

# Technoeconomic Boundary Analysis of Photobiological Hydrogen Producing Systems

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# Overview

## Timeline

- Start Date: April 2008
- End Date: May 2009
- Percent Complete: 95%

## Barriers

- AK. Diurnal Operation Limitations
- AJ. Systems Engineering
- AS. Waste Acid Accumulation

## Budget

- Total project: \$206,149
- FY08: \$206,149
- FY09: none
- No Contractor Share

## Partners

- DOE/NREL Bio H<sub>2</sub> Working Group
- Gerald C. Dismukes - Princeton University

# Objectives

- **Conceptual System Designs**
  - Photobiological H<sub>2</sub> production systems
  - Dark fermentation H<sub>2</sub> production systems
  - Microbial Electrolysis H<sub>2</sub> production systems
  - Integrated H<sub>2</sub> production systems
- **Hydrogen Cost Calculations**
  - Calculate Capital costs, Operating costs, Feedstock costs for conceptual systems
  - Compute levelized hydrogen costs for conceptual systems
  - Determine key factors affecting cost estimates

# Approach

## Photobiological Systems

- **5 Organisms:**  
Characterize H<sub>2</sub> production
- **4 Reactor Concepts:**  
Define operation process
- **5 Plant Designs:**  
Design a reactor and plant for each organism

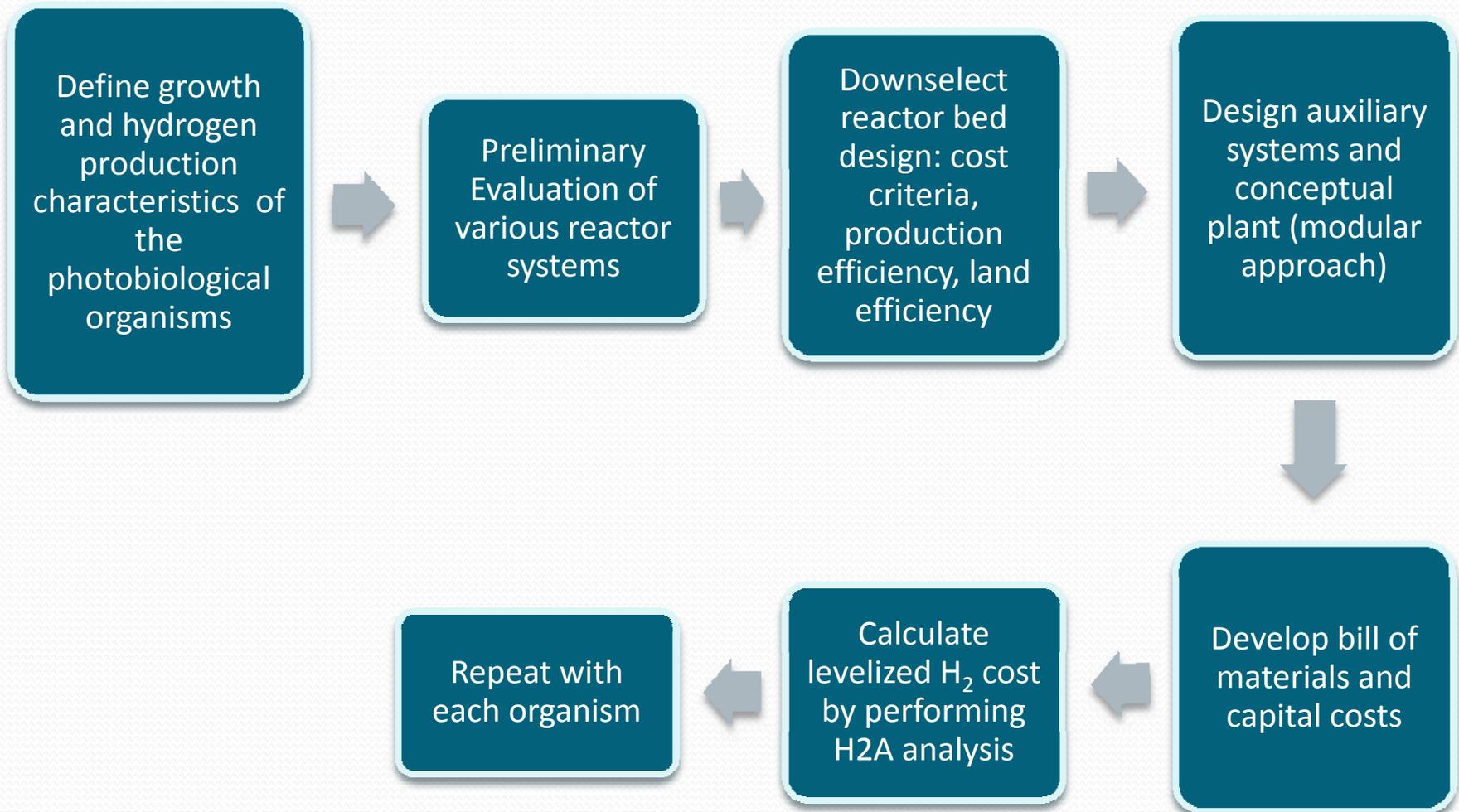
## Fermentation & Microbial Electrolysis Systems

- Fermentation using waste organisms from photobiological systems
- Fermentation using lignocellulose feed
- MEC (Microbial Electrolysis Cell) systems using acetate feedstocks

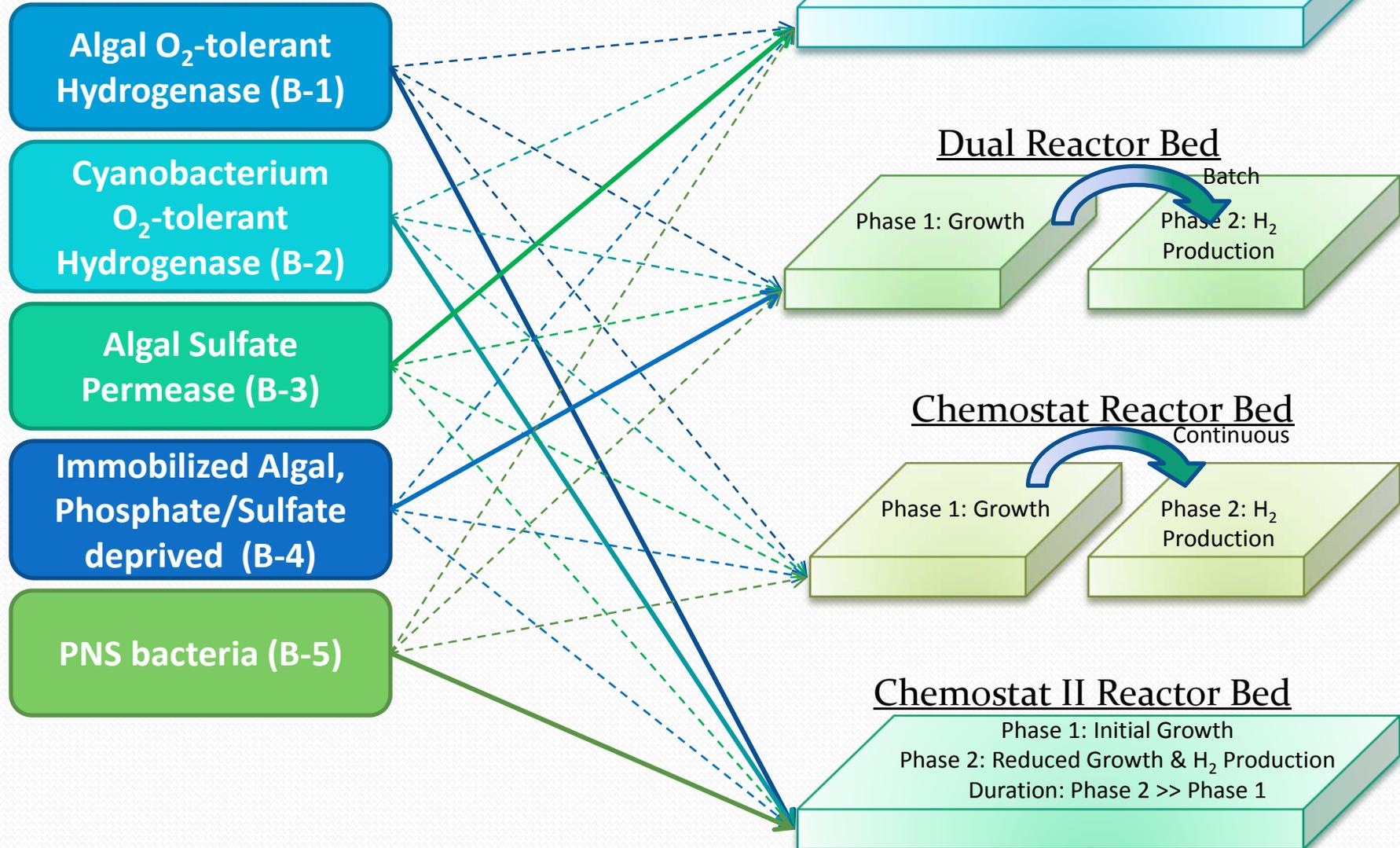
## Integrated Systems

- Combined photobiological systems
- Combined photobiological and fermentation systems
- Combined fermentation and MEC systems

# Photobiological Approach



# Organisms & Reactor Beds

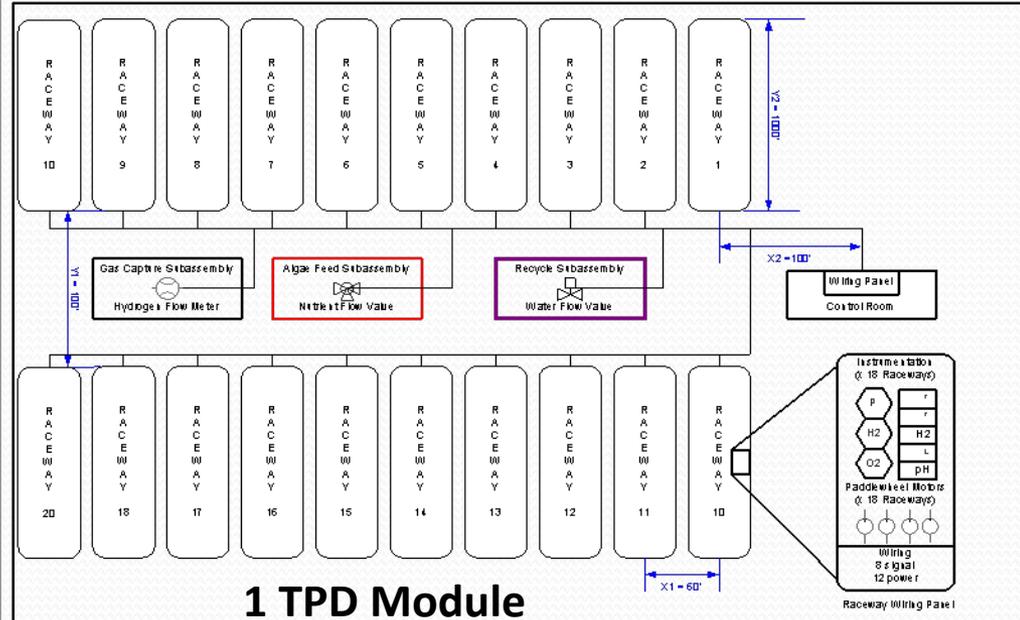
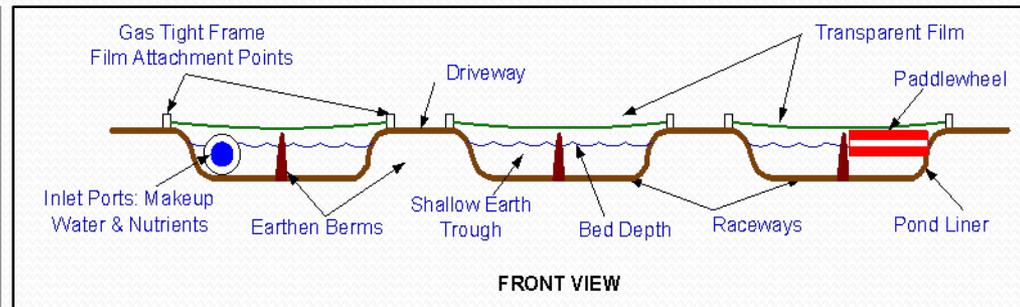
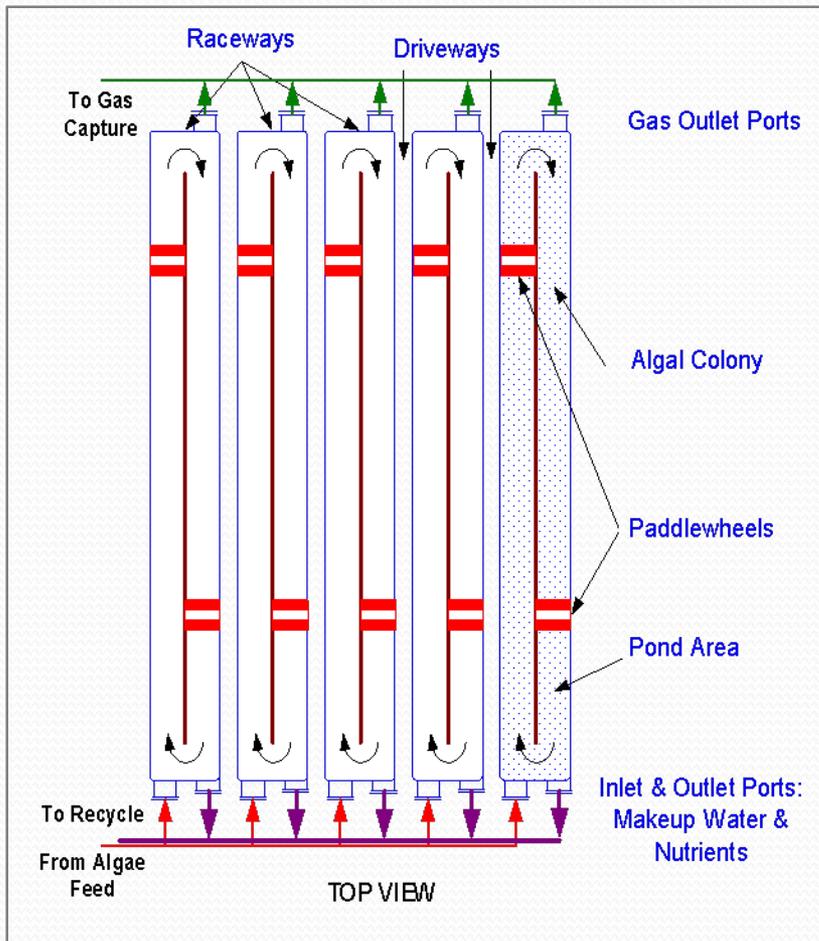


# Organism Characterization/Assumptions: 1 TPD Module

	Algal O2-tolerant Hydrogenase	Cyanobacteria O2-tolerant Hydrogenase	Algal Sulfate Permease Mutant	Immobilized Algal, Phosphate & Sulfate deprived	Purple Non-sulfur (PNS) Bacteria
Subsystem Path ID	B-1	B-2	B-3	B-4	B-5
Reactor Bed Type	Chemostat II	Chemostat II	Single-Bed	Dual-Bed	Chemostat II
H <sub>2</sub> Production Rate	1111 kgH <sub>2</sub> /day	1111 kgH <sub>2</sub> /day	1111 kgH <sub>2</sub> /day	1111 kgH <sub>2</sub> /day	1111 kgH <sub>2</sub> /day
Number of Raceways	20	20	36	64 Production 4 Growth	38
Dimensions of Raceways (ft) (LxWxD)	1090'x40'x0.33' (10 cm)	1090'x40'x0.33'	1090'x40'x0.33'	1060'x40'x0.33'	1060'x40'x 0.33'
Reactor Bed Area (acres)	20	20	35	65	37
Cell line	C. reinhardtii cc124	Synechocystis H2ase mutant	C. reinhardtii cc124	C. reinhardtii cc124	Rhodobacter sphaeroides RV
Antennae Type	LHC (Light Harvesting Complex) deletion Mutant	Phycobilin deletion Mutant	LHC deletion Mutant	LHC deletion Mutant	LHC - II deletion Mutant
Types of Macro- and Micro-Nutrients	Fertilizer containing K, N, and P, CO <sub>2</sub>	Fertilizer containing K, N, and P, CO <sub>2</sub>	Fertilizer containing K, N, and P	Fertilizer containing K, N, and P	Fertilizer containing K, N, and P, Organic acids
Cell Concentration (g/L – Dry Wgt)	0.2	0.2	0.2	26	0.2
Deprivations from media (During H <sub>2</sub> Production)	CO <sub>2</sub> deprived	CO <sub>2</sub> deprived	none	Phosphate and Sulfate deprived	Nitrogen deprived
Duration of Production Cycle (days)	Inf. continuous	Inf. continuous	3 days production 4 days growth	25 (300 hrs)	Inf. continuous
Product Gases Produced	H <sub>2</sub> , O <sub>2</sub>	H <sub>2</sub> , O <sub>2</sub>	H <sub>2</sub> , CO <sub>2</sub>	H <sub>2</sub> , CO <sub>2</sub>	H <sub>2</sub> , CO <sub>2</sub>
Theoretical Product Gas Ratio	2 mol H <sub>2</sub> 1 mol O <sub>2</sub>	2 mol H <sub>2</sub> 1 mol O <sub>2</sub>	2 mol H <sub>2</sub> 1 mol CO <sub>2</sub>	2 mol H <sub>2</sub> 1 mol CO <sub>2</sub>	2 mol H <sub>2</sub> 1 mol CO <sub>2</sub>
STH Energy <i>upper bound</i>	9.2%*	9.2%*	5.2%*	3%	5%
Efficiency: <i>current level</i>	-	-	-	0.8%	2.5%

\* level based on 100% utilization of PAR photons for growth and H<sub>2</sub> production and with no light saturation limit

# Reactor Bed Design & Plant Layout



10 TPD Plant Capacity = 1 TPD Module x 10

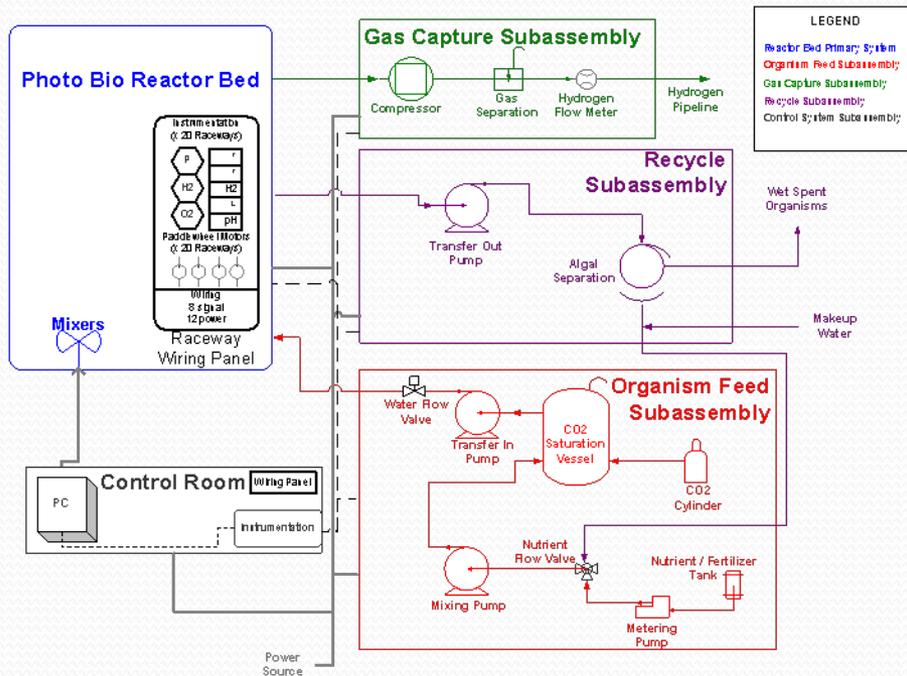
1 TPD Module (at 9.2% STH efficiency) = 20 reactor beds (raceways) over 26 acres

1 Raceway = 1090 ft x 40 ft x 0.33ft

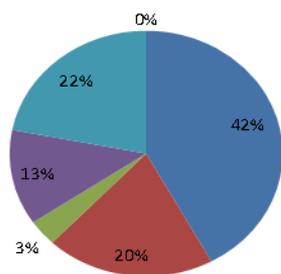
# Plant Design

## Algal O<sub>2</sub>-tolerant Hydrogenase (B-1)

## Process Diagram



## Capital Expenditures



- Photo Bioreactor Subassembly
- Gas Capture Subassembly
- Algae Feed Subassembly
- Recycle Subassembly
- Control System

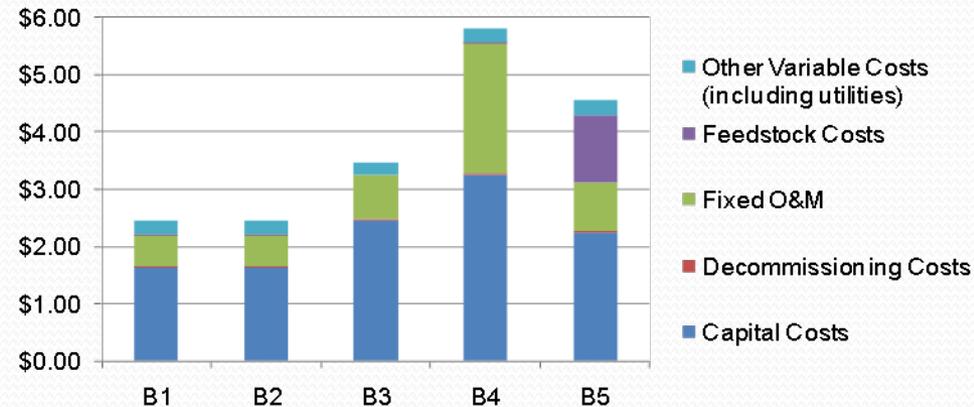
## Bill of Materials: 1 TPD Module

Description	Size Req'd	Units	Unit Size	Units	Unit cost	Qty Req'd	Total Cost
<b>Photo Bio Reactor Bed Subassembly</b>							
Transparent Film	87080 m2	1	m2	\$ 0.54	87,080	\$ 46,871	
Pond Lining	93998 m2	1	m2	\$ 0.47	93,998	\$ 44,412	
Pond Edging	13982 m	1	m	\$ 7.00	13,982	\$ 97,876	
Installation of Ponds		1	raceway	\$ 26,083.00	20	\$ 521,660	
Paddlewheel Mixers		1	each	\$ 5,000.00	40	\$ 200,000	
Inlet Water Valve	0.5 in	1	each	\$ 43.46	20	\$ 869	
Outlet Water Valve	0.5 in	1	each	\$ 43.46	20	\$ 869	
Outlet Gas Valve	1.0 in	1	each	\$ 67.23	20	\$ 1,345	
Flanges	0.5 in	1	each	\$ 8.00	60	\$ 480	
<b>Gas Capture Subassembly</b>							
Compressor	37 kgmol/hr	37	kgmol/hr	\$ 9,233.00	1	\$ 338,347	
PSA				\$ 89,215.16	1	\$ 89,215	
Piping - 4"	1180 ft	1	ft	\$ 6.18	1180	\$ 7,292	
Piping - 1"	40 ft	1	ft	\$ 1.00	40	\$ 40	
<b>Organism Feed Subassembly</b>							
Transfer In Pump	150 gpm	150	gpm	\$ 10,252	1	\$ 10,252	
Nutrient Metering Pumps	1468 Gal/Hr.	7	\$ 2,594	7	\$ 18,158		
Mixing Pump	150 gpm	150	gpm	\$ 10,252	1	\$ 10,252	
CO2 Cylinder	50 lb	50	lb	\$ 360	1	\$ 360	
CO2 Saturation Vessel	15000 gal	15000	gal	\$ 30,000	1	\$ 30,000	
Nutrient Tank	8 gal	10	gal	\$ 30.00	1	\$ 30	
Initial Medium	3.80 lb/Acre/yr	1	Acre	\$ 0.76	20	\$ 15.21	
CO2 Gas	156 lb CO2	50	lb CO2	\$ 35.00	3	\$ 112	
Water	2142022 gal	1	gal	\$ 0.001665	2,142,022	\$ 3,566	
Piping - 1/2"	40 ft	1	ft	\$ 0.52	40	\$ 21	
Piping - 1.5"	1180 ft	1	ft	\$ 1.57	1180	\$ 1,853	
Piping - 2"	180 ft	1	ft	\$ 2.12	180	\$ 382	
<b>Recycle Subassembly</b>							
Rotary Drum filter	9639 gph	3750	gph	\$ 87,000.00	3	\$ 261,000	
Transfer Out Pump	150 gpm	150	gpm	\$ 10,252	1	\$ 10,252	
Piping - 1/2"	40 ft	1	ft	\$ 0.52	40	\$ 21	
Piping - 1.5"	1180 ft	1	ft	\$ 1.57	1180	\$ 1,853	
<b>Control System</b>							
Control Room	160 ft2	1	ft2	\$ 50.00	160	\$ 8,000	
Control Room Wiring Panel		1	\$ 3,000.00	1	\$ 3,000.00		
Raceway wiring Panel		1	\$ 146.00	20	\$ 2,920		
Computer and Monitor		1	\$ 1,500.00	1	\$ 1,500.00		
Labview Software		1	\$ 4,299.00	1	\$ 4,299.00		
Level Indicators		1	\$ 3,000.00	20	\$ 60,000.00		
Pressure Sensors		1	\$ 4,700.00	20	\$ 94,000.00		
Hydrogen Area Sensors		1	\$ 5,500.00	20	\$ 110,000.00		
Air Temperature Indicator		1	\$ 1,800.00	20	\$ 36,000.00		
Water Temperature Indicator		1	\$ -	20	\$ -		
pH level Indicator		1	\$ 1,200.00	20	\$ 24,000.00		
Oxygen Area Sensors		1	\$ 5,500.00	20	\$ 110,000.00		
Nutrient Flow Valve		1	\$ 5,500.00	1	\$ 5,500.00		
Water Flow Valve		1	\$ 5,500.00	1	\$ 5,500.00		
Hydrogen Flow Meter		1	\$ 5,500.00	1	\$ 5,500.00		
Instrument Wiring	69170 ft	1	ft	\$ 0.02	69170	\$ 1,343.84	
Power Wiring	102150 ft	1	ft	\$ 0.02	102150	\$ 1,981.71	
Conduit	4810 ft	1	ft	\$ 0.58	4810	\$ 2,788.84	
<b>System Initial Cost</b>						\$ 2,173,735	

# Study Results - Photobio

	B-1	B-2	B-3	B-4	B-5
Bed Type	Chemostat II	Chemostat II	Single Bed	Dual Bed	Chemostat II
Total Bed Area (m <sup>2</sup> )	809,680	809,680	1,433,230	2,493,830	1,496,300
Solar to H <sub>2</sub> Efficiency (%)	9.2%*	9.2%*	5.2%*	3.0%	5.0%
Production (kg H <sub>2</sub> /day)	10,000	10,000	10,000	10,000	10,000
Capital Cost (\$M)	21.73	21.73	32.84	43.43	33.92
<b>Cost (\$/kgH<sub>2</sub>)</b>	<b>2.41</b>	<b>2.41</b>	<b>3.47</b>	<b>5.67</b>	<b>4.41</b>
Product Mix	2 mol H <sub>2</sub> + 1 mol O <sub>2</sub> (Potential Combustion Issues)		2 mol H <sub>2</sub> : 1 mol CO <sub>2</sub>		

\* level based on 100% utilization of PAR photons for growth and H<sub>2</sub> production and with no light saturation limit



Plant Capital Costs minimized by accumulating product H<sub>2</sub> in pond headspace and sizing gas processing for 24 hr/day operation.

# Dark Fermentation & MEC Systems

- **Fermentation of Algae or Bacteria**
  - Evaluate H<sub>2</sub> production capability from photobiological system waste
  - Feedstock of 2.3 TPD, Generates 7 kg/day H<sub>2</sub>
- **Fermentation of Corn Stover**
  - Developed from NREL report on ethanol production from corn stover<sup>1</sup>
  - Use bacteria developed by NREL for H<sub>2</sub> production with acetate byproduct
  - Size based on feedstock of 2,000 TPD corn stover, Generates 41 TPD H<sub>2</sub>
- **Microbial Electrolysis Cell (MEC)**
  - Uses byproduct acetate from fermentor, or purchased acetate
  - Process design based on experimental work done at Penn State<sup>2</sup>
  - System Generates 104 TPD H<sub>2</sub>
- **All Systems**
  - Design plant, develop bill of materials, compute capital cost, operating cost, feedstock cost
  - Perform levelized hydrogen cost computations

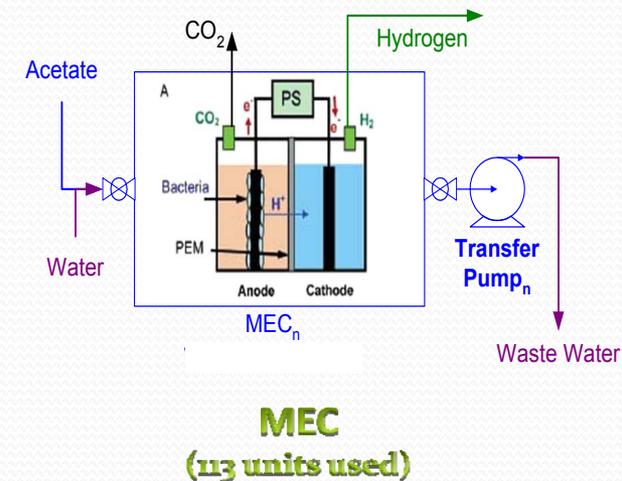
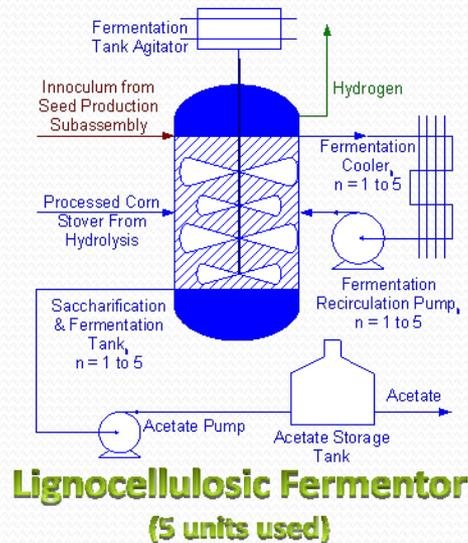
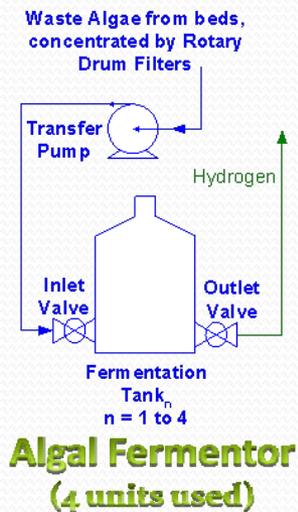
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<sup>1</sup> A. Aden, et al., "Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover", NREL/TP-510-32438, June 2002.

<sup>2</sup> D. Call, et al "High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells", Environ. Sci. Technol, 2009.

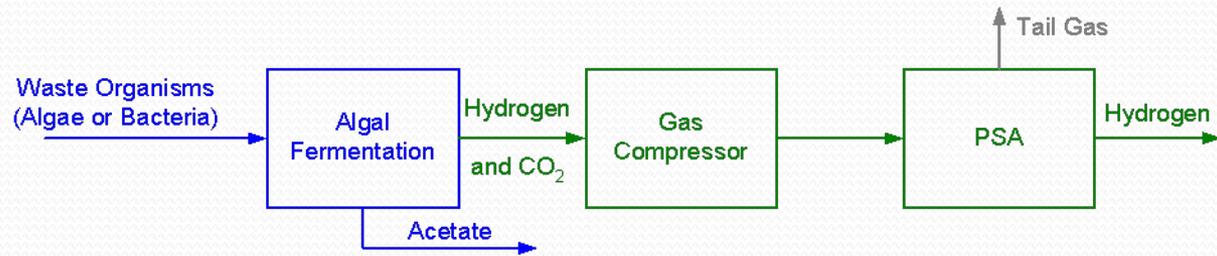
# System Designs

Parameters	Algal Fermentor	Lignocellulosic Fermentor	MEC
Design Basis	NREL Research	NREL / TP-510-32438 (ethanol) NREL H <sub>2</sub> Bacteria Research	Penn State Research, NREL Research
Feedstock	Waste Algae/ Bacteria from Photobio	Corn Stover	Acetic Acid
Feedstock Usage (kg/day)	2,312– 4,272	2,000,000	852,530
Reactor Parameters	55 °C Fermentation	150 °C Hydrolysis 55 °C Saccharification & Fermentation	40 °C 0.9 Volt Potential
Electricity Usage (kWhr/day)	43-58	163,356	3,340,862
Residence Time (hours)	72	36	24
# of primary reaction Vessels	4 (2500 – 4500 gallons)	5 (1 million gallons each)	113 (1 million gallons each)
H <sub>2</sub> Production Rate (kg/day)	~7-13	41,315	104,410
Mass Conversion rate (kg H <sub>2</sub> /kg feedstock)	0.4%	2.5%	12%

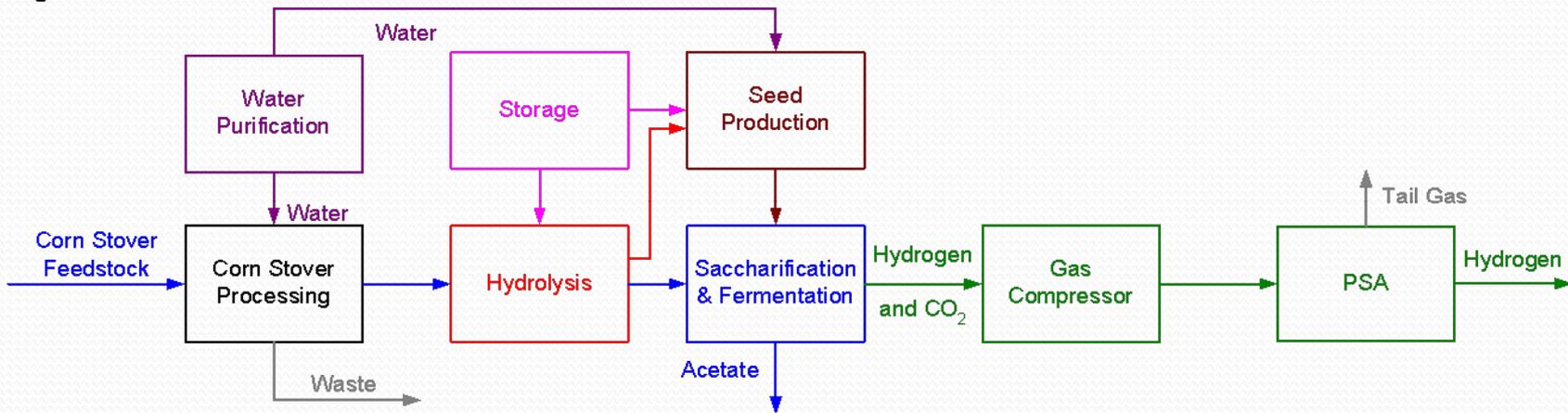


# Fermentation Plant Process Diagrams

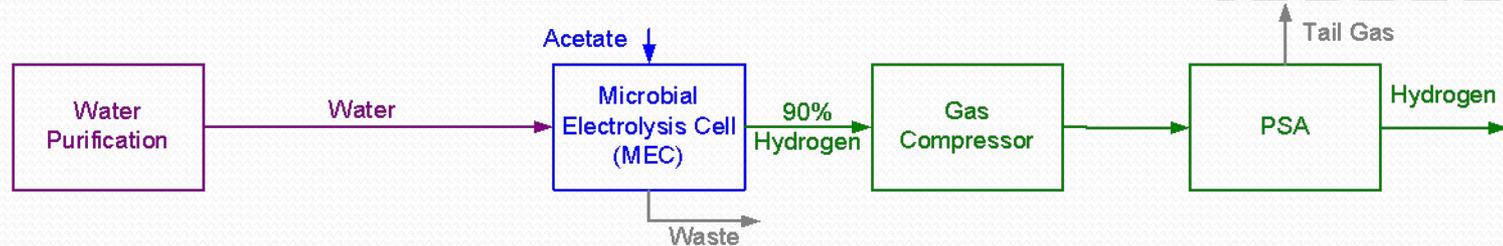
## Algal Fermentation



## Lignocellulosic Fermentation

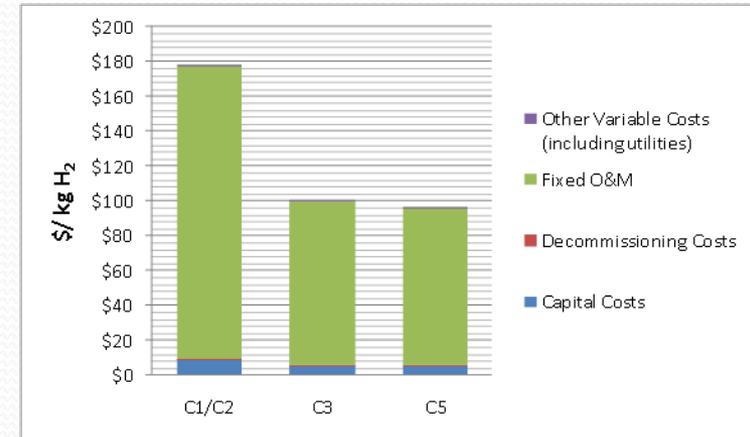


## MEC System



# Algal Fermentation Results

System Criteria	C-1	C-3	C-5
Organism Input Basis	B-1 or B-2	B-3	B-5
Feedstock	Algal or Cyanobacterium O <sub>2</sub> -tolerant Hydrogenase	Algal Sulfate Permease	PNS Bacteria
Feedstock Usage (kg/day)	2,312	4,092	4,272
Production (kg H <sub>2</sub> /day)	7	12	13
Capital Cost (\$)	\$52,198	\$80,351	\$86,211
Cost (\$/kg H <sub>2</sub> )	<b>\$178.40</b>	<b>\$103.45</b>	<b>\$98.99</b>
Mass Conversion (kg H <sub>2</sub> /kg feedstock)	0.4%	0.4%	0.4%

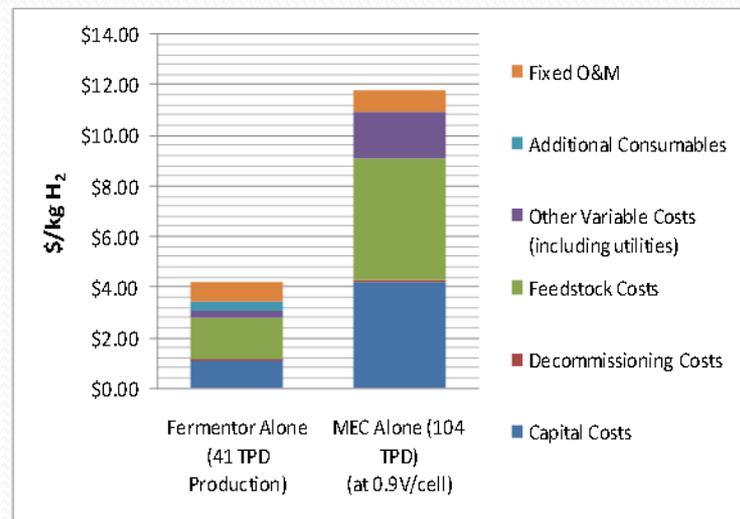


- Feedstock is spent waste from single 10TPD Photobio System
- Stand-alone system costs assume no cost algae feedstock
- Current low conversion rate yields high Capital Cost / per kg H<sub>2</sub>
- Systems are too small: labor (in fixed O&M) is very high % of cost  
(with zero labor cost , hydrogen cost would be \$6.54-\$7.47/kg H<sub>2</sub>)

System requires algal waste of very large photobiological systems to achieve suitable throughput volume. Also, organism waste transportation will add additional expenses.

# Lignocellulose Fermentor and MEC Results

	Lignocellulosic Fermentor	MEC
Feedstock	Corn Stover (\$30/ton dry)	Acetate + Electricity (at \$0.60/kg acetate)
Area (acres)	11 (+ 500 acres for long term corn stover storage)	10
Production (Tonnes H <sub>2</sub> /day)	41	104
Mass Conversion (kg H <sub>2</sub> /kg Feedstock)	2.6%	12.9%
Capital Cost (\$M)	\$47.5M	\$563.9M
H <sub>2</sub> Cost (\$/kg H <sub>2</sub> )		
- No acetate sale	\$4.18/kg H <sub>2</sub>	\$11.79/kg H <sub>2</sub>
- \$0.20/kg acetate sales	\$0.65/kg H <sub>2</sub>	NA

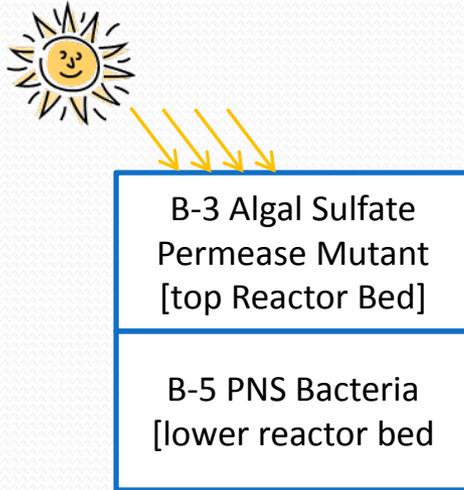


- MEC sized for potential integration with fermentor as acetate byproduct processor
- High Fermentor/MEC integration potential: raw fermentor byproduct readily used as MEC feedstock
- Sale of fermentor byproduct acetate drives down fermentor H<sub>2</sub> cost: acetate purification cost needs to be quantified
- Fermentor design based on production ethanol plant and thus has higher cost confidence than MEC design
- MEC H<sub>2</sub> cost is dominated by high cathode cost and high acetate dilution % (high system volume): and further developments to reduce these would greatly improve system cost effectiveness

Lignocellulose fermentor offers pathway to ~\$1/kg H<sub>2</sub> due to byproduct acetate sales

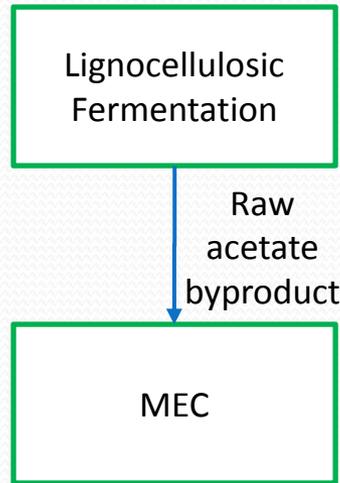
# Integrated Systems

## Photobiological Stacked Beds



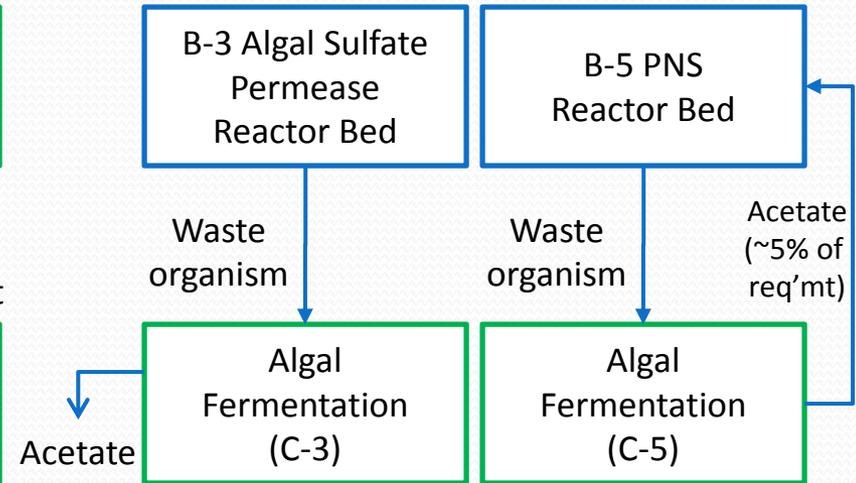
- Lower bed organism captures photons outside of photosynthesis band of top bed organism
- Shared excavation and labor costs
- Resized BOP subassemblies

## Fermentor/MEC Integration



- Ligno byproduct stream = MEC feedstock
- Shared water purification system
- Separate gas processing systems

## Photobio-Fermentor Integration (Two options)



- C-3 and C-5 are sized to accept B-3 and B-5 waste respectively.
- Integration reduces labor and gas processing costs associated with Algal Fermentation
- IB-5/C-5 Integration slightly reduces acetate costs for PNS

These combinations were selected from several possible combinations and others can be explored based on the synergies of their flowstreams.

# Integrated Systems Results

Photobiological Stacked Beds	
System	\$/kg H <sub>2</sub>
Stand alone B-3 (10 TPD)	\$3.47
Stand alone B-5 (10 TPD)	\$4.41
Integrated (12 TPD)	\$4.33

Photobio & Organism Fermentor		
System	\$/kg H <sub>2</sub>	\$/kg H <sub>2</sub>
Stand alone Photobio 10 TPD	\$3.47 (B-3)	\$4.41 (B-5)
Stand alone Algae Fermentation (~0.02 TPD)	\$103.45 (C-3)	\$98.99 (C-5)
Integrated (~10.02 TPD)	\$3.62	\$4.96

Lignocellulose Fermentator & MEC	
System	\$/kg H <sub>2</sub>
Fermentor alone 41 TPD	\$4.18 (~\$1.00 with acetate sale)
MEC alone 104 TPD (not optimized for lowest cost)	\$11.79
Integrated 144 TPD (unoptimized)	\$4.18 from fermentor \$6.48 from MEC \$5.83 combined

- Algal Fermentation & MEC a possibility for future integration
- MEC based on PSU research data, not optimized for lowest capital cost
- Integration of more than 2 systems possible, but can be logistically difficult

Integrated systems make best use of land and waste products.  
Further developments can yield more cost effective systems.

# Collaborations

<b>Collaborator</b>	<b>Organization</b>	<b>Role/Expertise</b>
Bio-Hydrogen Working Group	DOE	System and Organism Guidance
- Tasio Melis	UC - Berkeley	Photobiological systems
- Maria Ghirardi	NREL	Photobio organisms & Fermentation processes
- PinChing Maness	NREL	PNS organisms & Fermentation processes
- Mike Seibert	NREL	Immobilized Algal systems, Sulfur deprived (B-4)
Gerald C. Dismukes	Princeton Univ.	Consultant, Photobio
Bruce Logan	Penn State Univ.	MEC system data

# Summary

- Technoeconomic Boundary Analysis Conducted
  - Defined and Evaluated 4 different H<sub>2</sub> Production approaches
    - Photosynthesis with algae and bacteria, waste algae fermentation, lignocellulose fermentation, and microbial electrolysis
    - Approaches included multiple system embodiments and system integrations
  - Estimated concepts' feasibility, performance, and cost and resultant \$/kg H<sub>2</sub>
  - Provided systems contexts and issues to researchers
- Plant performance based on component performance projections
  - Photosynthesis systems
    - Postulated advanced truncated antenna mutants without light saturation limit yield 5-9% STH efficiency (best case result)
    - Such mutants are in development, however, current STH efficiency is much lower <1%
    - Large shallow reactor beds with thin film cover are most economic approach
    - Results point to future H<sub>2</sub> costs with mutants ~\$2.40-6.00/kg H<sub>2</sub>
  - Algal Fermentation
    - Based on experimental results, Utilizes waste organisms from photobio systems
    - Resulting high cost due to effects of labor cost and low H<sub>2</sub> Production ~\$100/kg H<sub>2</sub>

# Summary (continued)

- Lignocellulose Fermentation
  - Complicated process, but well defined from ethanol production examples
  - Assumed Hydrolysis process and fermentation bacteria are technical advances
  - Predicted H<sub>2</sub> price of \$4.18/kg could be lowered to ~\$1.00/kg with byproduct sales (exact byproduct composition and treatment not yet defined)
- Microbial Electrolysis Cell
  - Promising experimental results used as basis for analysis
  - Significant scale-up issues for production not yet resolved
  - Current immature production concept suggests H<sub>2</sub> price of \$11/kg using purchased acetate or \$5.80/kg using no-cost acetate from fermentor
  - Extensive cost reduction potential from system component development
- Integrated systems
  - 4 integrated systems examined
  - Significant symbiotic effect with Fermentor/MEC combination but not with others
  - Examination of additional concepts may lead to additional improvement
- Extensive collaboration/coordination with DOE Bio-Hydrogen Working Group

# Proposed Future Work

- Integrated Systems
  - Validate costs and scaling benefits and alternative pathways
- Photobio Systems
  - Sensitivity analysis including effects of algae photon utilization rate saturation (e.g., electron transport rate saturation of truncated antenna mutants)
  - Alternative reactor bed concepts
  - More mature design study addressing mixing and pH control, thermal control, CO<sub>2</sub> absorption
- Algae Fermentation Systems
  - Pre-treatment of algae (e.g., hydrolysis) to increase conversion rate
  - Large-scale production using high glucose algae grown specifically for fermentation
- Lignocellulose Fermentation System
  - More detailed analysis/verification of subsystems
  - Analysis of byproduct utilization and consequent reduction in effective \$/kgH<sub>2</sub>.
- MEC System
  - Optimized production process and components for low capital cost system
    - Increased solution density, Increased pressure operation
    - Low cost cathodes and anodes
    - Cathode and anode optimization for large reactors
  - Determination of ion transport loss increases in large scale reactors