Techno-economic Boundary Analysis of Biological Pathways to Hydrogen Production (2009)

24 September 2013

Presentation to:
Biological Hydrogen Production Workshop

By:
Brian D. James
Strategic Analysis Inc.
Bjames@sainc.com
(703) 778-7114

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Overview of 2009 Directed Technologies Inc. (DTI) Analysis

Timeline

- Start Date: April 2008
- End Date: Sept 2009

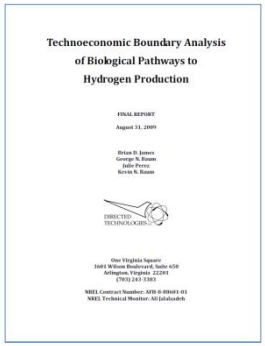
Barriers

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

Deliverables

- Written Report (207 pages)

Full documentation is needed.


Technoeconomic Boundary Analysis of Biological Pathways to Hydrogen Production

FINAL REPORT

August 31, 2009

Brian D. James
George N. Baum
Julie Perez
Kevin N. Baum

DIRECTED TECHNOLOGIES, INC.

One Virginia Square
3601 Wilson Boulevard, Suite 650
Arlington, Virginia 22201
(703) 243-3383

NREL Contract Number: AFH-0-88601-01
NREL Technical Monitor: Ali Jalalzadeh

Partners/Collaborators

- DOE/NREL Bio H_2 Working Group
  - Roxanne Garland, DOE
  - Ali Jalalzadeh-Azar, NREL
  - Mike Seibert, NREL
  - Maria Ghirardi, NREL
  - Pin-Ching Maness, NREL
  - Tasio Melis, UC Berkeley
- Gerald C. Dismukes - Princeton University
- Bruce Logan, Penn State
- DTI Team
  - Brian James
  - George Baum
  - Julie Perez
  - Kevin Baum

Strong Technical Team is a must. Analysis will be interactive and collaborative. Should not be conducted in isolation by one group.

Objectives

- **Conceptual System Designs**
  - Photobiological H_2 production systems
  - Dark fermentation H_2 production systems
  - Microbial electrolysis H_2 production systems
  - Integrated H_2 production systems

Conceptualization of systems was more than half the battle.

H2A Model was main $/kgH2 evaluation tool.

- **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

Defining scope at beginning of project is critical. Agree on simplifying assumptions early. Can always add detail later on.

Photobiological Systems

- 5 Organisms:
  Characterize H_2 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 fermentation and MEC systems
- Combined Photobiological and Fermentation systems

Fundamental decision is the technology timeframe.
Is it current, near-future, or far-future systems that are to be examined?

Photobiological Approach

Mostly Excel computations for system performance computations. PowerPoint diagrams of system concepts for ease of discussion.

In association with Tech Team augmented by literature references, commercial company practices.

Define growth and hydrogen production characteristics of the photobiological organisms

Preliminary evaluation of various reactor systems

Downselect reactor bed design: cost criteria, production efficiency, land efficiency

Design auxiliary systems and conceptual plant (modular approach)

Develop bill of materials and capital costs

In Excel with scaling parameters (since design and assumptions will change numerous times).

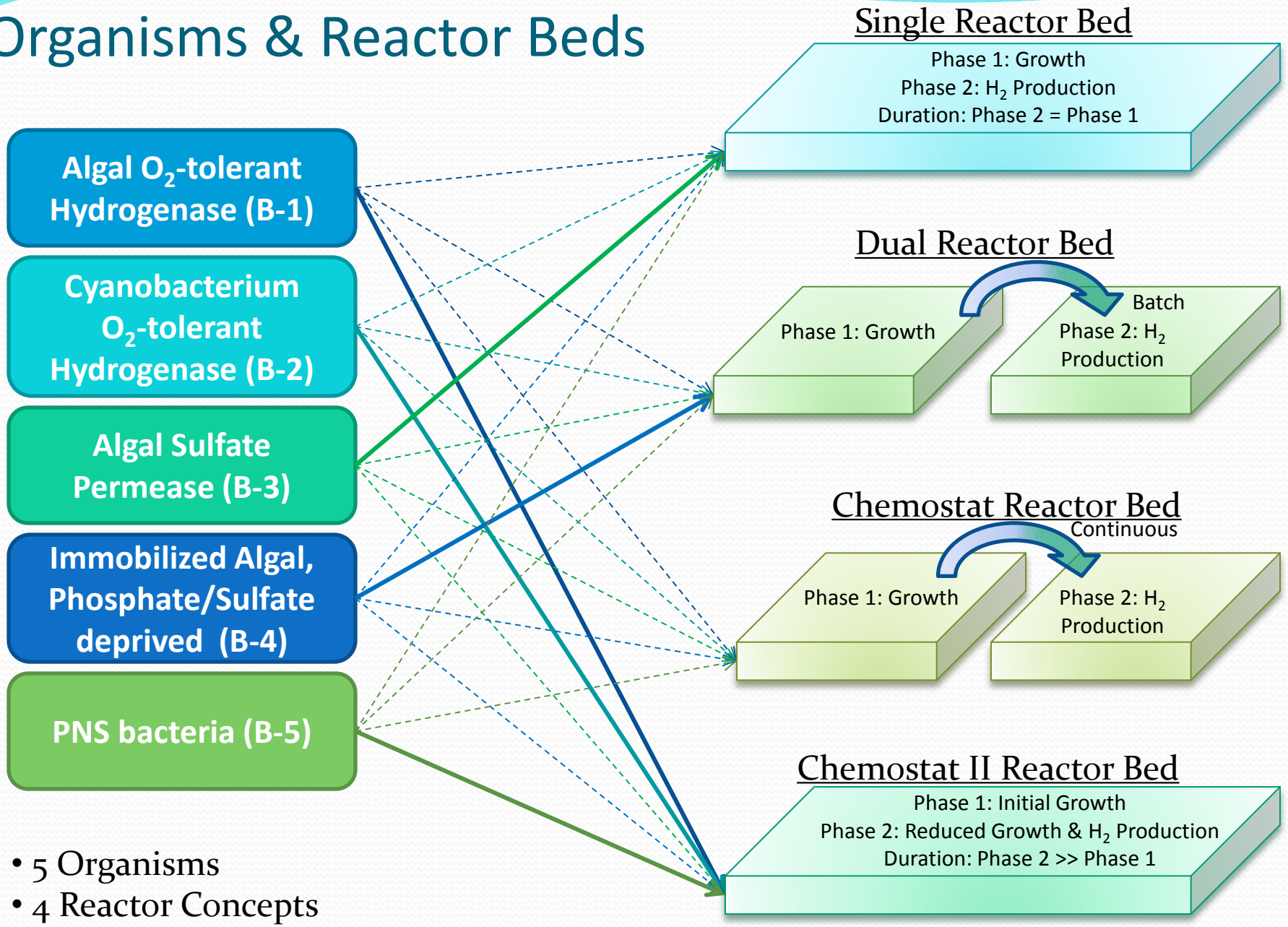
Calculate levelized H_2 cost by performing H2A analysis

Using H2A Model.

Repeat with each organism

While shown as sequential, in practice the approach had much iteration and back-tracking. This led to much better product.

Organisms & Reactor Beds



- 5 Organisms
- 4 Reactor Concepts

Organism Characterization/Assumptions: 1 TPD Module

A "Key Attributes" table (frequently updated) was vital to understanding and achieving consistency between pathways.

Much discussion went into how forward-looking to be in regards to operation and efficiency.

Parameters / Varialbes	B-1	B-2	B-3	B-4	B-5
Organisms	Algal O_2-tolerant Hydrogenase	Cyanobacteria O_2-tolerant Hydrogenase	Algal Sulfate Permease Mutant	Immobilized Algal, Phosphate& Sulfate deprived	Purple Non-sulfur (PNS) Bacteria
Reactor Bed Type	Chemostat II	Chemostat II	Single-Bed	Dual-Bed	Chemostat II
H_2 Production Rate	1,111 kgH_2/day	1,111 kgH_2/day	1,176 kgH_2/day	1,176 kgH_2/day	1,111 kgH_2/day
Number of Raceways	20	20	38	90 Production 2 Growth	54
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	38	87	54
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, CO2	Fertilizer containing K, N, and P, CO2	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	4.91	2.8	0.2
Deprivations from media (During H_2 Production)	None	None	none	Phosphate deprived, Sulfate limited	Nitrogen deprived
Duration of Production Cycle (days)	Semi-infinite Continuous	Semi-infinite Continuous	3 days production 4 days growth	3 days production, 1 day growth for ~180 days total	Semi-infinite continuous
Product Gases Produced	H_2, O_2	H_2, O_2	H_2, CO_2	H_2, CO_2	H_2, CO_2
Theoretical Product Gas Ratio	2 mol H_2 1 mol O_2	2 mol H_2 1 mol O_2	2 mol H_2 0.86mol CO_2	2 mol H_2 0.6 mol CO_2	2 mol H_2 0.05 mol CO_2
STH Energy Effic. Upper Bound Near Term	9.2%* 2%	9.2%* 2%	5.2%* 1.3%	2.25% 1.5%	3.5% 1.5%

* level based on 100% utilization of PAR photons for growth and H2 production and with no light saturation limit

Solar Conversion Efficiency

STH Efficiency = Solar-to-Hydrogen Energy Conversion Efficiency

$$= \frac{(\text{LHV of Net } H_2 \text{ out of System})}{(\text{total solar energy input into system collector})}$$

Full spectrum energy

Full active area, not space in-between panels/beds

- Need to specify location (since it affects insolation)
- Be mindful of daily and seasonal solar fluxuations
  - Affects sizing of equipment
- Be aware of H_2 loss mechanisms
  - H_2 leaks
  - Solar absorption in transparent films.

Approach Specific Metrics

- Three Approaches examined
  - Photolytic Bio H2
  - Photosynthetic Bacterial
  - Dark Fermentation and Macrobial Electrolysis Cells (MECs)

- Tables appear in DOE 2012 Multiyear Research Development & Demonstration Plan (MYRD&D) http://www1.eere.energy.gov/hydrogenandfuelcells/mypp/pdfs/production.pdf

- Tables have extensive footnotes

Table 3.1.10 Technical Targets: Photolytic Biological Hydrogen Production [a]

Characteristics	Units	2011 Status	2015 Target [c]	2020 Target [d]	Ultimate Target [e]
Hydrogen Cost [b]	$/kg	NA	NA	9.20	2.00
Reactor Cost [f]	$/m^2	NA	NA	14	11
Light utilization efficiency (% incident solar energy that is converted into photochemical energy) [g]	%	25 [h]	28	30	54
Duration of continuous H_2 production at full sunlight intensity [i]	Time Units	2 min [j]	30 min	4 h	8 h
Solar to H_2 (STH) Energy Conversion Ratio [k]	%	NA	2%	5%	17%
1-Sun Hydrogen Production Rate [l]	kg/s per m^2	NA	1.6E-7	4.1E-7	1.4E-6

Table 3.1.11 Technical Targets: Photosynthetic Bacterial Hydrogen Production [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target [b]
Efficiency of Incident Solar Light Energy to H_2 (E0*E1*E2) [c] from organic acids	%	NA	3	4.5
Molar Yield of Carbon Conversion to H_2 (depends on nature of organic substrate) E3 [d]	% of maximum	NA	50	65
Duration of continuous photoproduction [e]	Time	NA	30 days	3 months

Table 3.1.12 Technical Targets: Dark Fermentative Hydrogen Production and Microbial Electrolysis Cells (MECs) [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target [b]
Feedstock Cost [c]	cents/lb. sugar	13.5	10	8
Yield of H_2 production from glucose by fermentation [d]	mol H_2 /mol glucose	3.2 [e]	4	6
Yield of H_2 production from glucose by integrated MEC – fermentation [f]	mol H_2 /mol glucose	-	6 [e]	9 [e]
Duration of continuous production (fermentation)	Time	17 days [g]	3 months	6 months
MEC cost of electrodes	$/m^2	2,400 [h]	300	50
MEC production rate	L-H_2 / L-reactor-day	-	1	4

This presentation does not

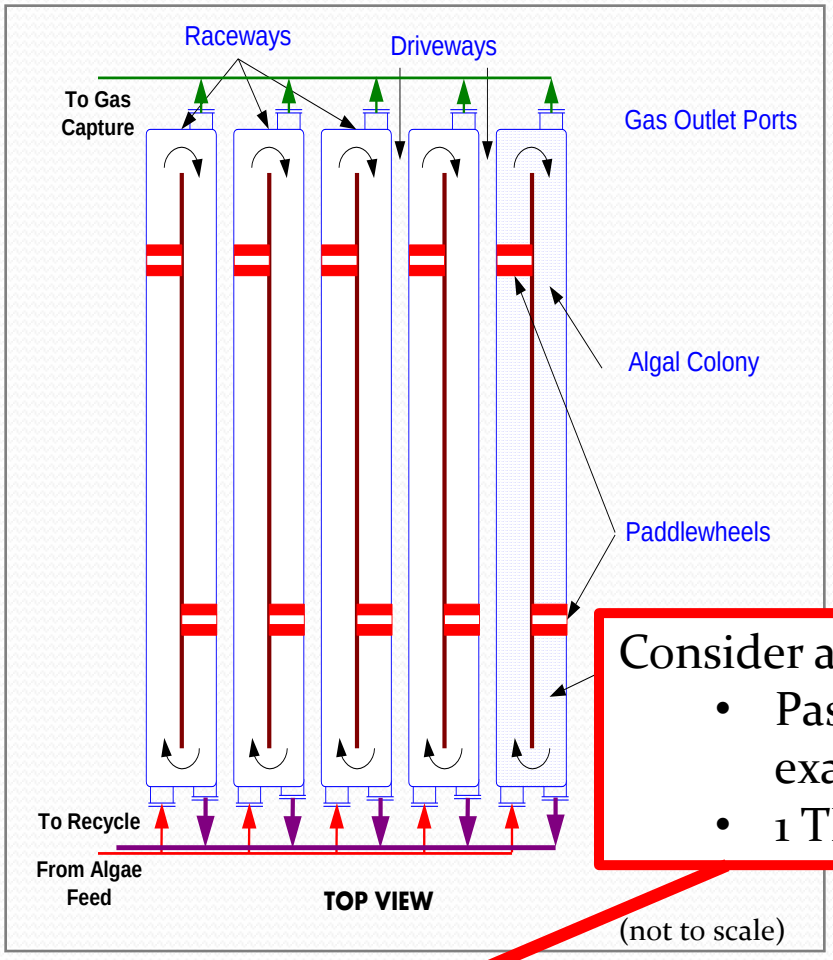
Key Assumptions in Analysis

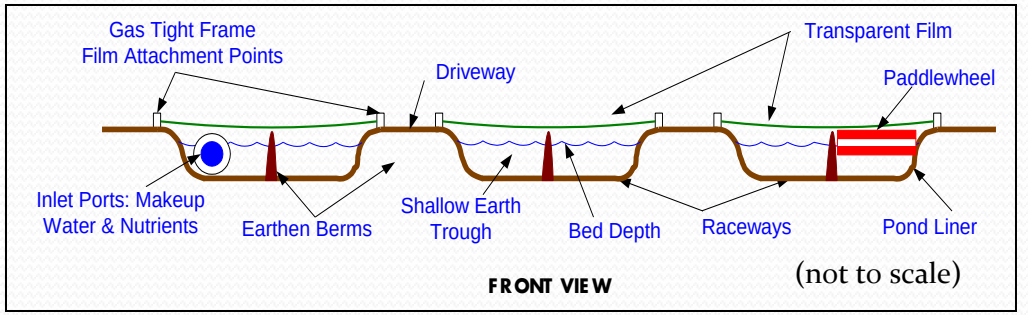
Clearly state performance assumptions and level of technical aggressiveness.

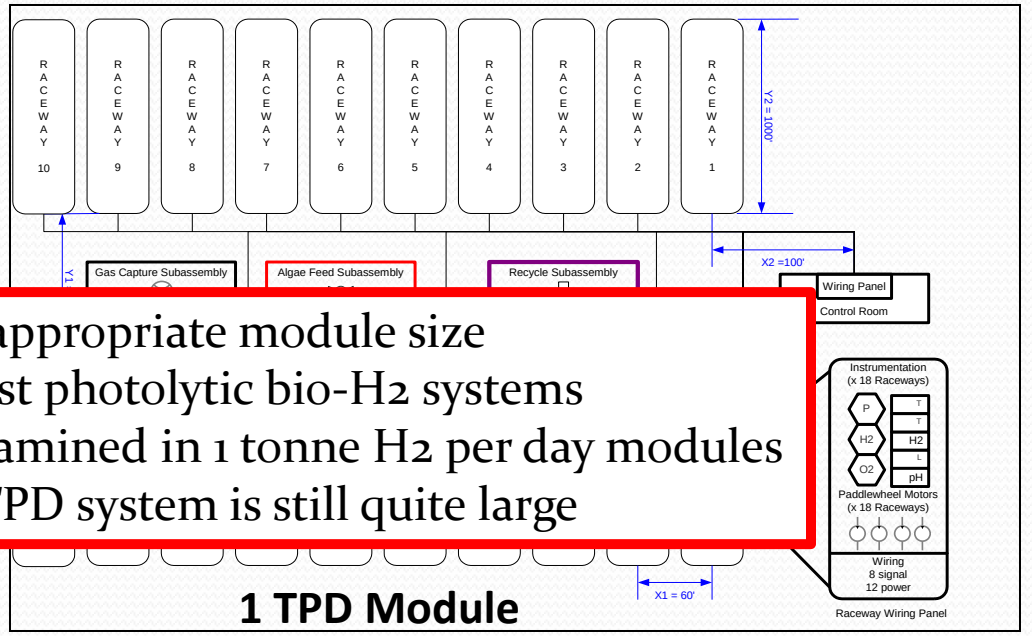
- Photosynthesis H_2 Production
  - Solar PAR (Photosynthetically Active Radiation) energy is 44% for B1-B4 and 71% for B5
  - Mutant developed with highly truncated chlorophyll antenna for better solar utilization
    - Mutants have been developed with truncated antennas
    - Current development aimed at increasing H_2 production
  - Mutant developed without ETR (Electron Transfer Rate) limitation in intense sunlight
    - Current ETR saturation limits STH to ~2%
    - Increasing ETR limit is significant challenge
  - Chemostat II postulated, not yet demonstrated
    - Simultaneous growth and H_2 production
    - 10% of culture removed each day to maintain constant organism mass
- Fermentation H_2 Production
  - Algae fermentation output based on lab data on sulfur and phosphate-deprived algae
  - Corn Stover fermentation system based on NREL Lignocellulose/Ethanol Report
    - Sacchrification process carried out using bacteria
    - Fermentor Bacteria convert 95% of Cellulose and Hemicellulose to H_2 and Acetate over 24 hrs
- Microbial Electrolysis cell H_2 Production
  - Feedstock is liquid organic output of Fermentor or purchased acetate
  - Reactor volumes based on lab-scale tests
  - Cathode and anode areas based on lab-scale tests
  - Conversion efficiency and ion transport losses are comparable to lab tests

Reactor Bed Design & Plant Layout

Commercial algae systems used as inspiration. But with modifications for H2 capture.







Consider appropriate module size

- Past photolytic bio-H2 systems examined in 1 tonne H2 per day modules
- 1 TPD system is still quite large

10 TPD Plant Capacity = 1 TPD Module x 10

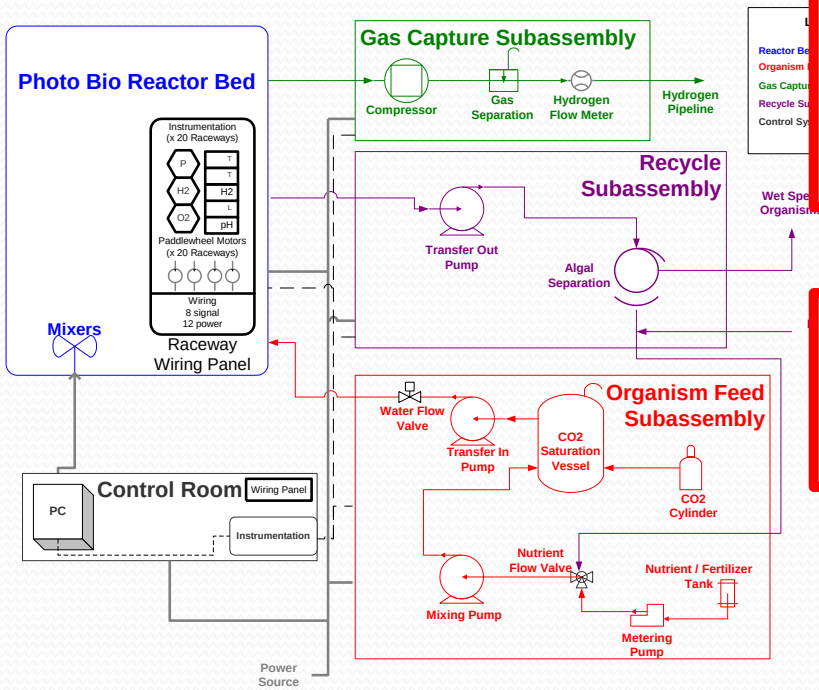
1 TPD Module (at 9.2% STH efficiency) = 20 reactor beds (raceways) over 26 acres

1 Raceway = 1090 ft x 40 ft x 0.33ft (deep)

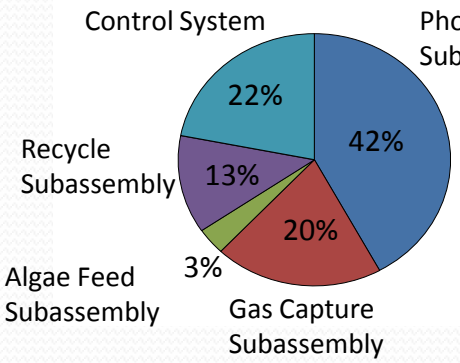
Plant Design

Algal O_2-tolerant Hydrogenase (B-1)

Process Dia



Capital Expenditures



~$2.2M capital cost for 1 TPD Module

Bill of Materials: 1 TPD Module

Description	Size Req'd	Units	Unit Size	Units	Unit cost	Qty Req'd	Total Cost
Photo Bio Reactor Bed Subassembly							
Transparent Film	87,080	m2	1	m2	$ 0.54	87,080	$ 46,871
Pond Lining	93,998	m2	1	m2	$ 0.47	93,998	$ 44,412
Pond Edging	13,982	m	1	m	$ 7.00	13,982	$ 97,876
Organism Feed Subassembly							
Transfer In Pump	**150**	gpm	150	gpm	$ 10,252	2	$ 20,503
Nutrient Metering Pumps	**1468**	gph	1	each	$ 2,594	1	$ 2,594
Transfer Out Pump	**150**	gpm	150	gpm	$ 10,252	2	$ 20,503
Main Slurry Feed Pipe	1080	ft	1	ft	$ 2.12	1080	$ 2,290
Raceway Slurry Feed Pipe	40	ft	1	ft	$ 1.00	40	$ 40
Consumables							
Initial CO2	5241	lb	50	lb	$ 35.00	105	$ 3,675
Initial Nutrients	0.42	lb	1	lb	$ 0.20	0	$ 0.1
Initial Water	2,142,278	gal	1	gal	$ 0.0017	2,142,278	$ 3,567
Control System							
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		$ 714.00	20	$ 14,280.00
Pressure Sensors			1		$ 345.00	20	$ 6,900.00
Hydrogen Area Sensors			1		$ 7,600.00	10	$ 76,000.00
Air Temperature Meter					$ 599.00	1	$ 599.00
Air Temperature Indicator			1		$ 38.00	20	$ 760.00
Water Temperature Indicator			1		$ -	20	$ -
pH level Indicator			1		$ 435.00	20	$ 8,700.00
Oxygen Area Sensors			1		$ -	20	$ -
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	69270	ft	1	ft	$ 0.02	69270	$ 1,343.84
Power Wiring	85350	ft	1	ft	$ 0.02	85350	$ 1,655.79
Conduit	4860	ft	1	ft	$ 0.58	4860	$ 2,817.83
						System Initial Cost	**$ 2,164,488**

Don't forget the Balance of Plant (BOP)

- Sensors turned out to be expensive
- Purification (PSA) significantly affected Net H2 production

Useful metrics:

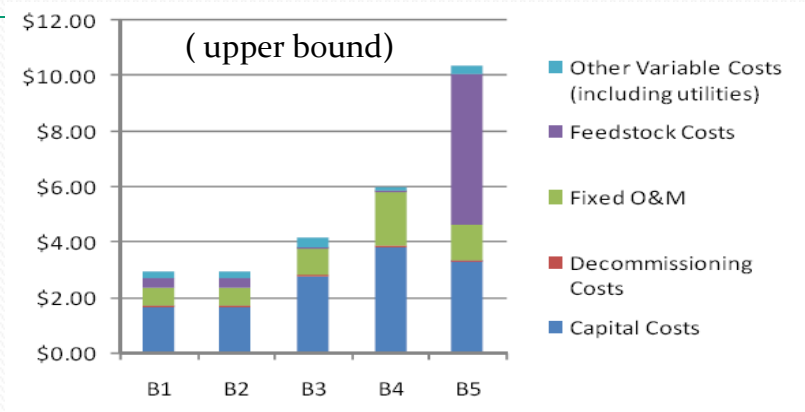
- Reactor cost in $/m2
- BOP cost in $/(kg/day)

Study Results – Photobio Upper Bound Performance

	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^2)	809,680	809,680	1,517,540	3,520,700	2,162,280
Solar to H_2 Efficiency (%)	9.2%*	9.2%*	5.2%*	2.25%	3.5%
Production (kg H_2/day)	10,000	10,000	10,000	10,000	10,000
Capital Cost ($M)	21.64	21.64	35.62	48.44	40.34
Cost ($/kg$H_2$) (upper bound performance)	**2.99**	**2.99**	**4.17**	**6.02**	**10.36**
Product Mix	2 mol H_2 + 1 mol O_2 (Potential Combustion Issues)		2 mol H_2 : 1 mol CO_2		

* level based on 100% utilization of PAR photons for growth and H2 production and with no light saturation limit

Plant Capital Costs minimized by accumulating product H_2 in pond headspace and sizing gas processing for 24 hr/day operation.

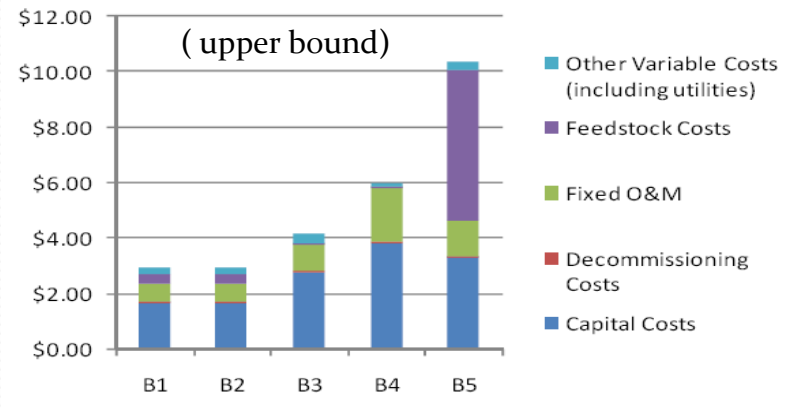


Study Results – Upper Bound vs. Near Term

	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^2)	809,680	809,680	1,517,540	3,520,700	2,162,280
Solar to H_2 Efficiency (%)	9.2%*	9.2%*	5.2%*	2.25%	3.5%
Production (kg H_2/day)	10,000	10,000	10,000	10,000	10,000
Capital Cost ($M)	21.64	21.64	35.62	48.44	40.34
Cost ($/kg$H_2$) (upper bound performance)	**2.99**	**2.99**	**4.17**	**6.02**	**10.36**
Cost ($/kg$H_2$) (near term performance)	**8.15**	**8.15**	**10.48**	**8.44**	**13.95**
Product Mix	2 mol H_2 + 1 mol O_2 (Potential Combustion Issues)		2 mol H_2 : 1 mol CO_2		

* level based on 100% utilization of PAR photons for growth and H2 production and with no light saturation limit

Plant Capital Costs minimized by accumulating product H_2 in pond headspace and sizing gas processing for 24 hr/day operation.



Dark Fermentation & MEC Systems

- **Fermentation of Algae or Bacteria**
  - Evaluate H_2 production capability from photobiological system waste
  - System waste of 1.7 TPD generates 7 kg H_2/day
- **Fermentation of Corn Stover**
  - Developed from NREL report on ethanol production from corn stover[1]
  - Size based on feedstock of 2,000 TPD corn stover generates 37 TPD H_2 and 658 TPD acetate byproduct
  - Use bacteria developed by NREL for H_2 production with acetate byproduct
- **Microbial Electrolysis Cell (MEC)**
  - Uses byproduct acetate from fermentor, or purchased acetate
  - Process design based on experimental work done at Penn State[2]
  - System generates 88 TPD H_2 (from 658 TPD Acetate)
- **All Systems**
  - Design plant, develop bill of materials, compute capital cost, operating cost, feedstock cost
  - Perform levelized hydrogen cost computations

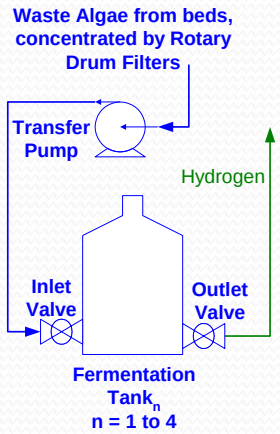
[1] A. Aden, et al., "Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover", NREL/TP-510-32438, June 2002.
[2] D. Call, et al "High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells", Environ. Sci. Technol, 2009.

System Designs

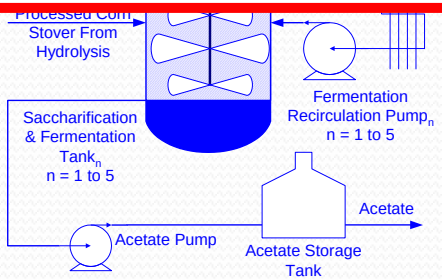
Mass conversion rate used as practical evaluation factor for fermentation systems.

Parameters	Algal Fermentor	Lignocellulosic Fermentor	MEC
Design Basis	NREL Research	NREL / TP-510-32438 (ethanol) NREL H_2 Bacteria Research	Penn State Research, NREL Research
Feedstock	Waste Algae/ Bacteria from Photobio	Corn Stover	Acetic Acid (& Glucose)
Feedstock Usage (kg/day)	1,751 - 4,677	2,000,000	767,277
Reactor Parameters	55°C Fermentation	150°C Hydrolysis 55 °C Saccharification & Fermentation	30°C 0.9 Volt Potential
Electricity Usage (kWh/day)	43-58	152,389	3,288,962
Residence Time (hours)	72	36	24
# of primary reaction vessels	4 (2500 – 4500 gallons)	5 (1 million gallons each)	113 (1 million gallons each)
Net H_2 Production Rate (kgH_2/day)	~7-18	37,181	88,085
Mass Conversion rate (net kg H_2/kg feedstock	0.4%	1.9%	12%

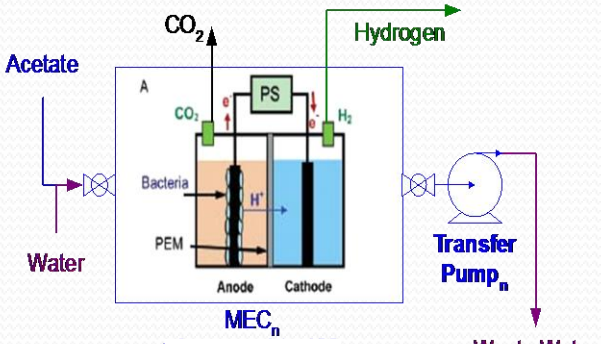
(Past) Fermentation systems marked by low conversion rates to H2.



Algal Fermentor
(4 units used)

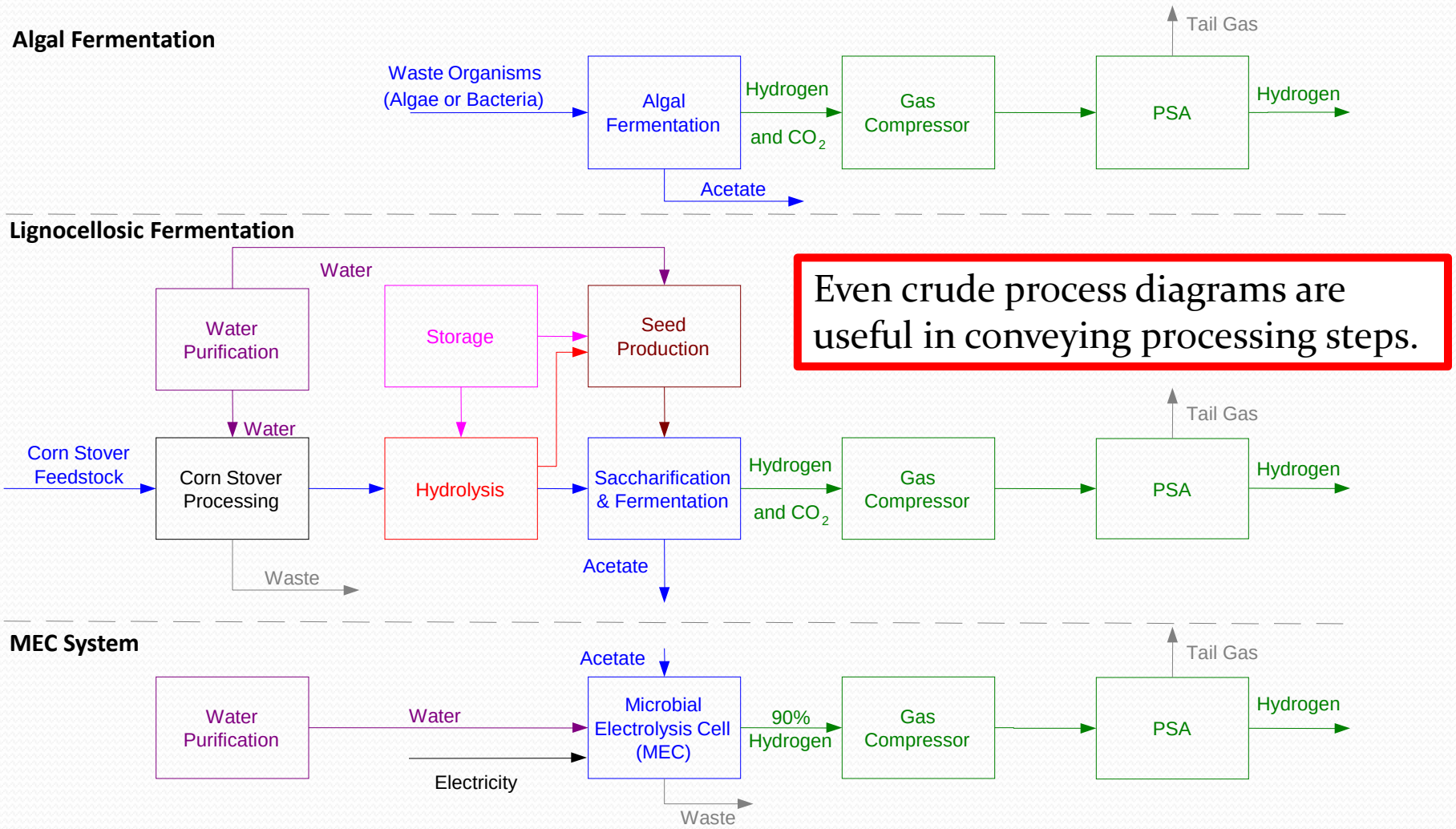


Lignocellulosic Fermentor
(5 units used)



MEC
(113 units used)

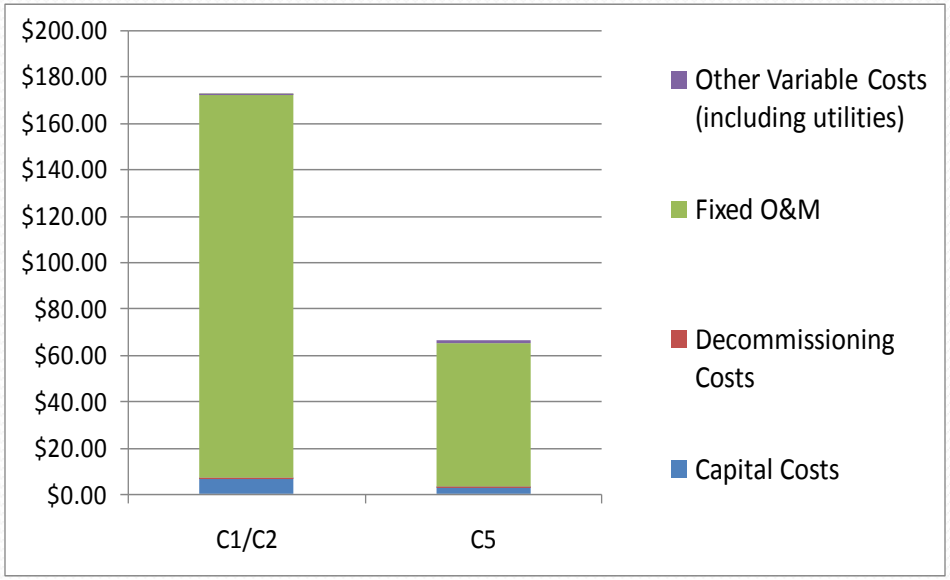
Fermentation Plant Process Diagrams



Even crude process diagrams are useful in conveying processing steps.

Algal Fermentation Results

System Criteria	C-1/C2	C-5
Organism Input Basis	B-1 or B-2	B-5
Feedstock	Algal or Cyanobacterium O_2-tolerant Hydrogenase	PNS Bacteria
Feedstock Usage (kg/day)	1,751	4,677
Production (kg H_2/day)	7	18.7
Capital Cost ($)	$37,142	$76,281
Cost ($/kg H_2)	$172.73	$66.17
Mass Conversion (kg H2/kg feedstock)	0.4%	0.4%



- Feedstock is spent waste from single 10TPD Photobiological System
- Stand-alone system costs assume no cost algae feedstock
- Current low conversion rate yields high Capital Cost / per kg H_2
- Systems are too small: labor (in fixed O&M) is very high % of cost

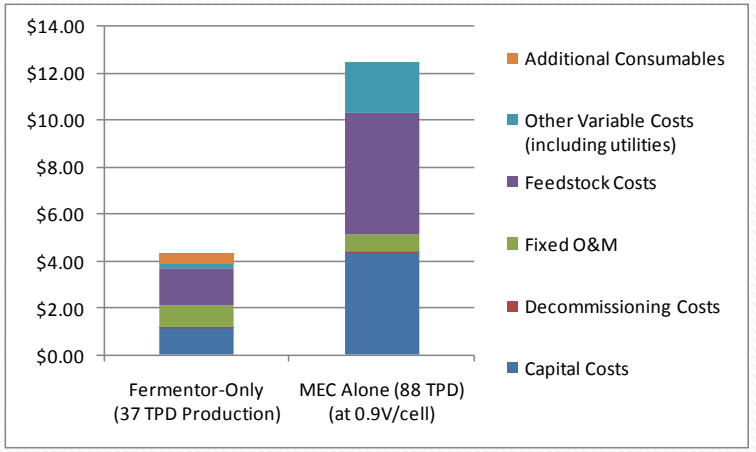
  (with zero labor cost , hydrogen cost would be $4.06-$7.04/kg H_2

Scale of examined system was too small. Resulted in a very high cost.

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

Lignocelloulose Fermentor and MEC Results

	Lignocellulosic Fermentor	MEC
Feedstock	**Corn Stover ($30/ton dry)**	**Acetate + Electricity (at $0.60/kg acetate)**
Area (acres)	**11 (+ 500 acres for long term corn stover storage)**	**10**
Net H_2 Production (Tonnes H_2/day)	**37.2**	**88.1**
Mass Conversion (net kg H_2/kg feedstock)	**1.9%**	**12.1%**
Capital Cost ($M)	**$44.9M**	**$558.7M**
H_2 Cost ($/kg H_2) - No acetate sale - $0.20/kg acetate sales	**$4.33/kg H_2 $0.60/kg H_2**	**$12.43/kg H_2 NA**



Waste byproducts may be valuable sources of revenue.

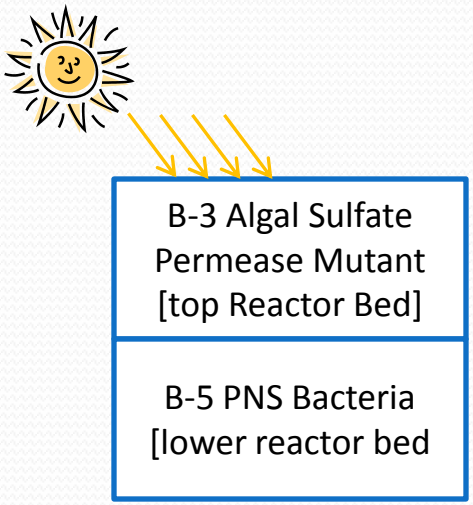
- MEC sized for potential integration with fermentor as acetate byproduct processor
- High Fermentor/MEC integration potential: raw fermentor byproduct readily used as MEC feedstock
- Sale of fermentor byproduct acetate drives down fermentor H_2 cost: acetate purification cost needs to be quantified
- Fermentor design based on production design for ethanol plant
- MEC H_2 cost is dominated by high cathode cost and very low concentration of acetate resulting in high system volume. Further developments to reduce these could greatly improve system cost effectiveness.

Lignocellulose fermentor offers pathway to <$1/kg H_2 due to byproduct acetate sales

Integrated Systems

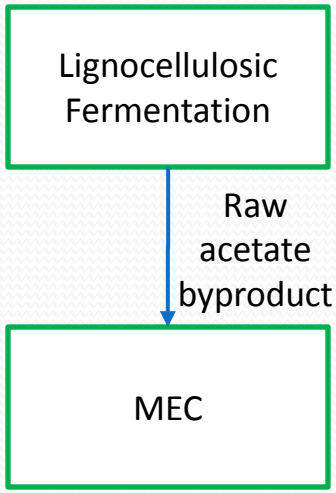
There are many complex combinations of subsystems. Consider the simplest configurations first.

Photobiological Stacked Beds



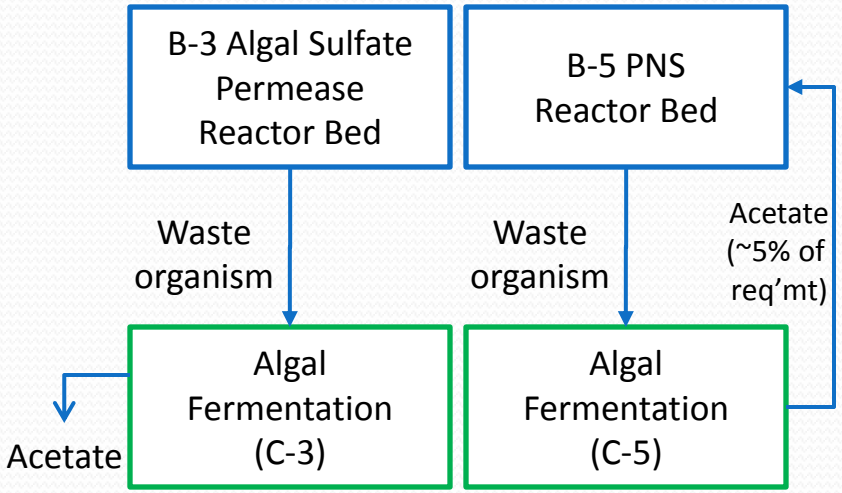
- Lower bed organism captures photons outside of photosynthesis band of top bed organism
- Shared excavation and labor costs
- Resized BOP subassemblies

Fermentor/MEC Integration



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

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
- B-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_2
Stand alone B-3 (10 TPD)	$4.17
Stand alone B-5 (10 TPD)	$10.36
Integrated (10.6 TPD)	$5.25

Photobio & Organism Fermentor		
System	$/kg H_2	$/kg H_2
Stand alone Photobio (10 TPD)	$2.99 (B-1/B-2)	$10.36 (B-5)
Stand alone Algae Fermentation (7-13kg/day)	$172.73 (C-1/C-2)	$66.17 (C-5)
Integrated (~10.0 TPD)	$3.21	$11.04

Lignocellulose Fermentor & MEC	
System	$/kg H_2
Fermentor alone (37 TPD)	$4.33 (~$0.60 with acetate sale)
MEC alone (88 TPD)	$12.43
Integrated (125 TPD)	$6.61

- MEC based on PSU research process , not yet optimized for lowest capital cost
- Integration of more than 2 systems possible, but can be logistically difficult

Sensitivity analysis (Tornado Charts) is a convenience and useful tool to determine most sensitive parameters.

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

Collaborations

Collaborator	Organization	Role/Expertise
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_2 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_2
  - 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_2 costs with mutants ~\$2.99 - \$4.17/kg H_2
  - Algal Fermentation
    - Based on experimental results, utilizes waste organisms from photobio systems which have low glucose content
    - Resulting high cost due to effects of labor cost and low H_2 production >\$100/kg H_2

Summary (continued)

- Lignocellulose Fermentation
  - Complicated process, but well defined from ethanol production systems configuration
  - Assumed Hydrolysis process and fermentation bacteria are key technical advances
  - Predicted H_2 price of $4.33/kg could be lowered to ~$0.60/kg with acetate byproduct sales
- 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 price of $12.43/kg H_2 using purchased acetate
  - Extensive cost reduction potential from system component development
- Integrated systems
  - Four 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

2009 Proposed Future Work

- Integrated Systems
  - Validate costs and scaling benefits and alternative pathways
- Photobiological 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_2 absorption
- Algae Fermentation Systems
  - Pre-treatment of algae (e.g., hydrolysis) to increase conversion rate
  - Large-scale production using high glucose content algae grown specifically for fermentation
- Lignocellulose Fermentation System
  - More detailed analysis/verification of subsystems
  - Analysis of byproduct utilization and consequent large reduction in effective \$/kg H_2.
- MEC System
  - Optimized production process and components for low capital cost system
    - Increased acetate solution density, Increased pressure operation
    - Low cost cathodes and anodes
    - Determination of increased ion transport loss in large reactors
  - Determination of ion transport loss increases in large scale reactors

DOE MYRDD Plan Technical Target Tables: Photolytic Bio H_2

https://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html

Table 3.1.10 Technical Targets: Photolytic Biological Hydrogen Production [a]					
Characteristics	**Units**	**2011 Status**	**2015 Target [c]**	**2020 Target [d]**	**Ultimate Target [e]**
Hydrogen Cost [b]	$/kg	NA	NA	9.20	2.00
Reactor Cost [f]	$/m^2	NA	NA	14	11
Light utilization efficiency (% incident solar energy that is converted into photochemical energy) [g]	%	25 [h]	28	30	54
Duration of continuous H_2 production at full sunlight intensity [i]	Time Units	2 min [j]	30 min	4 h	8 h
Solar to H_2 (STH) Energy Conversion Ratio [k]	%	NA	2%	5%	17%
1-Sun Hydrogen Production Rate [l]	kg/s per m^2	NA	1.6E-7	4.1E-7	1.4E-6

Footnotes for Bio Tables

Table 3.1.10

[a] The targets in this table are for research tracking with the Ultimate Target values corresponding to market competitiveness. Targets are based on an initial analysis utilizing the H2A Central Production Model 3.0 with standard H2A economic parameters (www.hydrogen.energy.gov/h2a_production.html.)

[b] Hydrogen cost represents the complete system hydrogen production cost for purified, 300 psi compressed gas. Projections assume photolytic production of hydrogen gas by genetically engineered organisms (algal or bacterial) suspended in a water solution under solar illumination, modeled as algae, with an O_2-tolerant hydrogenase, grown in large, raceway-type, shallow bed reactors that are covered by a thin, optically transparent film, and provided with nutrients, CO_2, and sunlight. The evolved gas will be collected, purified to 99.999+ hydrogen purity by pressure swing adsorption (PSA), and compressed to 300 psi for hydrogen pipeline transport. Plant capacity is 50,000 kg H_2/day for all years. All targets are expressed in 2007 dollars. Cost calculations are documented in the H2A v3 Future Case Study for Photolytic Biological Production of Hydrogen (http://www.hydrogen.energy.gov/h2a_prod_studies.html). Further analysis assumptions may be found in "Technoeconomic Boundary Analysis of Biological Pathways to Hydrogen Production," Directed Technologies, Inc., Final Report to U.S. Department of Energy, 31 August 2009 (http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/46674.pdf).

[c] The 2015 target is based on analysis of the best technologies projected to be available in 2015 and assumes integration into a single, non-hybrid organism. Specifically, the 2015 target is based on a model of a *Chlamydomonas reinhardtii* strain with an O_2-tolerance hydrogenase system and a reduced chlorophyll antennae light harvesting complex (LHC), in which all the improvements listed in the table have been integrated.

[d] For 2020, all assumptions of the 2015 target system apply (such as reactor system design and organism type) except the organism is assumed to be further improved in the target parameters indicated in the table.

[e] For the 2015 and 2020 targets, the organism modeled is assumed to be an algal strain with a native photosynthesis system (i.e., with Photosystems I and II). For the Ultimate Target, previous assumptions (such as reactor system design) apply, but the modeled organism is both optimized and has a genetically modified hybrid photosynthetic system combining the native algal Photosystem II with a bacterial Reaction Center, achieving greater hydrogen production rates by extending the light spectrum that can be collected and improving the efficiency of other conversion steps. Fundamental genetic engineering advances are required to reach the hybrid organism's ultimate target efficiency values. If the hybrid organism was not successfully genetically engineered, performance would be limited to a light utilization efficiency of 34%, an STH ratio of 9.8%, and a cost of $2.6/kg H_2.

[f] Installed cost per square meter of organism bed reactor equipment includes the containment structure, film covering, and any reactor interior flow control equipment. It does not include cost of complementary equipment

Footnotes for Bio Tables Table 3.1.10 (continued)

such as compressors, PSA, Control Room, etc. Square meters are defined as the solar capture area. Future designs for the reactors will need to address safety measures to deal with the co-production of hydrogen and oxygen (e.g., replacing PSA systems with Temperature Swing Apparatus systems), which may increase costs. Due to the early stage of development, photobioreactor designs and the required organismal characteristics will likely undergo modifications before widespread commercial use to address issues such as temperature, salinity, and pH control.

g The light utilization efficiency is the conversion efficiency of incident solar energy into photochemically available energy and is the product of two values: the light collection efficiency and the photon use efficiency at full sunlight intensity. The first value, light collection efficiency, is the fraction of solar incident light that is within the photosynthetically active radiation (PAR) wavelength band of the organism. For green algae, the light collection efficiency is estimated to be 45% ("Light and photosynthesis in aquatic ecosystems," Kirk, Cambridge University Press, 1994), and is considered fixed for the 2015 and 2020 targets; the hybrid organism modeled for the ultimate target is estimated to have a light collection efficiency of up to 64% ("Integrated biological hydrogen production," Melis and Melnicki, International Journal of Hydrogen Energy, September 2006) http://www.sciencedirect.com/science/article/pii/S0360319906002308). The second value, photon use efficiency, is the efficiency of converting the absorbed photon energy into chemical energy through photosynthesis at full sunlight intensity (2,500 micromol photons per square meter per second). At low-light conditions (i.e., with no light saturation), the average photon use efficiency for algae is 85% ("Absolute absorption cross sections for photosystem II and the minimum quantum requirement for photosynthesis in *Chlorella vulgaris*." Ley and Mauzerall, Biochim. Biophys. Acta 1982). Experimentally, photon use efficiency is determined by measuring the rate of photosynthesis (via oxygen evolution) per photon at different light intensities and comparing the rates at full sunlight and at sub-saturating light levels, with the maximum value set at the 85% efficiency level.

h "Maximizing Light Utilization Efficiency and Hydrogen Production in Microalgal Cultures," Melis, 2008 Annual Progress Report for DOE's Hydrogen Program (http://www.hydrogen.energy.gov/pdfs/progress08/ii_f_2_melis.pdf).

i For purposes of conversion efficiencies and duration reporting, full sunlight (2,500 micromol photons per square meter per second) conditions are assumed. Since in actual practice light intensity varies diurnally, only 8 hours of continuous duration is needed for a practical system. The duration values assume a system where the enzyme is regenerated at night with respiration scavenging oxygen.

j Brand et al., 1989, Biotechnol. Bioeng.

k STH energy conversion ratio is defined as the energy of the net hydrogen produced (LHV) divided by net full-spectrum solar energy consumed. For systems utilizing solar energy input only, the consumed energy is calculated based on the incident irradiance over the total area of the solar collector. For hybrid systems, all additional non-solar energy sources (e.g., electricity) must be included as equivalent solar energy inputs added to the denominator of the ratio. For photolytic biological hydrogen production, this can be thought of as the product of three components: E_0*E_1*E_2. The maximum potential value is calculated by determining the highest possible conversion efficiencies at three steps: E_0, the percent of solar energy (at sea level) that is absorbed by the organism; E_1, the percent of absorbed energy that is utilized for charge separation by the photosystems; and E_2, the energy for charge separation that is utilized for water splitting. The E_2 value is reduced by 20% to account for the fact that some photon energy will go to other processes, such as cellular maintenance, rather than hydrogen production. The hydrogen cost calculation takes into consideration reductions due to reactor light transmittance (10% loss) and the loss of production over a full production day due to durations less than 8 h. Cost calculations are documented in the H2A v3 Future Case Study for Photolytic Biological Production of Hydrogen (http://www.hydrogen.energy.gov/h2a_prod_studies.html).

l The hydrogen production rate in kg/s per total area of solar collection under full-spectrum 1-sun incident irradiance (1,000 W/m^2). Under ideal conditions, STH can be related to this rate as follows: STH = H_2 Production Rate (kg/s per m^2) * 1.23E8 (J/kg) / 1.00E3 (W/m^2). Measurements of the 1-sun hydrogen production rate can provide an invaluable diagnostic tool in the evaluation of loss mechanisms contributing to the STH ratio.

DOE MYRDD Plan Technical Target Tables: Photosynthetic Bacterial Bio H_2

https://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html

Table 3.1.11 Technical Targets: Photosynthetic Bacterial Hydrogen Production [a]				
Characteristics	**Units**	**2011 Status**	**2015 Target**	**2020 Target [b]**
Efficiency of Incident Solar Light Energy to H_2 (E0*E1*E2) [c] from organic acids	%	NA	3	4.5
Molar Yield of Carbon Conversion to H_2 (depends on nature of organic substrate) E3 [d]	% of maximum	NA	50	65
Duration of continuous photoproduction [e]	Time	NA	30 days	3 months

Footnotes for Bio Tables Table 3.1.11

[a] The targets in this table are for research tracking. The final targets for this technology are costs that are market competitive. This table will be updated in a future version of this plan to incorporate hydrogen cost target and current technology assumptions.

[b] Technology readiness targets (beyond 2020) are 5.5% efficiency of incident solar light energy to H_2 (E0*E1*E2) from organic acids, 80% of maximum molar yield of carbon conversion to H_2 (depends on nature of organic substrate) E3, and 6 months duration of continuous photoproduction. See Figure 3.1.2 for a schematic representation of conversion steps and associated efficiencies.

[c] E0 reflects the light collection efficiency of the bacteria in the photoreactor and the fact that only a fraction of incident solar light is photosynthetically active (theoretical maximum is 68%, from 400 to 1000 nm). E1*E2 is equivalent to the efficiency of conversion of absorbed light to primary charge separation then to adenosine-5'-triphosphate; both are required for hydrogen production via the nitrogenase enzyme. E0*E1*E2 represents the efficiency of conversion of incident solar light to hydrogen through the nitrogenase enzyme (theoretical maximum is 10% for 4-5 electrons). This efficiency does not take into account the energy used to generate the carbon substrate.

[d] E3 represents the molar yield of H_2 per carbon substrate (the theoretical maximum is 7 moles per mole carbon in the substrate, based on the average yield of acetate and butyrate).

[e] Duration reflects continuous production in the light, not necessarily at peak efficiencies. It includes short periods during which ammonia is re-added to maintain the system active.

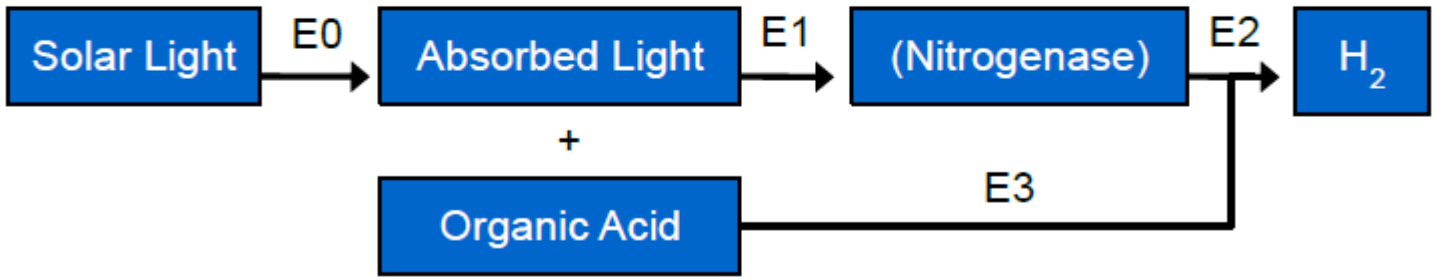


Figure: 3.1.2 Photosynthetic Bacterial System Overview Illustrating E0, E1, E2 and E3 Conversion Processes

DOE MYRDD Plan Technical Target Tables: Dark Fermentation & MECs

https://www1.eere.energy.gov/hydrogenandfuelcells/mypp/index.html

Table 3.1.12 Technical Targets: Dark Fermentative Hydrogen Production and Microbial Electrolysis Cells (MECs) [a]

Characteristics	Units	2011 Status	2015 Target	2020 Target [b]
Feedstock Cost [c]	cents/lb. sugar	13.5	10	8
Yield of H_2 production from glucose by fermentation [d]	mol H_2 /mol glucose	3.2 [e]	4	6
Yield of H_2 production from glucose by integrated MEC – fermentation [f]	mol H_2 /mol glucose	-	6 [e]	9 [e]
Duration of continuous production (fermentation)	Time	17 days [g]	3 months	6 months
MEC cost of electrodes	$/m^2	2,400 [h]	300	50
MEC production rate	L-H_2 / L-reactor-day	-	1	4

Footnotes for Bio Tables

Table 3.1.12

[a] The targets in this table are for research tracking. The final targets for this technology are costs that are market competitive. This table will be updated in a future version of this plan to incorporate hydrogen cost targets and feedstock assumptions.

[b] Technology readiness targets (beyond 2020) are 10 molar yield of H_2 production from glucose, 6 cents/lb. sugar feedstock cost, and 12 months duration of continuous production.

[c] Targets are from the DOE Biomass Program Multi Year Program Plan 2007-2012, August, 2005, for sugar from lignocellulosic biomass. The targets have been shifted 2-5 years in Table 3.1.12 for purposes of FCT planning pending further analysis of this pathway.

[d] The theoretical maximum from known fermentative pathways is 4, although the H_2 content of 1 mole of glucose and the H_2O required for fermentation is 12. Clearly, in order to achieve molar yields greater than 4, the feasibility of developing new pathways or discovering new microbes needs to be assessed.

[e] In 2010, NREL reported a H_2 molar yield of 3.2 by supplying limited amounts of cellulose substrate during fermentation (2010 Annual Progress Report DOE Hydrogen Program; (http://www.hydrogen.energy.gov/pdfs/progress10/ii_h_3_maness.pdf).

[f] The yield assumes a system where the effluent from the glucose-fed fermentation system is used as feedstock for an MEC (e.g., in 2015 the target for fermentation is 4 mol H_2/mol glucose while that for MEC is 2 mol H_2/mol glucose, for a total combined target of 6 mol H_2/mol glucose). The goal is for continuous flow operation conditions.

[g] Van Ginkel, S., Sung, S. 2001. Environ. Sci. Technol. 35: 4726-4730.

[h] Estimated for replacing Pt with MoS_2, based on Tokash, J.C. and B.E. Logan. 2011. "Electrochemical evaluation of a molybdenum disulfide catalyst for the hydrogen evolution reaction under solution conditions applicable to microbial electrolysis cells." Int. J. Hydrogen Energy. 36(16): 9439-9445.