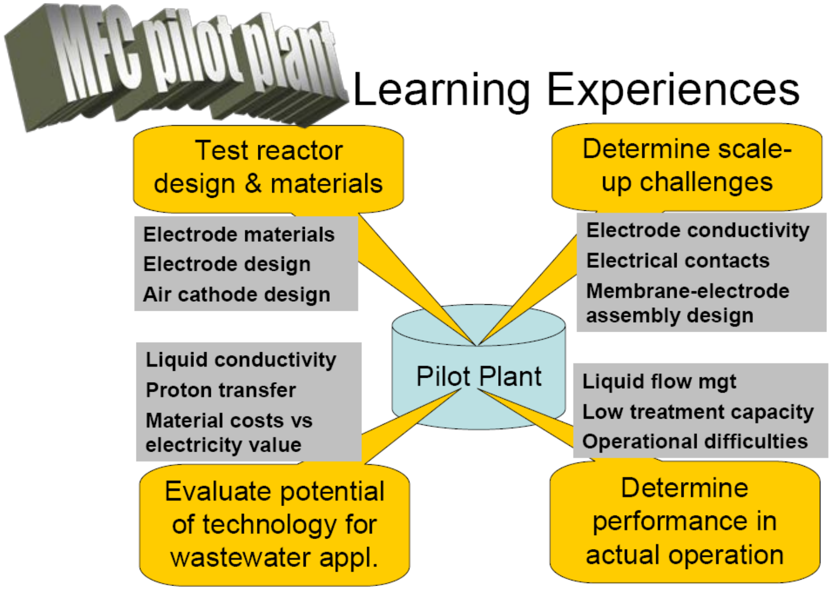
Process steam and electricity

Export electricity

Borole AP, **Biofuels, Bioproducts & Biorefining,** *Improving energy efficiency and enabling water recycle in biorefineries using bioelectrochemical cells.*, 5(1):28-36 (2011).

MEC Scale-up issues

- Study by J. Keller and group
  - Current: maximal 2A / cell at 400mV
  - COD removal as current: ≈ 0.2 kgCOD m^{-3} d^{-1}
  - Power density: 0.5 W/m^2 membrane area
    8.5 W/m^3 reactor volume
  - Loop operation essential for pH stability
- Low power output
- Engineering vs. Biocatalyst issues at pilot-scale
- Low coulombic efficiency
  - Presence of dissolved oxygen
  - Growth of unwanted (aerobic) biofilms
- MEC scale up
  - 1000L
  - 7.4 A/m^3, 0.19 L/L-day H_2.
  - 86% methane in product



Learning Experiences

Test reactor design & materials
Electrode materials
Electrode design
Air cathode design

Determine scale-up challenges
Electrode conductivity
Electrical contacts
Membrane-electrode assembly design

Pilot Plant

Liquid conductivity
Proton transfer
Material costs vs electricity value

Evaluate potential of technology for wastewater appl.

Liquid flow mgt
Low treatment capacity
Operational difficulties

Determine performance in actual operation

Borole, AP; US Patent 7,695,834, April 2010.
Microbial fuel cell with improved anode.

Bio-oil production and aqueous phase bio-oil separation for MEC experiments from switchgrass using pyrolysis unit at UTK CRC

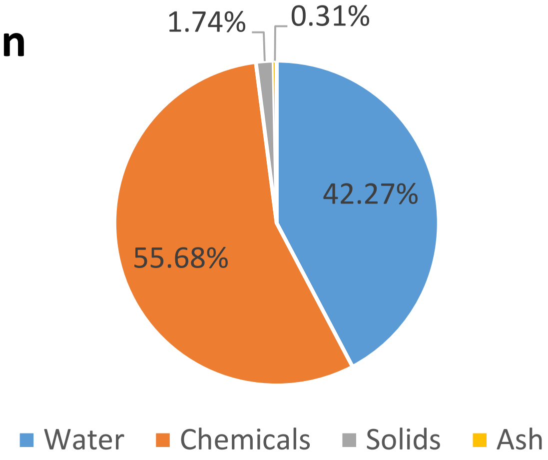
Bio-oil production by pilot auger pyrolysis reactor at UTK CRC

- Source: switch grass particle size: less than 2mm
- Feeding rate: 10kg/hr
- Reaction temperature: 500°C and 550°C
- Bio-oil yield: 40-50wt%, biochar: 25-30wt%, gas:20-25wt%
- The bio-oil is combined by three condensers

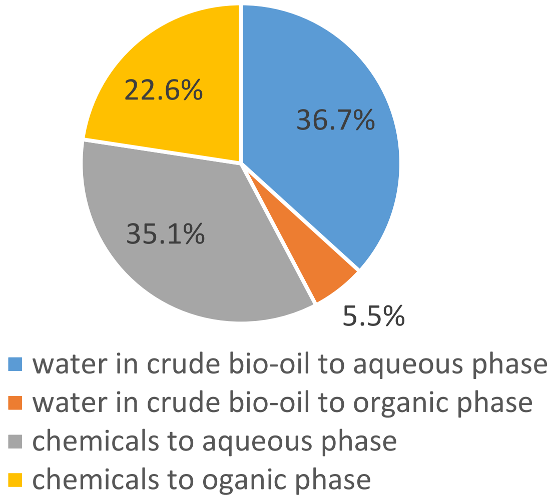
Pilot auger pyrolysis reactor at UTK CRC

Aqueous phase bio-oil separation

- Water: oil: 4:1
- Vigorous shaking
- Standing for overnight at 4°C
- Centrifugation: 5000rpm/min for 30min



Fractions of crude bio-oil (wt%) before separation



Fractions of bio-oil (wt% of crude bio-oil) after separation

Note: The data on this slide should not be distributed, forwarded or cited.

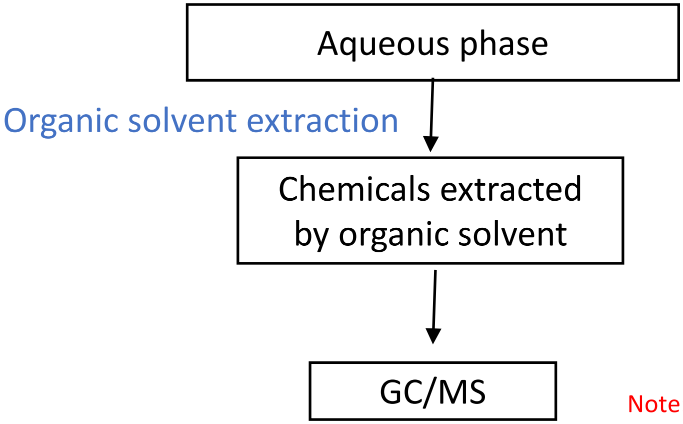
Characterization of crude and aqueous phase bio-oil

Properties of crude and aqueous phase bio-oil

Properties	Crude bio-oil	Aqueous phase bio-oil
Water content (wt%)	42.27±0.66	91.72±1.03
Total solid (wt%)	1.74±0.25	Not detected
pH value	2.84±0.07	3.02±0.01
Density (g/ml)	1.13±0.001	1.01±0.004
Ash (wt%)	0.31±0.04	0.085±0.004
Viscosity at 40 °C centistokes (cSt)	6.5±0.82	0.75±0.01
TAN, mg KOH/g	137.39±2.96	30.13±1.28

Major chemicals identification and quantification in aqueous phase bio-oil

chemicals identification

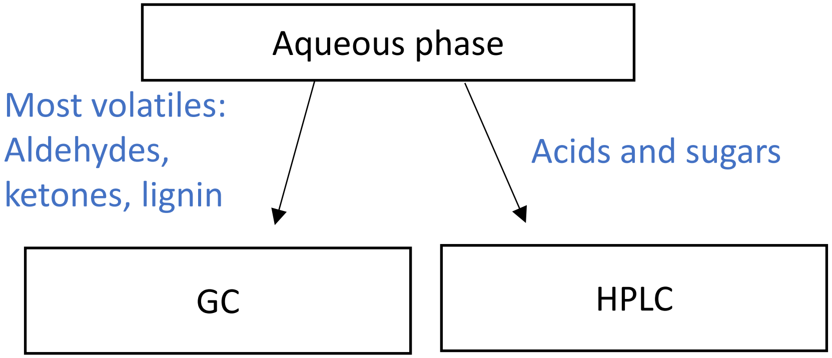

Aqueous phase

Organic solvent extraction

Chemicals extracted by organic solvent

GC/MS

chemicals Quantification


Aqueous phase

Most volatiles: Aldehydes, ketones, lignin

Acids and sugars

GC

HPLC

Note: The data on this slide should not be distributed, forwarded or cited.

Removal of Water from Bio-oil

Liquid-Liquid Extraction of Bio-oil Components

Investigators: Sotira Yiacoumi and Costas Tsouris
Ph.D. Student: Kyoung Eun (Lydia) Park

School of Civil and Environmental Engineering
Georgia Institute of Technology

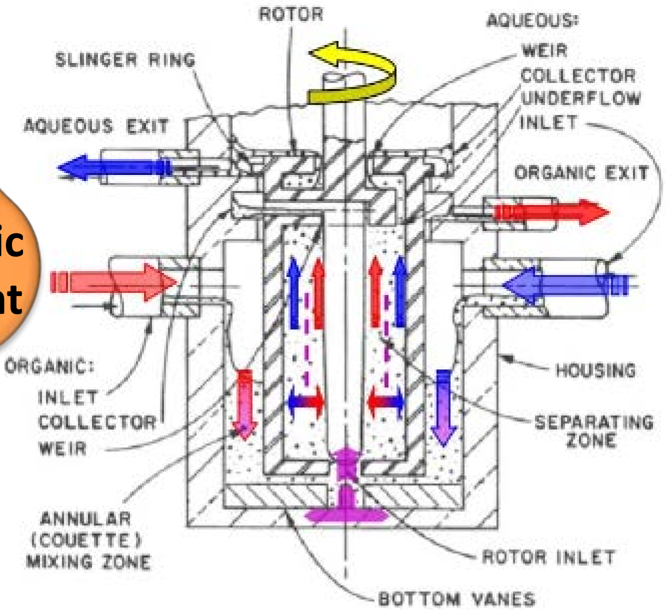
Aqueous Extraction of Bio-oil with the Centrifugal Contactor

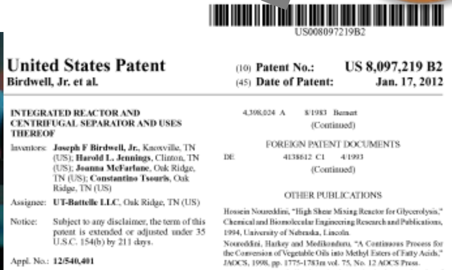
+

Aqueous Solution

/

Organic Solvent





US008097219B2

United States Patent
Birdwell, Jr. et al.

(10) **Patent No.:** **US 8,097,219 B2**
(45) **Date of Patent:** **Jan. 17, 2012**

INTEGRATED REACTOR AND CENTRIFUGAL SEPARATOR AND USES THEREOF

Inventors: **Joseph F Birdwell, Jr.**, Knoxville, TN (US); **Harold L. Jennings**, Clinton, TN (US); **Joanna McFarlane**, Oak Ridge, TN (US); **Constantino Tsouris**, Oak Ridge, TN (US)

Assignee: **UT-Battelle LLC**, Oak Ridge, TN (US)

Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 211 days.

Appl. No.: **12/540,401**

4,398,024 A 8/1983 Bernert
(Continued)

FOREIGN PATENT DOCUMENTS

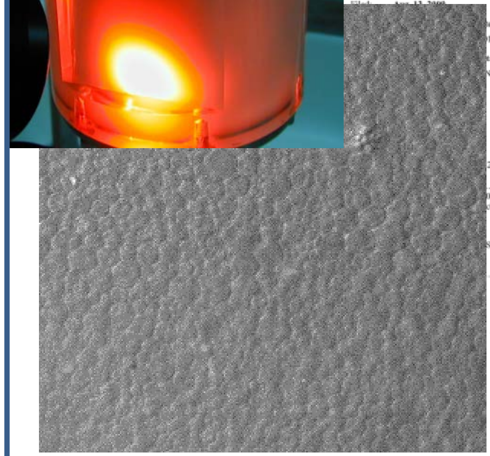
DE 4138612 C1 4/1993
(Continued)

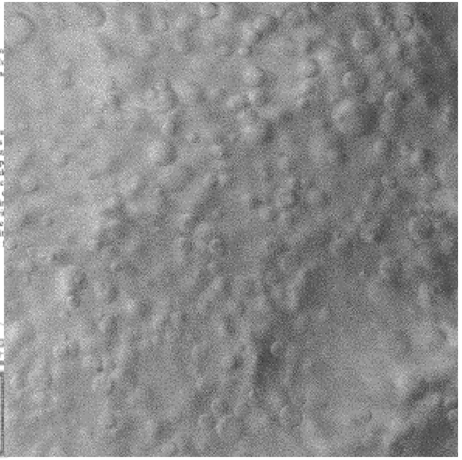
OTHER PUBLICATIONS

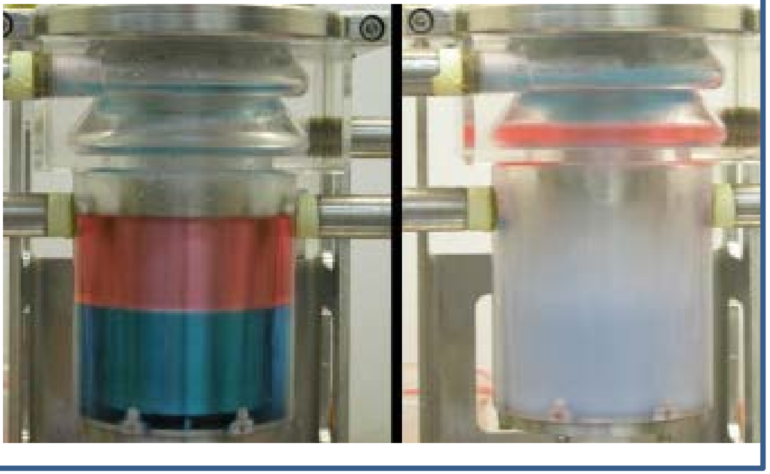
Hossein Noureddini, "High Shear Mixing Reactor for Glycerolysis," Chemical and Biomolecular Engineering Research and Publications, 1994, University of Nebraska, Lincoln.

Noureddini, Harkey and Medikonduru, "A Continuous Process for the Conversion of Vegetable Oils into Methyl Esters of Fatty Acids," JAOCS, 1998, pp. 1775-1783m vol. 75, No. 12 AOCS Press.

Jon van Gerpen, "Biodiesel Production Technologies," University of Idaho, 2004.







Options for Solvent Extraction of Bio-oil

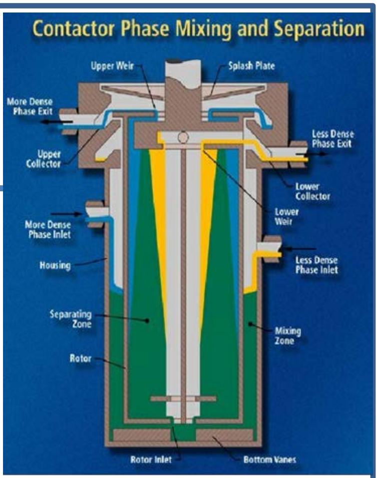
Extraction Options

Sequential Extraction

Simultaneous Extraction

Aqueous Phase — MEC for H_2 production

Organic Phase — **Fuel**



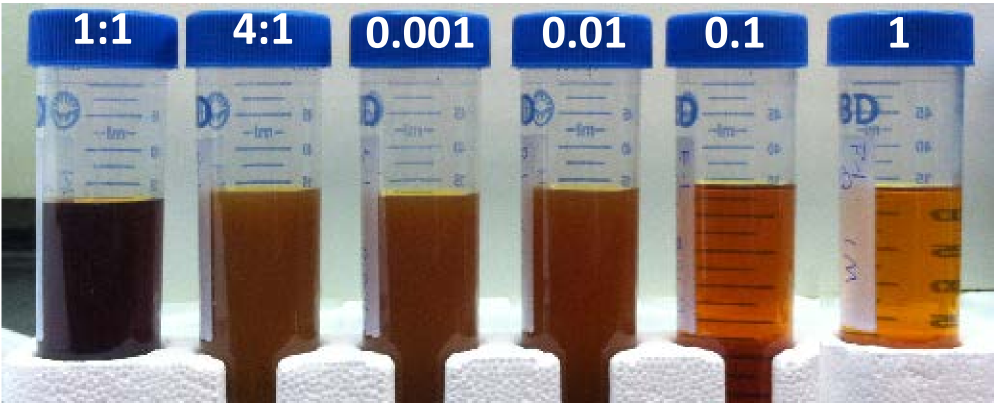
Extraction Parameters: Solvent type, pH, ionic strength, volume ratio, etc.

Batch experiments to determine range of parameters:

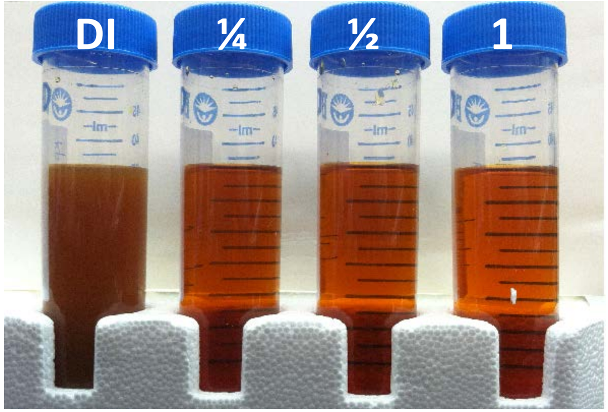
Volume ratio

NaCl (Ionic strength) (M)

Aqueous solutions after extraction



Microbial growth media (phosphate buffer)



Measurements: Partitioning, pH, conductivity, chemical composition

Note: The data on this slide should not be distributed, forwarded or cited.

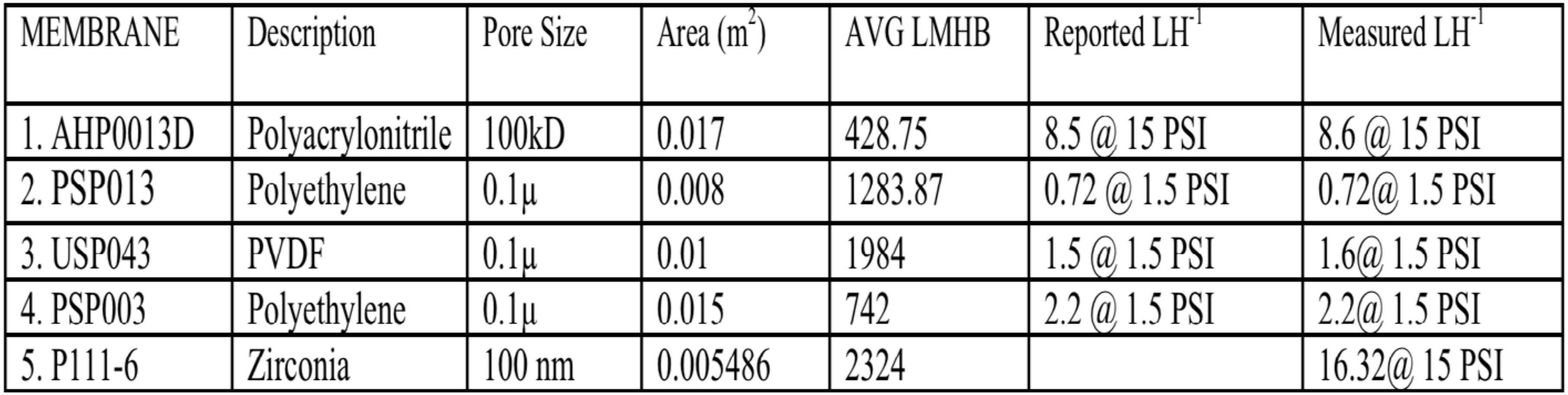
– Bio-oil contains a significant fraction of water and water-soluble species

– The water to bio-oil volume ratio and ionic strength affect the extraction of bio-oil species

Membrane Separations-Objectives

- **Removal of cellular debris in the MEC effluent.**
- **Evaluate impact of carryover oil, fines and contaminants in recycle water on downstream processes.**
- **Produce clean water for recycle to aqueous phase.**
- **Feed volumes from microbial reactor: <1L -10L**
- **Identify and develop process parameters using hollow fiber and tubular ceramic membranes- hydrophobic (PVDF) and hydrophilic (PAN) and zirconia.**
- **Flux stability over time, membrane fouling, back pulsing and membrane regeneration.**
- **Process optimization, integration, reliability and scalability.**
- **Obtain engineering data for scale-up and assess energy requirements.**

Verification of water flux for Pall membranes



MEMBRANE	Description	Pore Size	Area (m^2)	AVG LMHB	Reported LH^{-1}	Measured LH^{-1}
1. AHP0013D	Polyacrylonitrile	100kD	0.017	428.75	8.5 @ 15 PSI	8.6 @ 15 PSI
2. PSP013	Polyethylene	0.1µ	0.008	1283.87	0.72 @ 1.5 PSI	0.72@ 1.5 PSI
3. USP043	PVDF	0.1µ	0.01	1984	1.5 @ 1.5 PSI	1.6@ 1.5 PSI
4. PSP003	Polyethylene	0.1µ	0.015	742	2.2 @ 1.5 PSI	2.2@ 1.5 PSI
5. P111-6	Zirconia	100 nm	0.005486	2324		16.32@ 15 PSI

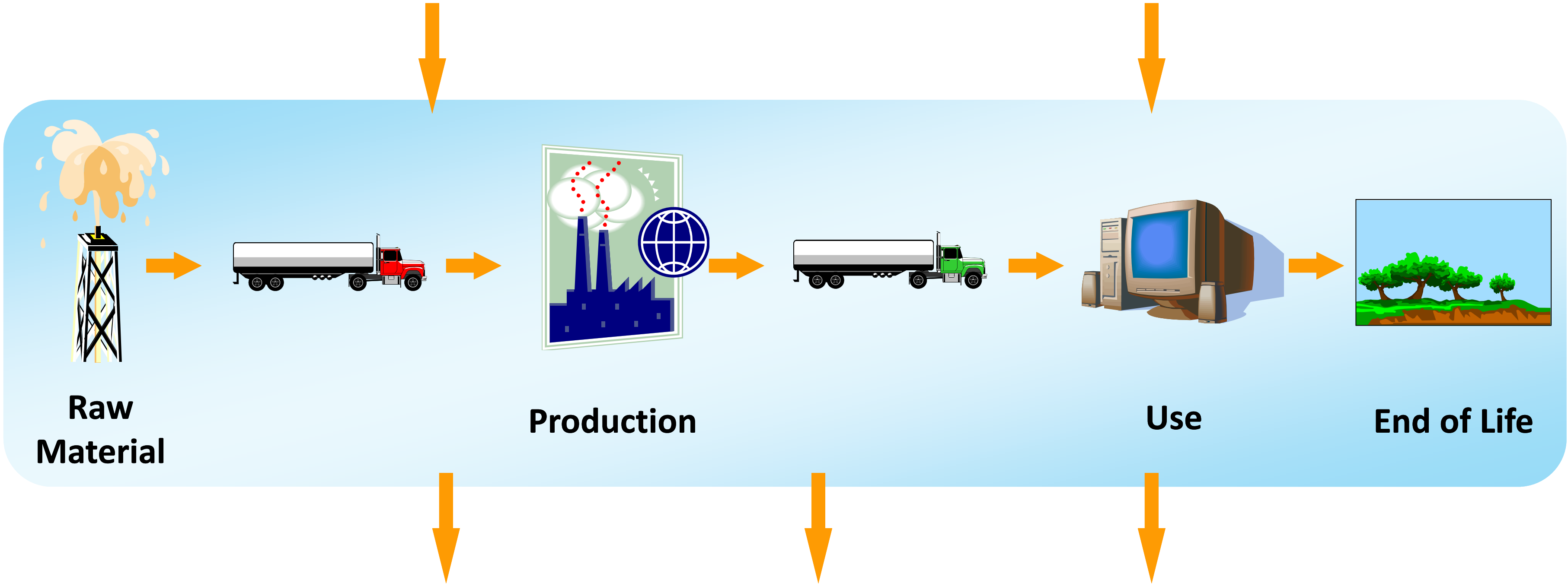
Where:

- LMHB – Liter/Hr-M^2-bar
- LH^{-1} – Liters/Hr
- kD – kilo Dalton

Note: The data on this slide should not be distributed, forwarded or cited.

Life Cycle Assessment Defined

Raw material and energy consumption



Raw Material

Production

Use

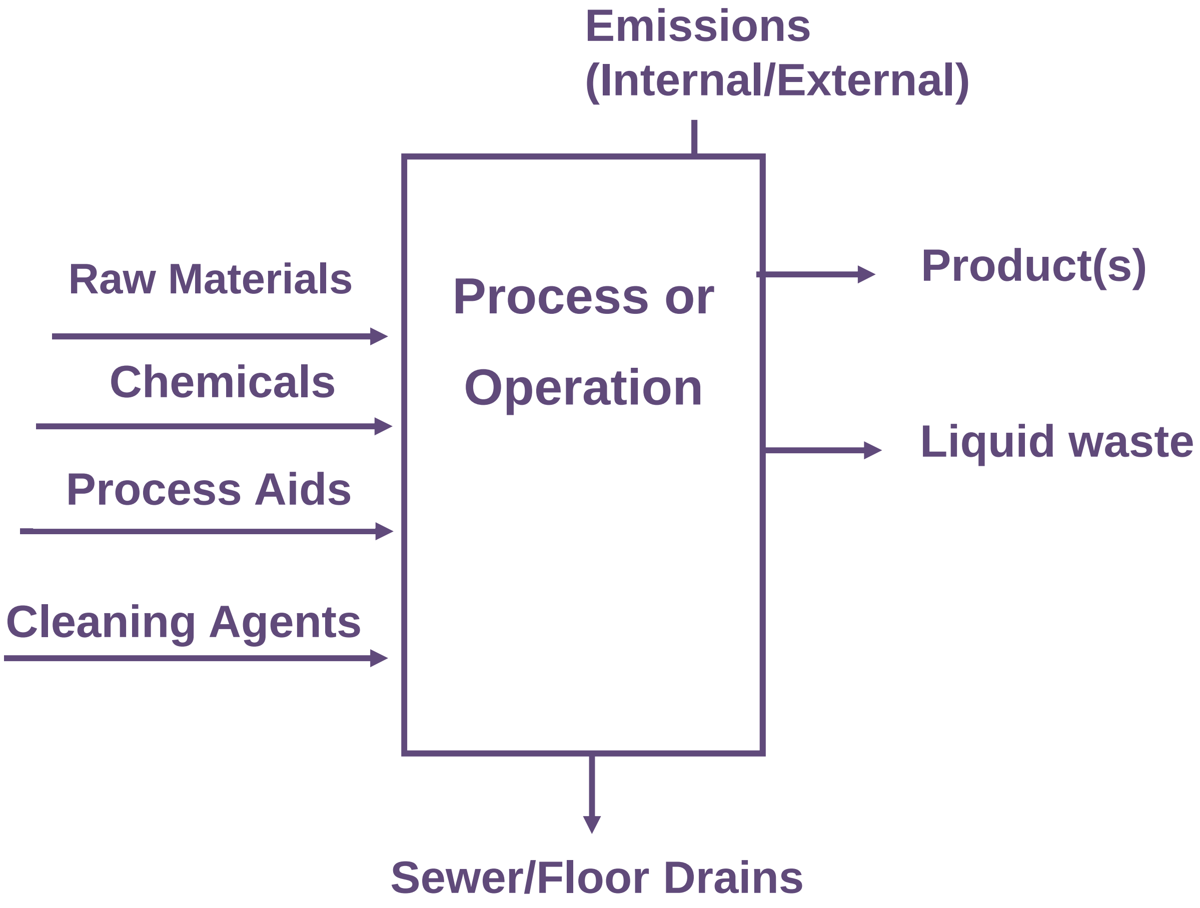
End of Life

Emissions to air, water and soils

Cradle-to-Grave Product System Boundary

FOUR ELEMENTS LLC

Simplified Mass Balance



Emissions
(Internal/External)

Raw Materials

Chemicals

Process Aids

Cleaning Agents

Process or

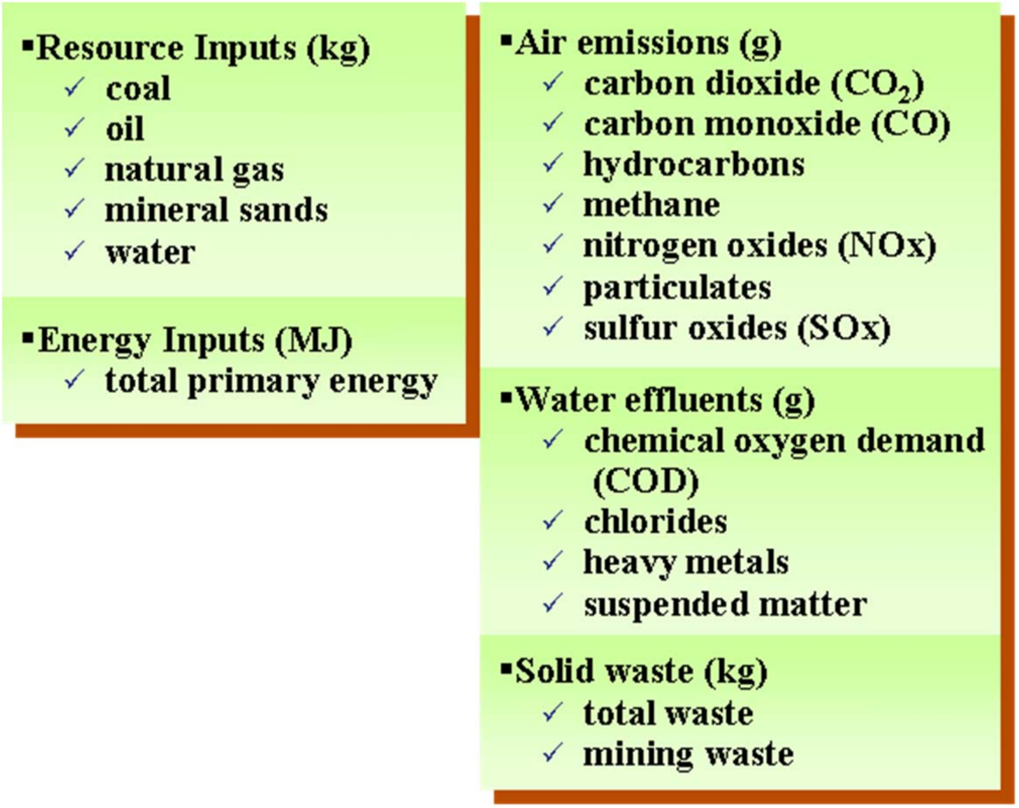
Operation

Product(s)

Liquid waste

Sewer/Floor Drains

Life Cycle Inventory



- Resource Inputs (kg)
  - ✓ coal
  - ✓ oil
  - ✓ natural gas
  - ✓ mineral sands
  - ✓ water
- Energy Inputs (MJ)
  - ✓ total primary energy
- Air emissions (g)
  - ✓ carbon dioxide (CO_2)
  - ✓ carbon monoxide (CO)
  - ✓ hydrocarbons
  - ✓ methane
  - ✓ nitrogen oxides (NOx)
  - ✓ particulates
  - ✓ sulfur oxides (SOx)
- Water effluents (g)
  - ✓ chemical oxygen demand (COD)
  - ✓ chlorides
  - ✓ heavy metals
  - ✓ suspended matter
- Solid waste (kg)
  - ✓ total waste
  - ✓ mining waste

Balance sheet of environmental inflows and outflows

Sample list

Omni Tech
STRATEGIC. SUSTAINABLE. SCIENCE.

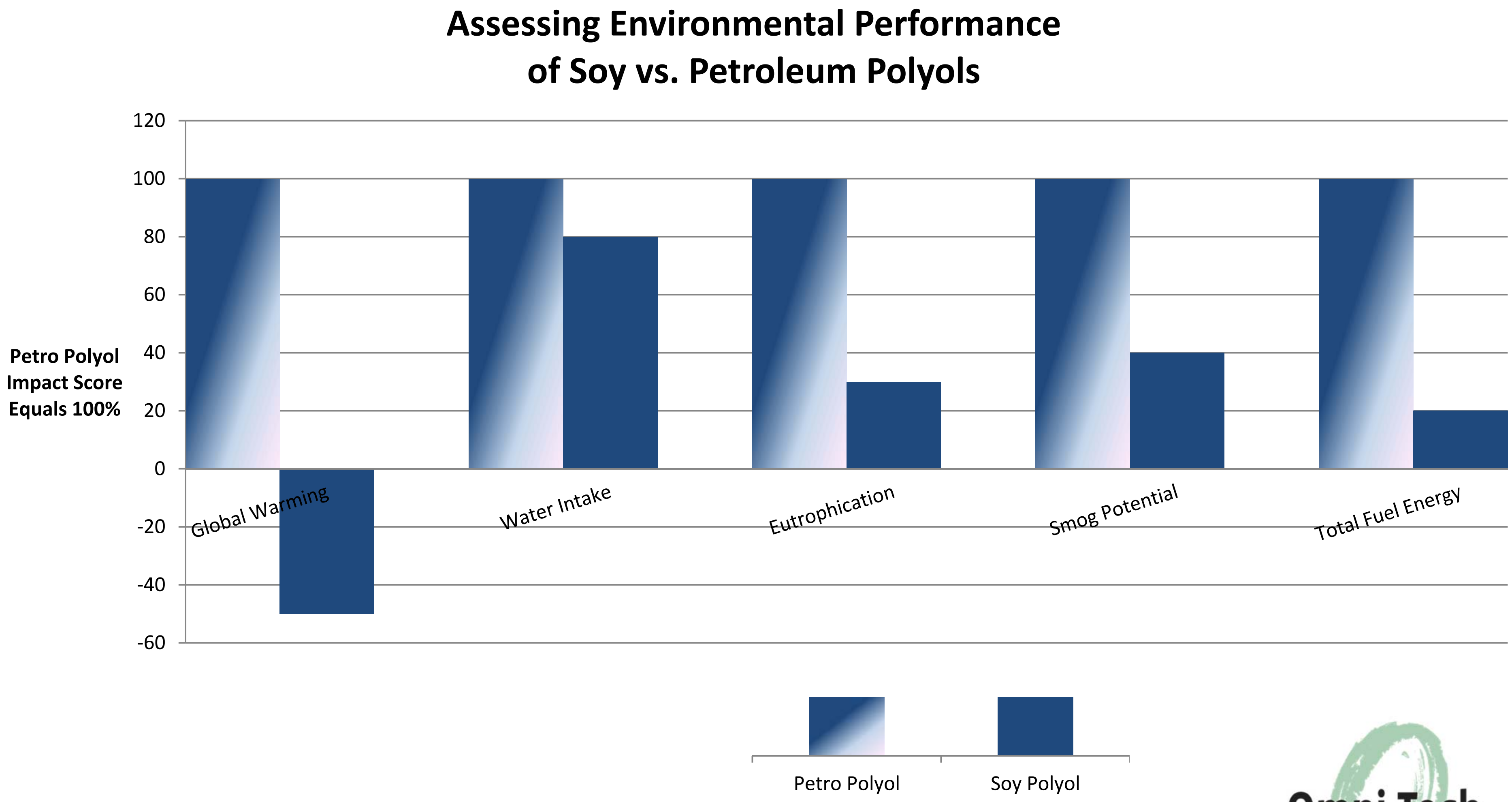
Sample Life Cycle Impact Assessment Calculation

Global Warming Potential

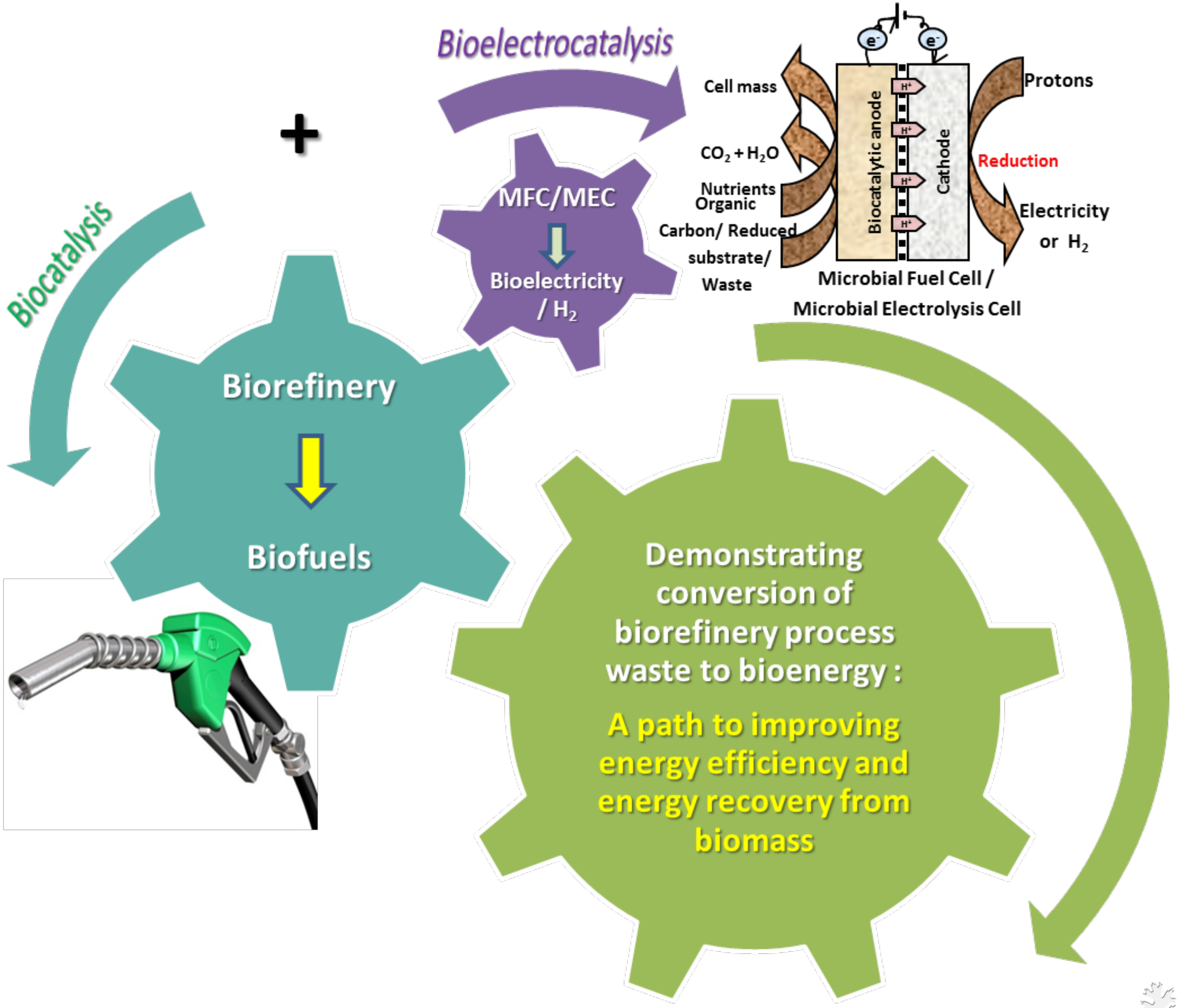
Corresponding characterization factors

	GWP equiv. factor	**LCI Result**	**LCIA Result**
Carbon dioxide	1	2000	2000
Methane	21	15	315
Nitrous Oxide	310	0.1	31
		Total Potential GWP (CO2-eq) -->	**2346**

Sample Comparative Results



Omni Tech
STRATEGIC. SUSTAINABLE. SCIENCE.



MFC/MEC

Bioelectricity / H_2

Biorefinery

Biofuels

Demonstrating conversion of biorefinery process waste to bioenergy :

A path to improving energy efficiency and energy recovery from biomass