The Role of Hydrogen in the 21st Century BioEconomy

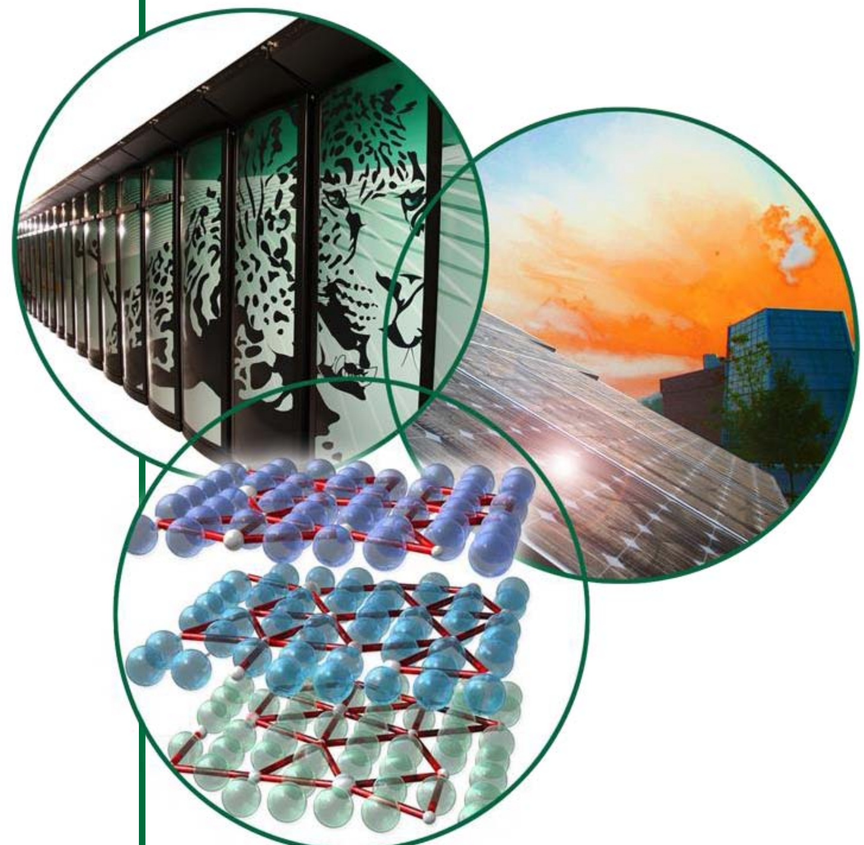
Abhijeet P. Borole, Ph.D.

Oak Ridge National Laboratory

July 12, 2017

2017 BIoEconomy Conference, Washington, DC

<u>Open Technical Session</u>: Enabling technologies and strategies to engineer net-zero or negative carbon utilization pathways



U.S. DEPARTMENT OF ENERGY

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Outline

- The Need for Hydrogen in BioEconomy
  Biofuels
  Bioproducts
- Renewable Hydrogen Production Pathways
- Waste to Hydrogen Concept
- Integration of Hydrogen Production and Biorefinery
- Path to Carbon-Negative Economy or Circular Economy
- Broader impact
  - Water-Energy Nexus
  - Resource recovery: P, N, metals, water

Hydrogen in Biomass to Biofuels Pathways

- Biomass contains 35-40% oxygen
- Deoxygenation requires significant amount of reductant to preserve carbon and minimize CO_2 release
- Typical hydrogen sources
  - Natural gas
  - Electricity (derived from fossil?)

- Increasing availability of renewable hydrogen sources – solar, wind, biomass
- Smart ways to incorporate these sources into the biorefinery are needed!

Hydrogen for Bioproducts

- Aromatics
  - High yields of aromatics from biomass are possible via Integrated Catalytic Pyrolysis:
    - Bio-oil + Hydrogen -> Aromatics (Hydrogenation) (Vispute et al.)
    - 46% reduction in coking, 36% higher yield of aromatics and olefins
  - Lignin to aromatics
    - Better use of carbohydrates after separation from biomass
    - Yields of aromatics better than from biomass feedstock
    - Potential to generate cyclohexane
- Longer chain fatty acids
  - Elongation of VFAs using H2
- Alcohols
  - Butanol
- Diols
  - Glycerol to 1,3-PDO, Succinic acid to 1,4-BDO

Brown et al., Biofpr, 2017
Vispute et al., Science 2010,

Hydrogen Source Plays an Important Role in Pathway Risk Determination (Zhao et al., 2017, Biofpr)

Pathways	Feedstock	Energy input	Energy output	Source
High T fasification and Fischer Tropsch	Corn Stover	Biomass, natural gas, electricity	Gasoline, diesel, electricity	Swanson et al. (2010)
Low T gasification Fischer Tropsch	Corn stover	Biomass, natural gas, electricity	Gasoline, diesel, electricity	Swanson et al. (2010)
Fast Pyrolysis and hydroprocessing	Corn stover	Biomass, hydrogen, electricity	Gasoline, diesel, electricity	Bittner et al (2015), Brown et al., (2013)
High Temperature Liquefaction	Hybrid poplar	Biomass, natural gas, electricity	Gasoline, diesel, heavy oil, electricity	Zhu et al. (2014)
Indirectly heated gasification and Acetic acid synthesis	Hybrid poplar	Biomass, CO, H2, electricity	Ethanol, Electricity	Zhu and Jones (2009)
Directly heated gasification and Acetic acid synthesis	Hybrid poplar	Biomass, natural gas, CO, H2, electricity	Ethanol, Electricity	Zhu and Jones (2009)
Methanol to Gasoline	Hybrid poplar	Biomass, electricity	Gasoline, electricity, liquefied petroleum gas	Zhu et al., (2012)

The Vibe of the US Transportation Industry

- The new movement towards Electrification
- Natural gas based transportation energy (electricity, CNG, LNG, etc.)
- Liquid biofuel industry – still in infancy
- Renewable biogas from lignocellulosics – Significant contribution to RFS2
  - 42.2 million gallons-equivalent of cellulosic biofuels – 98.5% as liquefied renewable natural gas
- Strategies for making biomass-derived fuels economically competitive are needed

Brown et al., Biofpr, 2017

Waste to H_2 to Biofuels and Chemicals Pathways

- Waste sources
  - Biorefinery
    - Pyrolysis aqueous phase (up to 20% carbon – potential loss)
    - Fermentation effluent (fermentation byproducts + remaining 5-10% sugars)
    - Stillage (concentrated effluent), Lignin
  - Bioproducts industry
  - Food waste
    - Households, restaurants, food processing, bakeries, groceries
  - Breweries and wineries
  - Paper and pulp industry
  - Municipal waste
    - Food component (30-40%)
    - 40% of all purchased food ends up in trash can

Technologies for H_2 Production

Biological

- Dark Fermentation
- Photo Fermentation
- Anaerobic digestion-Partial Oxidation-Separation

Thermo-chemical

- Steam Reforming
- Solar-thermal
- Biomass gasification
- Biomass Pyrolysis

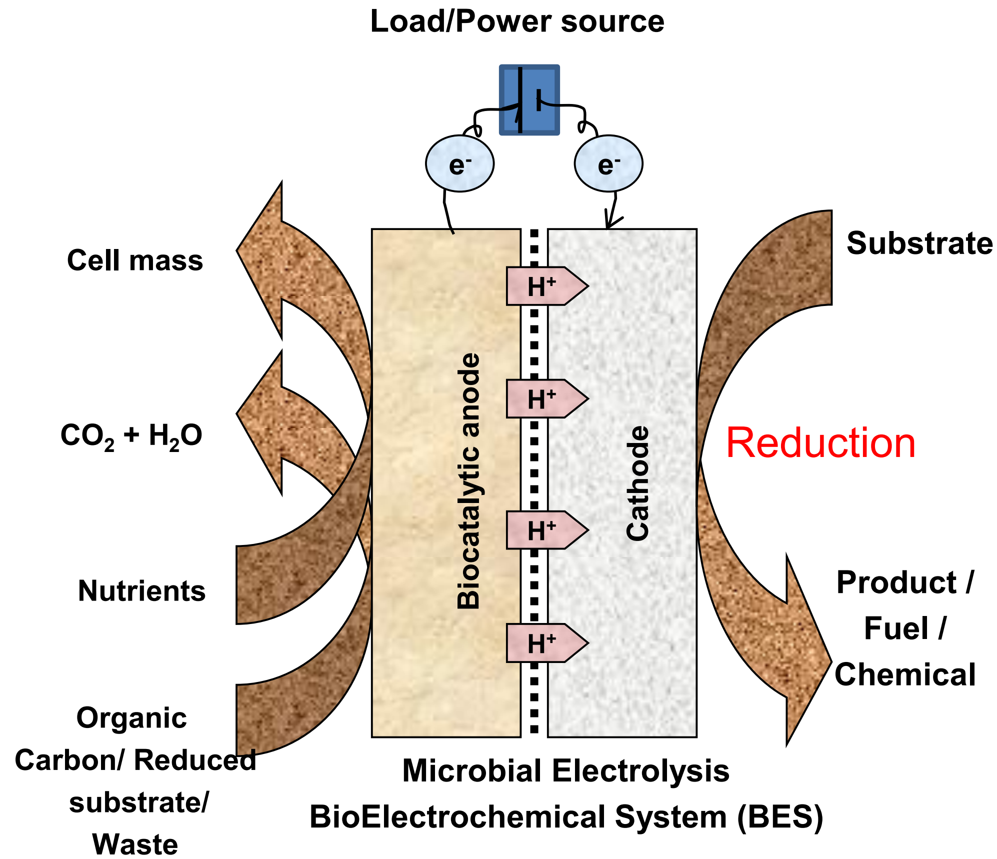
Electro-Chemical

- PV Electrolysis
- Wind Electrolysis

Waste (→ Biological, → Thermo-chemical)

Microbial Electrolysis Cell Technology

- Conversion of Waste to hydrogen
- Anode: Degradable organics to electrons, protons and CO_2
- Cathode: Proton reduction to hydrogen at applied potential of 0.3-1V.
- Uses electroactive biofilms with broad specificity and activity for biomass-derived components



Microbial Electrolysis
BioElectrochemical System (BES)

$C_xH_yO_z \rightarrow CO_2 + H^+ + e^-$ MEC: $H^+ + e^- \rightarrow H_2$

Pathway: Organics + water → electrons + protons (anode) → H_2 (cathode)

Borole*, A. P., US Patent 7,695,834, UT-Battelle, USA,* ***2010.***
Borole*, A. P., US Patent* 8,192,854 B2 *UT-Battelle, USA,* ***2012.***
Borole, A. and A. J. Lewis (2016) Provisional Patent Appl. No.: 62/351,322, UT Battelle, LLC.
Borole, A. P. and C. Tsouris (2009). US Patent 8,597,513 B2. USPTO. USA, UT-Battelle, LLC.
Borole, A. P., et.al., 2009, Biotechnol for Biofuels., *Controlling accumulation of fermentation inhibitors in biorefinery process water using Microbial Fuel Cells,* 2, 1, 7.
Borole, A. P., et al., 2011, Energy Environ. Sci., *Electroactive biofilms: Current status and future research needs* **4**: 4813-4834.
Borole, A. P., et al., Environ Sci Technol. ***2013, 47, 642.***
Borole, A. P., et al., Bioresour. Technol. ***2011, 102, 5098.***
Borole, A. P., et al., Biochem. Eng. J. ***2009, 48, 71.***

Hydrogen Production from Waste

- Waste/Biomass sugars (glucose) to H_2 :

	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.

Microbial electrolysis is a high efficiency, high yield, practical alternative available for hydrogen production.

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

Hydrogen Production Costs

$/kg H2	EERE [17]		Literature [19], [14].
	2011 status	2015 Target	
Wind + Electrolysis	4.10	3.00	6.64
PV-Electrolysis			6.18[†]
Biomass gasification	2.20	2.10	4.63
Biomass pyrolysis			3.80
Solar thermal	NA	14.50	
Photoelectrochemical cell	NA	17.30	
Photobiological	NA	9.20 (2020 Target)	
Nuclear thermal splitting of water			1.63
Natural gas reforming			1.03
Coal gasification			0.96
Microbial electrolysis	NA	12.43 [§]	5.40[‡] < 4.00 (ORNL study)
Reforming of bio-derived liquids[*] 1. Ethanol 2. Bio-oil aqueous phase [3]	6.60 31.84	5.90 3.00[£] (2017 Target)	

Table 1. Comparison of cost of hydrogen production [17], [19]. The costs reported in last column are based on 2003 $, except for MEC.

[†] Based on projected future technology

[§] Derived from [20]. A cost of $5.18 was deduced from the reported hydrogen production cost of $ 12.43, which was for production of substrate via fermentation. The FCTO MYPP reports cost of electrodes for MEC ($ 300/m^2, 2015 target), however, does not give estimated cost of hydrogen production. It assumes a hydrogen production rate of 1 L-H_2/L-reactor-day (2015 Target).

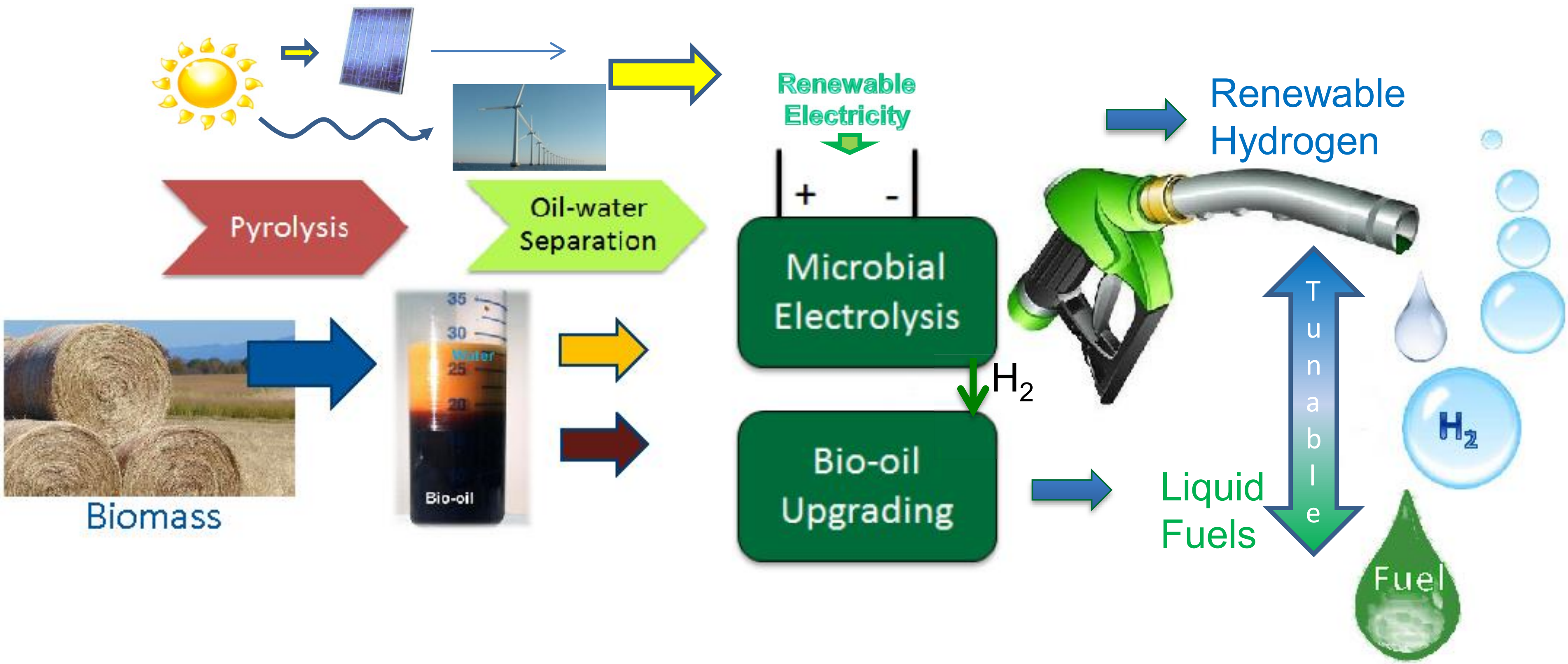
[‡] Derived from [14]-*Chemsuschem* **2012,** *5*, (6), 1012-1019 . Cost projected using future cost of electrode materials.

[*] For conversion of bio-derived liquids to hydrogen via steam reforming.

[£] The target of $ 3/kg of hydrogen production from bio-oil aqueous phase has been reported to be very difficult to meet [3].

The Electrochemical Society *Interface*., *Microbial Fuel Cells and Microbial Electrolyzers,* Spring Issue. Borole, A. P., 2015,

Microbial Electrolysis of Pyrolysis Aqueous Phase



Potential to generate hydrogen as intermediate for liquid fuel.

Borole & Lewis, Provisional Patent Appl. No.: 62/351,322, UT Battelle, LLC. submitted June 2016
Lewis, A. J., et al. (2015). "Hydrogen production from switchgrass via a hybrid pyrolysis-microbial electrolysis process." Bioresource Technology **195**: 231-241.

DOI: 10.1039/C7SE00060J

Hydrogen Production Metrics for MEC

	Targets for commercial consideration	June 2017
Hydrogen production rate	>20 L H_2/L-reactor-day	**11.7 L/L-anode-day for bio-oil aqueous phase**
Anode current density, A/m^2	20	14 for BOAP
Anode CE	>90%	60-79%
Applied voltage	< 0.6 V	0.9V
Cathode CE	>90% at 0.6V or less	87-96%
Potential Efficiency	>60%	NA
Resistance	< 80 mΩ m^2	NA
Capital costs*	<\$2000/m^3 reactor	NA

Performance and efficiency metrics for MEC development.

* The costs reported are for n^{th} reactor. The reduction in cost will come from improvements in MEC anode performance and use of non-Pt cathode electrode.

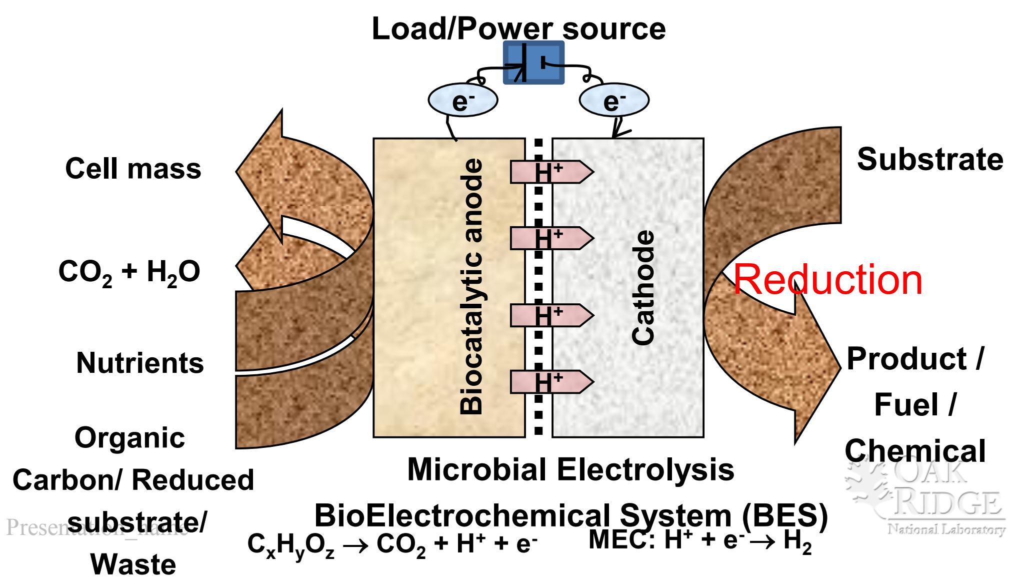
Demonstrated high performance in terms of H_2 yield and productivity.

Lewis, A. J., et al. (2015). Bioresource Technology **195**: 231-241.
Borole & Lewis (2017), Sustainable Energy & Fuels, DOI: 10.1039/C7SE00060J
Lewis, et al., 2017, Microbial Biotechnology, DOI: 10.1111/1751-7915.12756

Microbial Electrolysis for Chemicals

Type of BES		Cathode substrate	Product
MEC		Biomass - protons	Hydrogen
MFC		Oxygen	Electricity
BES		Glycerol	1,3-Propanediol
BES	H_2 +	Succinic Acid	1,4-Butanediol
BES		Acetate	Ethanol
BES		Oxygen	Hydrogen peroxide
MEC		Ag run-off/ Wastewater	Phosphate fertilizer/Struvite
MEC		Urine/Wastewater	Ammonia

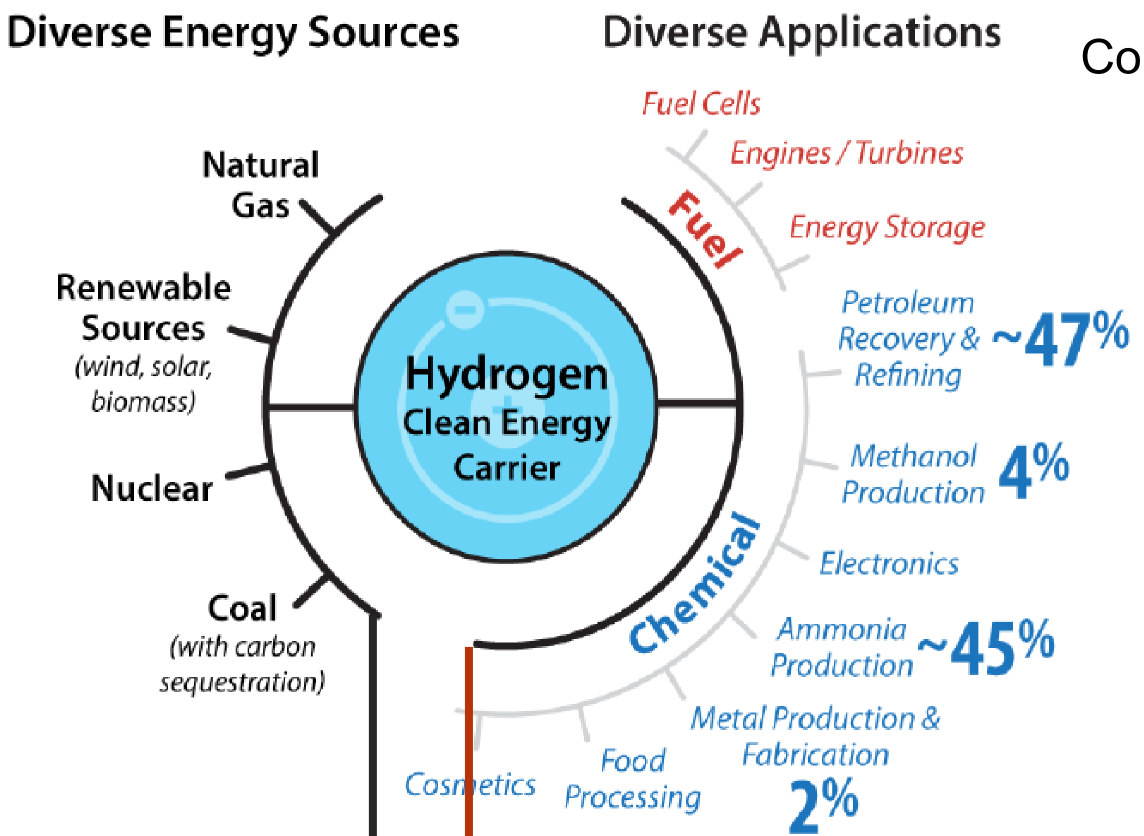
- Synergistic with Microbial Electrosynthesis or Electro-Fermentation and Electro-fuels
- H_2 evolution at cathode can improve yields of high value products synthesized via electrosynthesis.



Borole*, A. P., Bioelectrochemical Biorefining*, a book chapter in : Bioenergy & Biofuels, CRC Press, 2017

Beyond Current Hydrogen Sources / Applications

Courtesy: FCTO



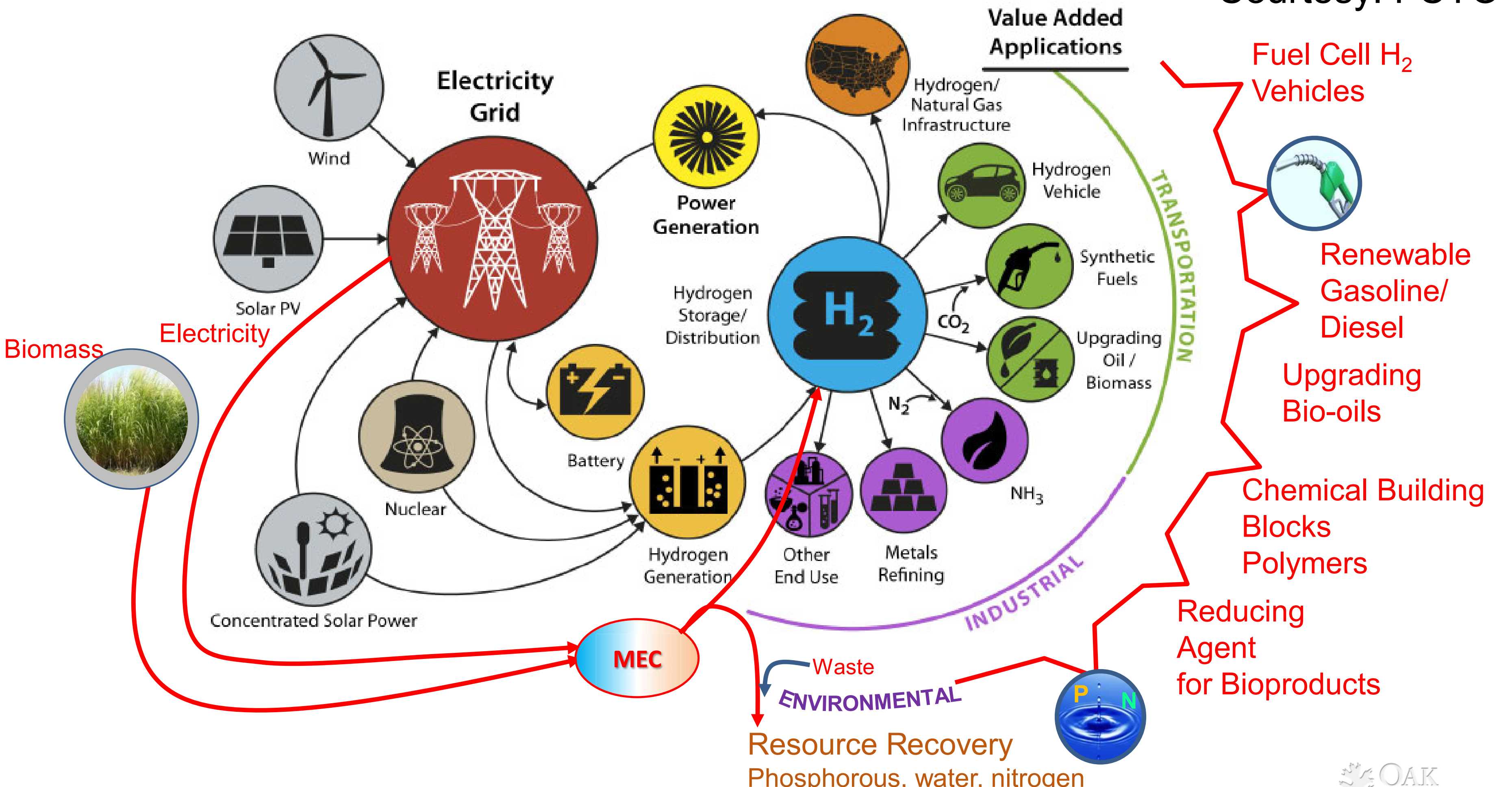
Biomass → H2 →

Biofuels (Renewable Gasoline/Diesel)
Chemicals (Building Blocks, Polymers)
Grid storage (Power to Gas-H_2)
Resource Recovery (N, P, water, metals)

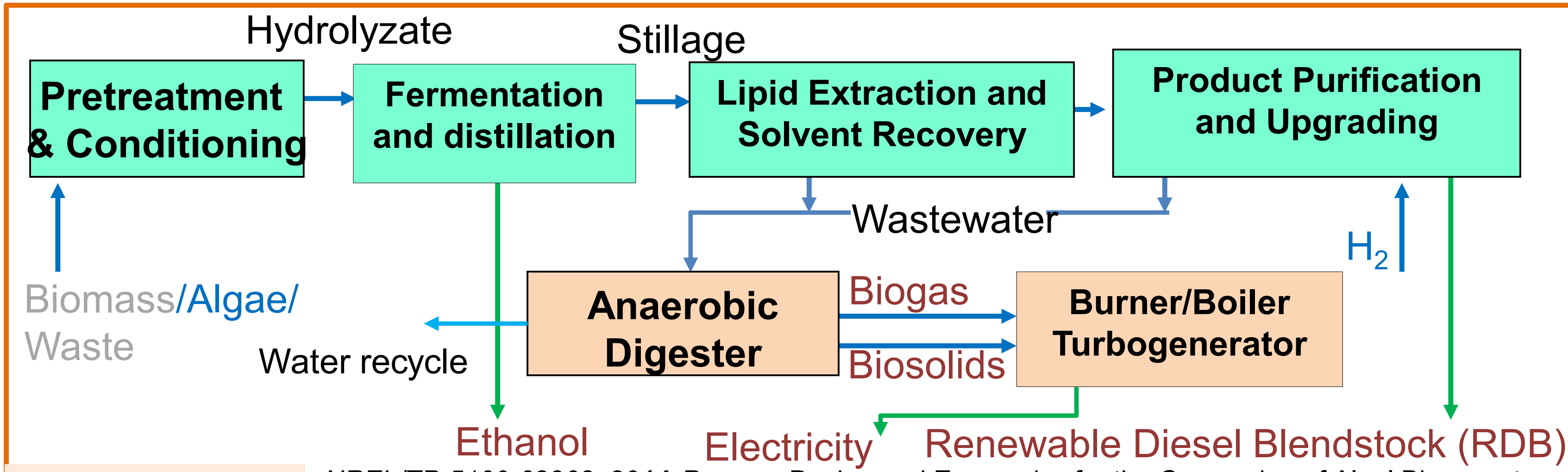
Integrating the Biomass Resource…
→ Enables A Holistic BioEconomy

Future Hydrogen Energy Systems Integrated with Biomass

Courtesy: FCTO

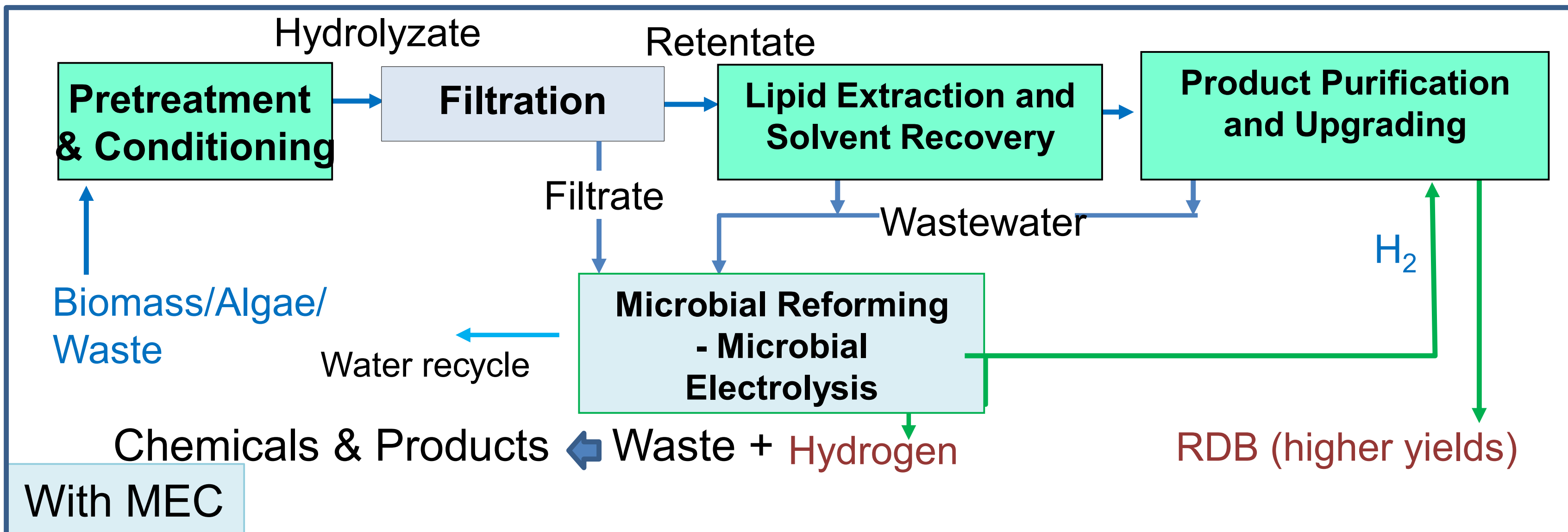


Process Optimization via Intensification

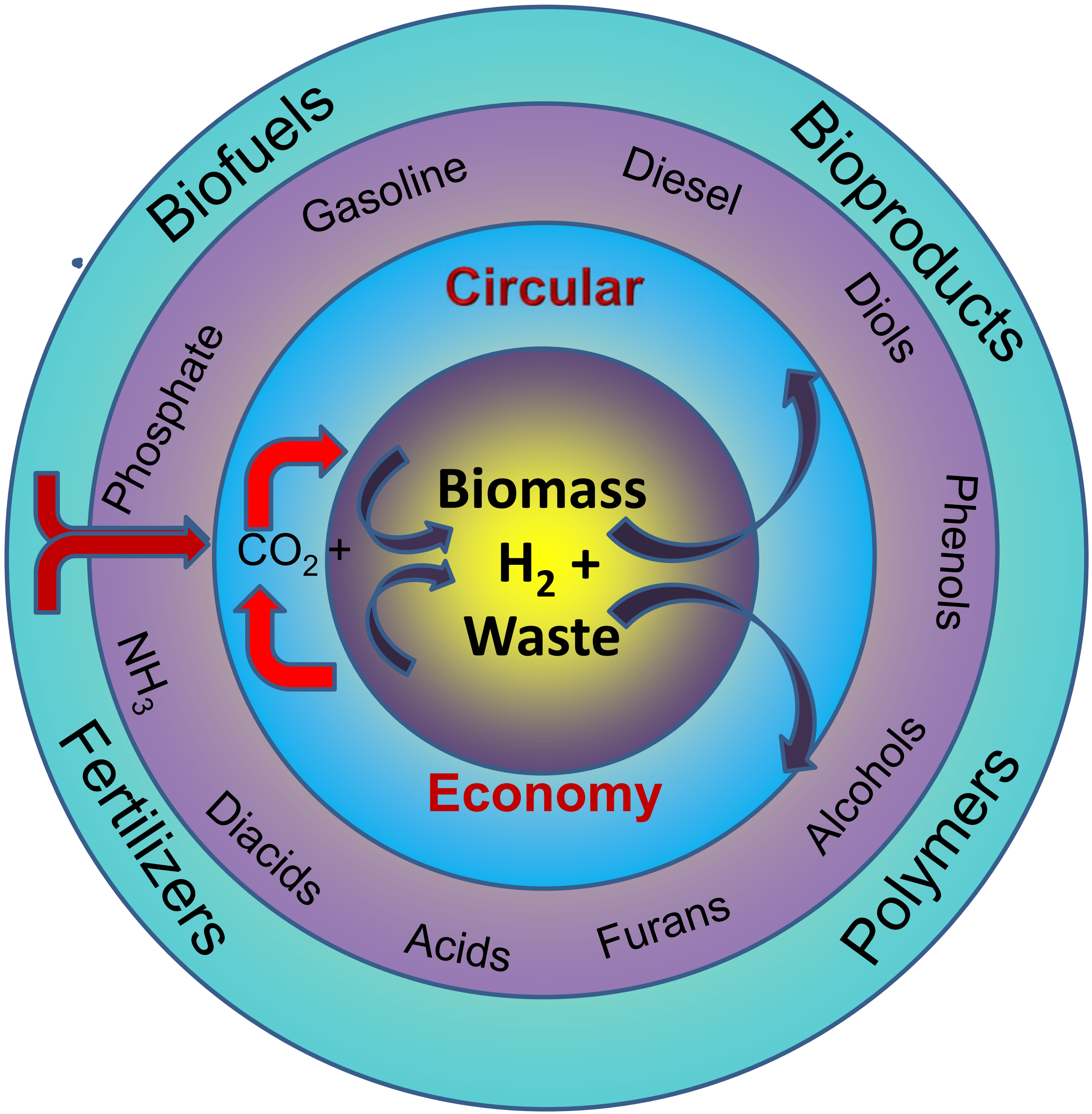


Without MEC

NREL/TP-5100-62368, ***2014.*** Process Design and Economics for the Conversion of Algal Biomass to Biofuels: Algal Biomass Fractionation to Lipid- and Carbohydrate-Derived Fuel Products, R. Davis, et al.



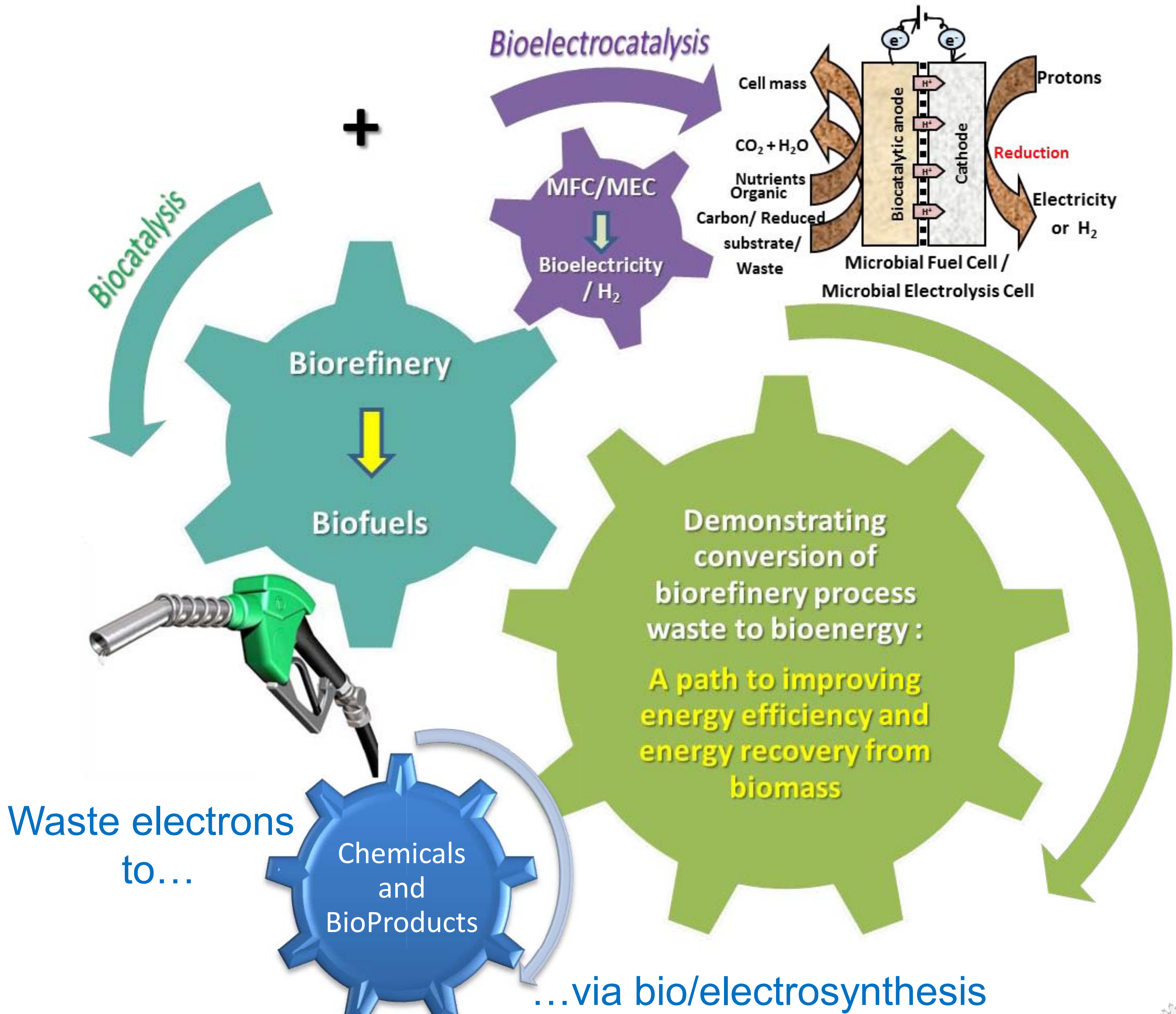
Sustainability, Special Issue: ***Sustainability in Bioenergy Production***,
Borole, A. P., 2015, Sustainable and Efficient Pathways for Bioenergy Recovery from Low-value Process Streams via Bioelectrochemical Systems in Biorefineries." 7(9): 11713-11726.


Biofuels
Bioproducts
Fertilizers
Polymers
Gasoline
Diesel
Diols
Phenols
Alcohols
Furans
Acids
Diacids
NH_3
Phosphate
Circular
Economy
CO_2 +
Biomass
H_2 +
Waste

Conclusion

- Waste to Hydrogen Technologies Need to be Implemented
- Value proposition for chemicals as well as biofuels production
- MEC - Potential game-changing technology
- Pros vs. anaerobic digestion – Direct H_2 production, minimize fugitive CH_4 release
- Cons – Nascent technology
- Hydrogen can play a significant role in bioeconomy
  - Extracting value out of waste
  - Providing a necessary reagent to generate high-value products
  - Introducing tunability in processes requiring hydrogen by diverting electrons from solar/wind to fuels & products

BioElectrochemical bioRefining (The BER Laboratory)



Environ Sci Technol *Conversion of residual organics in corn stover-derived biorefinery stream to bioenergy via microbial fuel cells*. **47**(1): 642-648. Borole, A. P., C. Hamilton, et al. (2013).