

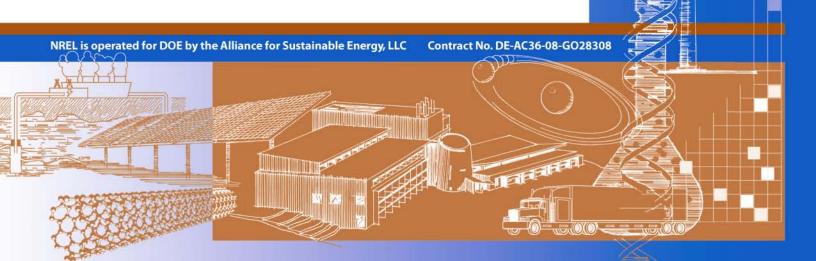
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Technoeconomic Boundary Analysis of Biological Pathways to Hydrogen Production

March 27, 2008 - August 31, 2009

B.D. James, G.N. Baum, J. Perez, and K.N. Baum *Directed Technologies, Inc. Arlington, Virginia*

Subcontract Report NREL/SR-560-46674 September 2009



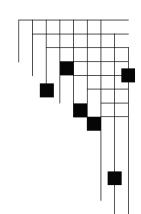
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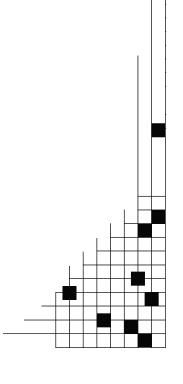
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Preface

The work described in this report was performed under contract to the National Renewable Energy Lab (NREL), under the technical guidance of members of the Biological Hydrogen Working Group.

The project considered multiple pathways for the biological production of gaseous hydrogen, including photobiological H₂ production from a variety of genetically engineered algae and bacteria, dark fermentation of waste photobiological organisms, dark fermentation of lignocellulosic biomass, and the microbial electrolysis of fermentative waste. Additionally, the integration of multiple systems for added hydrogen production and reduced cost was considered. This study was based on the best possible designs using data currently available, and is not inclusive of all potential designs.

Within the photobiological analysis, five different organisms were examined including:

- A truncated antennae Chlamydomonas mutant with an oxygen-tolerant hydrogenase
- A truncated antennae Cyanobacteria mutant with an oxygen-tolerant hydrogenase
- A sulfate-permease Chlamydomonas mutant with a truncated antennae
- An immobilized, sulfur-deprived Chlamydomonas mutant with a truncated antennae
- A truncated antennae Purple Non-Sulfur (PNS) photosynthetic bacterial mutant

For each organism, hydrogen production characteristics were defined, individual reactors conceptually designed, and levelized hydrogen costs calculated. In keeping with a technoeconomic boundary analysis, organism performance was based on the authors projection of future genetically modified organisms rather than current laboratory experimental measurements. Assumptions were carefully stated and compared to current demonstrated performance levels to allow the reader to assess the reasonableness of the future performance levels. Additionally, the hydrogen cost derived from photobiological systems achieving a near term energy efficiency were also computed to assist in bounding the expected future price of hydrogen.

For the fermentative systems, three main systems were examined:

- H₂ production using dark fermentation of photobiological systems algal waste
- H₂ production using dark fermentation of lignocellulosic feedstock (corn stover)
- H₂ production from a Microbial Electrolysis Cell (MEC) using fermentation waste as a feedstock.

While MEC systems produce hydrogen via electrolysis rather than fermentation, we group them with the fermentation systems for convenience as they are linked via a waste-product/feedstock relationship. The design and performance of the MEC plant draws heavily from the concepts and laboratory work conducted at Penn State University. The design of the lignocellulosic fermentation plant was based largely on a detailed NREL report analyzing the performance and cost of ethanol production from corn stover.

Fermentation for ethanol production and fermentation for hydrogen production share many characteristics. Consequently, the current project work product was greatly enhanced by making use of the analogous analysis. For each system, a plant design was selected, its capital cost and performance were estimated, and resulting levelized hydrogen cost computed. The DOE H2A cost estimation spreadsheet tool was used to estimate these levelized hydrogen costs so as to allow easy and transparent comparisons to other production options.

Finally, we integrated the most logical combinations of the above enumerated systems based on synergies in plant design, seeking to realize hydrogen cost reduction through combined utilization of reactor components and potential use of waste products as feedstock. Hydrogen cost from the integrated systems is then compared to hydrogen cost from the stand-alone systems.

Project results were reported in four sequentially prepared reports. This project final report consists of these four reports plus a comprehensive discussion section, all integrated under a common cover. Thus the report consists of five sections:

- Part I: Photobiological H₂ Production Systems
- Part II: Algae Fermentative H₂ Production Systems
- Part III: Lignocellulosic Fermentative H₂ Production Systems & Microbial Electrolysis Cell Systems
- Part IV: Integrated Systems
- Part V: Discussion of Project Results

Since the individual reports were done sequentially, Part V of the report contains a summary of all contract work, including recommendations for future actions. The reader is advised to look to Part V for an overall project summary and listing of conclusions.

Acknowledgements

The authors of this report would like to acknowledge the contributions of the Biological Hydrogen Working Group, whose members provided invaluable technical and/or programmatic guidance throughout the analysis project.

Working Group members included:

- Dr. Ali Jalalzadeh-Azar, Senior Engineer II and Technical Monitor, NREL
- Dr. Maria L. Ghirardi, Principal Scientist, NREL
- Ms. Pin-Ching Maness, Principal Scientist, NREL
- Dr. Michael Seibert, Research Fellow, NREL
- Dr. Anastasios Melis, Professor, UC Berkeley
- Dr. George Sverdrup, Laboratory Program Manager, NREL
- Ms. Roxanne Garland, Technology Development Manager, US DOE, EER&E

Additionally, other members of the hydrogen production community contributed to this analysis through their expert guidance. They are:

- Dr. G. Charles Dismukes, Professor, Princeton University
- Dr. Bruce E. Logan, Professor, The Pennsylvania State University

The work described in this report was performed under contract to the National Renewable Energy Lab (NREL) with sponsorship provided by the US Department of Energy, Office of Fuel Cell Technologies, DOE Office of Energy Efficiency and Renewable Energy.

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Part I: Photobiological H₂ Production Systems

Introduction

Directed Technologies Inc. (DTI) is under contract to the National Renewable Energy Lab (NREL) to conduct a techno-economic evaluation of photobiological hydrogen production systems. This report documents the biological and engineering characteristics of five algal and bacterial hydrogen production systems selected by DOE and NREL for evaluation. Those characteristics are divided into three areas, namely, basic science, biology, and engineering. Since basic science assumptions are strongly correlated with biological parameters, they are provided first. Hydrogen production capabilities are a function of the reactor bed design so those details are provided in the engineering section of this report. Because product hydrogen product is combined with other gases, the characteristics of a gas separation system will be given additional attention. The last section of this Task B report utilizes the information collected to estimate a final result, given as a cost per unit of produced hydrogen.

1. Basic Science

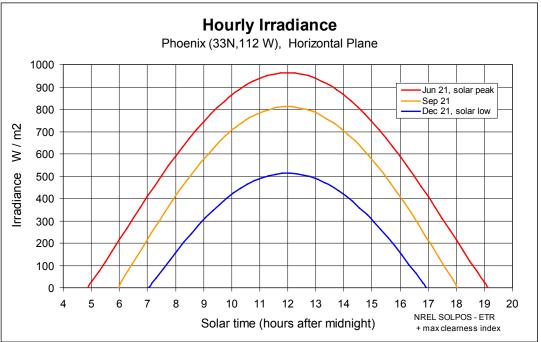
1.1 Solar Assumptions

Solar insolation is a key factor in determining algal growth and H₂ production rates. Selecting a geographical location provides ambient temperatures, hours of exposure, and amount of irradiance. For the purpose of this study we have based our solar input assumptions on the solar irradiance properties of the Phoenix, AZ area. Hourly solar irradiance (W/m² striking the horizontal reactor bed) for this area is shown in Figure 1-1. The NREL SOLPOS model is used for solar position angles and intensity¹. This model calculates extra terrestrial radiation (ETR) by the hour and day throughout the year. The total clearness index, Kt, is multiplied by the ETR to obtain the terrestrial irradiance on the horizontal surface. Kt values for the relevant months in the Phoenix area are obtained from the NASA Atmospheric Data Center / Surface meteorology and Solar Energy (SSE) database². The 3 curves plotted in Figure 1-1 show the solar peak at June 21, the autumnal equinox at September 21, and the solar minimum at December 21. These curves also show the seasonal peak radiation which determines the peak potential H₂ production for those periods. The peak June irradiance at 964W/m² is slightly below the nominal peak value of 1,000 W/m² due to the sun's maximum elevation angle being 80 degrees above the horizon.

¹ NREL MIDS SOLPOS (Solar Position and Intensity) model may be found at http://rredc.nrel.gov/solar/codesandalgorithms/solpos/.

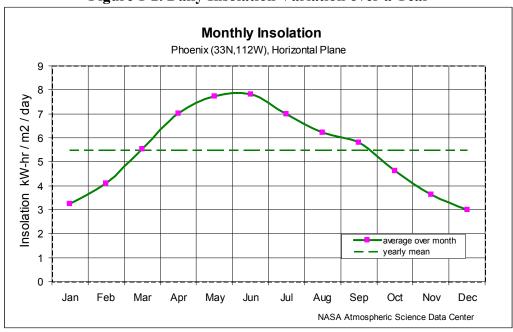
² NASA Atmospheric Data Center, Langley ASDC User Services, Surface meteorology and Solar Energy (SSE) data base (release 6.0).

Figure 1-1. Hourly Irradiance



The daily insolation energy (kW- $hr/m^2/day$) on a horizontal surface throughout the year for the Phoenix area was obtained from the NASA SSE database, and is plotted in Figure 1-2. These plotted values are averages for the respective months. The yearly mean value of 5.5kW- $hr/m^2/day$ is also shown.

Figure 1-2. Daily Insolation Variation over a Year



Note that the effects of clouds are implicitly included in these calculations, as the monthly data points are for the average day including the average amount of clouds. The normalized cell growth and hydrogen production parameters used in the following analyses have assumed an average sunlight of $5.5 \, \text{kW-hr/m}^2/\text{day}$ to generate a usable hydrogen production rate of $1,000 \, \text{kg/day}$ averaged over the year.

1.2 Bed Depth, Algal Concentration, & H₂ Production Rate Assumptions
The depth of the reactor bed and algal concentration are matched to ensure full photon capture by the organisms. If organism concentration is too dilute for a given total depth, light will penetrate to the bottom of the bed and photons will be "wasted". Should the organism be too concentrated, photons will be fully absorbed in only the upper layers of the bed potentially "starving" the organisms at the lower depths of photons and adversely affecting their health³. The organism concentration and bed depth are also important because they impact specifications for other system components such as pumps and valves, type of solids separation equipment, and type of mixing equipment.

Choice of bed depth and concentration depends on the mode of growth, batch versus continuous dilution. For batch mode, the ideal fixed-volume bioreactor to use for achieving constant light transmission throughout a growing population of dispersed cells would have to allow for continuous decrease in path length as the population grows to higher cell densities. Alternatively, a continuous dilution bioreactor of fixed volume could operate with a fixed cell density after reaching steady-state growth and thus would have constant absorbance. If the latter growth mode is not used and replaced with batch culture growth mode then the bed depth must be chosen so that the absorbance after reaching stationary phase, e.g., at beginning of the photo-hydrogen production stage, produces the maximum rate of hydrogen production.

1.2.1 Beers Law Photon Absorption Model

The rate of photon absorption and thus the maximum hydrogen production at a given bed depth increment can be determined by Beer's Law. At each depth increment, Δd , one calculates the number of photons absorbed and then multiplies that by the specific rate of H_2 production in molecules per photon (this is equivalent to the light saturation curve for photohydrogen production which is an experimental measurement distinct for each cell type or mutant).

Beer's law states that:

 $A = b*C*\varepsilon$ where A = Absorbance (unitless)

b= depth into liquid in cm

C= cell concentration in g_{drywt}/L

 ϵ = absorption coefficient in L/cm/g_{drywt}

Absorbance is defined as the negative logarithm of the ratio of exiting light intensity to entering (incident) light intensity:

A = -log(I/Io)

³ Proper bed mixing can mitigate or potentially eliminate the effects of shallow light penetration.

From this definition, I/Io (light intensity I, at a given bed depth, b) is derived from:

$$I/I_0 = 10^{-\epsilon bC}$$

To determine the required bed depth and cell concentration to maximize photon capture by the organisms, we integrate the above equation over the depth of the bed. Note that for this approach and Beer's law to be valid, we need to make multiple assumptions:

- 1. The cell volume and pigment content per cell must not change appreciably during the lifecycle of the sample. While most cells increase pigment content and volume as they age and, therefore, do not strictly obey Beer's law, we assume average rather than instantaneous cellular characteristics for purposes of the calculation. As shall be discussed later in the report, this assumption is most valid for the Chemostat II system, where a constant cell concentration is maintained.
- 2. The cells must not be allowed to aggregate, as commonly occurs without adequate mixing, resulting in biofilm formation. Consequently, this analysis is most applicable to planktonic (or free-floating) cells. With the exception of the B-4 System (see p. 25), all systems considered are free-floating cells in an actively mixed medium. This analysis is not relevant to the B-4 immobilized system.
- 3. The cell density must be sufficiently low that cell "shading" does not occur. In the present configuration shading is minimized by dilution: all systems, with the exception of B-3 and B-4 for which this analysis does not apply due to the necessity of higher cell concentration as a feedstock for oxidative respiration, maintain a cell concentration of less than $0.2g_{drywt}/L$.
- 4. Corrections for the light lost from the bioreactor arising from light scattering of cells (turbidity) are generally estimated to be low of order: 10% for the cell concentrations considered in this report and for a normal incident angle. Generally, visible light scattering by cells of the size of Chlamydomonas (10 microns) is predominantly forward scattering and thus most of the scattered light is retained in the bioreactor. Thus, no correction for light scattering is included in the analysis.

1.2.2 Light Saturation

While Beer's Law relates photon absorption to cell and bed characteristics, there is an additional limitation on H₂ production due to saturation of photon/electron conversion capability within the cells. There is a charge transfer limitation (alternately called a saturation limit) within the photosynthetic pathway that limits the rate at which photons/electrons can be processed by the PSII reaction. This consequently limits utilization of incident photons, limiting the rate of the PSI reaction and H₂ production, and thus lowering the Solar to Hydrogen (STH) energy conversion efficiency. At moderate-to-high light intensity, this saturation limit is greatly exceeded by wild type organisms and, to a lesser extent, by current truncated antenna mutants. Two analyses of the saturation limit effects are discussed in this and the following section.

To estimate this charge transfer limitation, we examine the measured quantum efficiency for electron transport by PSII as a function of Actinic Light Photon Flux Density (PFD) for whole cells of the green alga Chlorella. Figure 1-3 displays electron transfer rate (ETR) vs. actinic light for two methods of ETR calculation⁴. Actinic light generally refers to portion of light that causes a chemical change. In this specific case, light refers to the light within the PAR range. These data come from experiments and are qualitatively representative of data in the literature for other algae including *Chlamydomonas reinhardtii*.

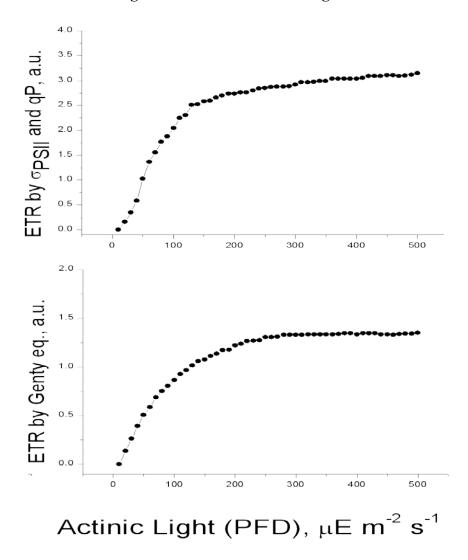


Figure 1-3. ETR vs. Actinic Light

Based on the theory of light absorption and following well-known Poisson statistics⁵ we postulate that the relationship between ETR and light intensity will follow the relationship,

⁴ Unpublished data from Gennady Ananeyev, Princeton University.

⁵ "Light Saturation Curves and Quantum Yields in Reaction Centers from Photosynthetic Bacteria", Blankenship et al. Journal of Biophysics, Volume 45 February 1984 455-461.

$$Y/Y_{max} = 1 - e^{-\sigma \Phi E}$$

where:

Ymax = Incident light intensity

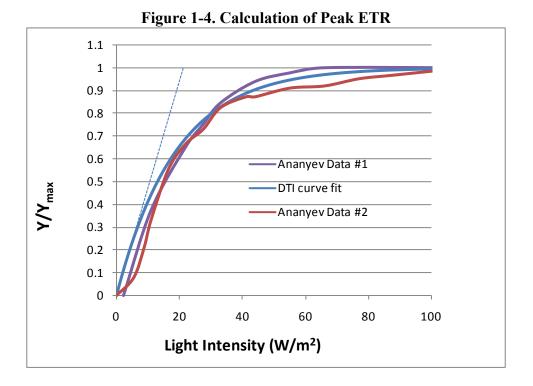
Y = Absorbed light intensity

 σ = optical cross section in cm²

 Φ = quantum yield, probability of charge separation/photon

 $E = Incident intensity in photons/cm^2/sec$

We next analytically determine the $\sigma\Phi$ value ($\sigma\Phi = 0.053346$) that results in a curve fit to the experimental data. As shown in Figure 1-4, a reasonably good curve fit was obtained. While this form of the data and analytic model indicate that ETR peaks at a light intensity of approximately 60W/m², it does not show the peak ETR. Consequently, to determine the peak ETR, we postulate that there are no charge transfer limitations at very low light levels and thus an extrapolation of the linear portion of the curve will yield an indication of the maximum electron transfer. By extrapolating the linear portion of the curve to its intersection with the maximum electron transfer (Y/Y_{max}=1), we estimate that the cells would be able to process photons at up to 19W/m² light intensity if they were unencumbered by rate limits. This allows us to compute the peak charge separation rate. Thus we now have a measure of both the peak H₂ production rate and shape of the light intensity vs. H₂ production rate. The light saturation curve can be used together with Beer's law to determine the rate of charge separation that occurs at every point within the bioreactor. This same approach can be used to calculate the H₂ production rate which is assumed to be a fixed fraction of the charge separation rate. Thereby the H₂ production rate can be obtained at each depth increment within the bioreactor and the total absorption summed from all such depth increments throughout the bioreactor to obtain the overall H₂ production throughout the reactor. The result is a substantial decrease in H₂ production rate due to light saturation effects of typical current organisms.



1.2.3 Alternative Model for Photon Absorption Saturation

An extensive analysis of saturation effects on hydrogen production was carried out for NREL by Wade Amos in NREL/MP 560-35539⁶. In this report, the hydrogen production rate in successive 0.2 mm layers of algae was predicted as a function of depth in the pond, the solar intensity, and the algae antenna saturation characteristics. For reduced antenna mutants, the analysis predicted major reduction in hydrogen production rate at depths shallower than 4 cm due to photon saturation. The photon saturation criterion assumed by Amos was that the maximum electron current able to be transferred to an external electron acceptor is 1 mole of electrons per gram (dry cell weight) of cells per day.

As an expansion of the Amos saturation analyses, we investigated the saturation effects using a hypothetical mutant (M2T) that had average absorption coefficient (ϵ) reduced by a factor of 5 relative to wild-type (WT). Figure 1-5, based on the Figure 15 of NREL/MP 560-35593, plots the rate of hydrogen production per m² per second for each 0.2mm increment of bed depth, for three varieties of algae. The thin green curve represents the rate of hydrogen production per depth layer of wild-type *Chlamydomonas reinhardtii* which has an average ϵ of 5.0, if all absorbed photons were successfully converted to hydrogen. The thick black line plots the analogous production curve for the Amos report Mutant-Type (MT) *Chlamydomonas reinhardtii* with a reduced antenna, which has an average ϵ of 2.07. The blue line plots the analogous production curve for a hypothetical improved Mutant-2-Type (M2T) *Chlamydomonas reinhardtii* with an average ϵ of 1.0. Figure 1-6 shows the

⁶ Amos, Wade, "Updated Cost Analysis of Photobiological Hydrogen Production from Chlamydomonas reinhardtii Green algae", NREL/MP 560-35593, January 2004 at page 7 (Gosset, 1995).

8

full extent of these curves. If all of the PAR photons were absorbed and converted to H_2 at the rate of 4 photons/one H_2 molecule, the hydrogen production would equal the integration of the area under each of these absorption curves and the STH energy efficiency would be 12.2% (assuming the Lower Heating Value (LHV) of $H_2 = 33.33$ kWh/kg).

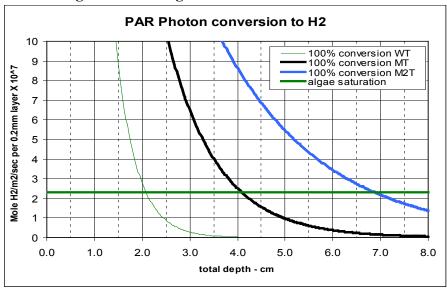
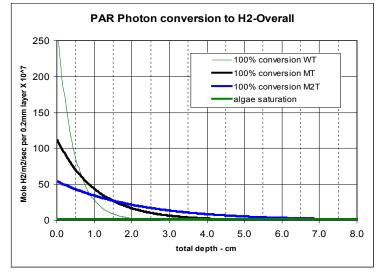


Figure 1-5. Biological Production Limits – detail





The thick green horizontal line on these curves denotes the algae saturation limit for hydrogen production based on the epsilon assumptions discussed above. Thus, with increasing depth, the actual H_2 production rate first follows the saturation thick green line for light intensities exceeding the saturation threshold and then follows the appropriate absorption curve predicted by Beer's Law. The ratio of the area below each set of two limiting curves to the solar photon flux represents the actual fraction of photons captured for H_2 production, and thus the process efficiency.

Shown in Figure 1-7, Figure 1-8 and Figure 1-9 are curves of the H_2 production efficiency for the wild-type and two mutant types as solar intensity is increased up to the max intensity of 1000W/m^2 . As can be seen, 100% photon utilization only takes place at low output for WT and at levels below 21 W/m² for MT and 45 W/m² for M2T. The higher efficiency of the Mutant-2-Type (M2T) *Chlamydomonas reinhardtii* results from the increased photon utilization throughout the pond depth.

H2 production - WT Density = 0.2 g/L, Algae saturation = $2.3 \times 10^{-7} \text{ mol H2/m2/s}$ (0.2 mm layer) 100% 90% 80% Photon Utilization for H2 70% 60% 50% 40% 30% 20% 10% 0 100 200 300 600 800 900 1000 400 500 700 solar irradiance W/m2

Figure 1-7. Hydrogen Production Efficiency - Wild-Type (WT)



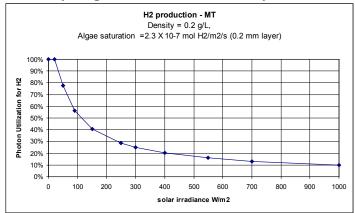


Figure 1-9. Hydrogen Production Efficiency – Mutant 2 (M2T)

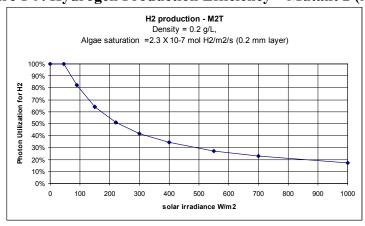


Figure 1-10, Figure 1-11 and Figure 1-12 show resultant hydrogen production rate for both wild-type and mutant types as solar irradiance is increased, with the early linear part of the curve reflecting full conversion. At full conversion intensities, the saturation limit is not exceeded and photon utilization can be 100% (i.e. 100% of the photons absorbed are able to be processed by the PSII and PSI reactions.) Output levels off as irradiance increases, with the Mutant-2-Type having significantly higher overall production levels.

Figure 1-10. Hydrogen Production - Wild-Type (WT)

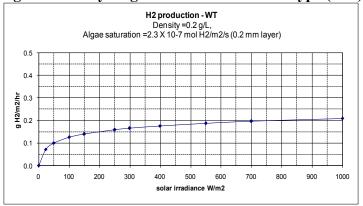


Figure 1-11. Hydrogen Production – Mutant 1 (MT)

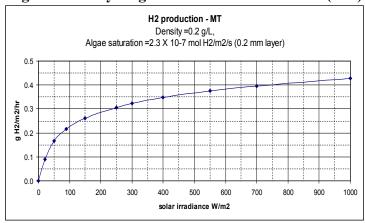
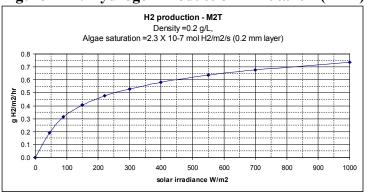


Figure 1-12. Hydrogen Production – Mutant 2 (M2T)



To illustrate the combined effects of cell saturation and seasonal and diurnal variation in light intensity, hourly hydrogen production curves were plotted in Figure 1-13 for June 21, September 21, and December 21. Integrating under the curve gives total daily H₂ production and allows an average STH energy conversion efficiency to be calculated. These values are shown in Figure 1-13.

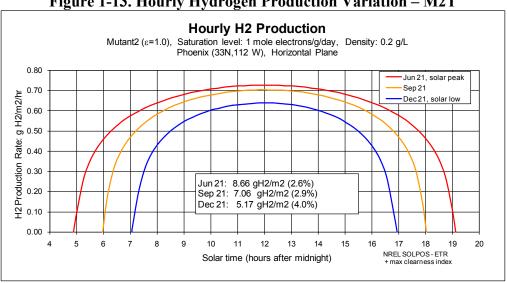


Figure 1-13. Hourly Hydrogen Production Variation – M2T

In summary, the above curves show H₂ production rate for a hypothetical M2T mutant antenna algae strain at the following conditions:

- An organism that obeys Beer's law
- Chlamydomonas reinhardtii at cell concentration = 0.2 g/L and a bed depth = 10 cm
- Mass absorption coefficient $\varepsilon = 1 \text{ L/cm/g}_{drywt}$ representing a 5:1 reduced antenna mutant relative to wild type
- Maximum charge transfer saturation limitation of 1 mole electrons per gram cell dry weight of cells per day
- Linear dependence of the H₂ production rate on light intensities below those needed to produce electron transfer at the maximum charge transfer limit
- Solar diurnal and yearly fluctuations as described in Section 2.1
- All photons absorbed by the cell are assumed to impact the chlorophyll antenna
- All photons successfully entering the PSII/PSI chain productively produce H₂ (i.e., no photons go toward growth, heat or fluorescence)

Integrating over the course of the year, we estimate that the resulting annual average STH energy conversion efficiency is 3.1%.

1.2.4 Absorption Parameters Used in This Study

The maximum STH efficiency is highly dependent on the saturation limit assumption. While the limitation mechanism is well understood, the upper saturation limit for future optimized organisms is poorly defined. The saturation model discussed in the prior sections is based on current organism properties. However, this study is focused on potential future production using developmental mutants of algae and bacteria which will not have the stringent saturation limits of current algae and bacteria. Consequently for this analysis the saturation limit was not imposed for the following reasons:

- 1. We wish to parametrically assess the cost of hydrogen resulting from multiple organism systems and configuration. Consequently, we want to establish a true "upper bound" efficiency to gauge the potential of biohydrogen.
- 2. We are interested in modeling hypothetical mutant strains that have optimized hydrogen generation capability and their exact production characteristics are not known.
- 3. Mutation of the chlorophyll antenna size is expected to be one approach to optimizing STH efficiency and the limits of antenna truncation are not known.
- 4. The removal of the saturation limit leads the STH conversion efficiency to be constant with respect to light intensity. This in turn means the STH efficiency is constant throughout the year and greatly simplifies the reactor bed sizing analysis (because it allows us to merely sum total incident photons rather than carefully assessing the incident photon variations over the course of the day and year).

Assumed STH conversion efficiencies for each of the examined biological systems are detailed in the next section.

2. Photobiological Systems - Biological and System Parameters

"Certain algae and cyanobacteria photoproduce hydrogen for short times as a way to get rid of excess energy." Recognizing the potential of using these biological systems as a source of energy, scientists have sought out ways to extend and control the duration of hydrogen production from these organisms.

Our analysis focuses on the hydrogen production potential of 5 photobiological systems. These are:

- 1. green algae that co-produces H₂ and O₂ gases and possesses an O₂-tolerant hydrogenase,
- 2. cyanobacteria that co-produces H₂ and O₂ gases and possesses an O₂-tolerant hydrogenase⁸,
- 3. sulfate-permease algal mutants that produce only H₂ gas due to the effects of a mutated sulfate permease gene on the chloroplast,
- 4. immobilized sulfate-deprived green algae that produce H₂ for extended periods of time, and
- 5. purple non-sulfur (PNS) bacteria that produce H₂ gas in light.

The baseline conditions that have been used for each of the pathways are summarized in Figure 2-1. The Reactor Bed Mode of Operation refers to the process that is used to grow algae and produce hydrogen. This mode of operation results in different solar to hydrogen (STH) efficiencies for a given organism. The Reactor Bed Mode of Operation is described in more detail in the Engineering Parameters section of this report.

⁷ Photobiological Production of Hydrogen (Fact Sheet). FS-560-42285. NREL. Colorado. November 2007. http://www.nrel.gov/docs/fy08osti/42285.pdf.

⁸ This strain of cyanobacteria does not currently exist and needs to be genetically engineered.

Figure 2-1. Biological Parameters of Photobiological Systems

B-1: B-2: B-3: B-4: B-5:							
	Algae	Cyanobacteria	Algae	Immobilized	PNS Bacteria		
	O ₂ -tolerant	O ₂ -tolerant	Sulfate	Algae, Sulfur			
	Hydrogenase	Hydrogenase	Permease	deprived			
Organism 9	C. reinhardtii	Synechocystis Hydrogenase ¹⁰	C. reinhardtii	C. reinhardtii cc124	Rhodobacter sphaeroides RV ¹¹		
Antennae Type	LHC (Light	Phycobilin deletion	LHC deletion	LHC deletion	LHC - II deletion		
	Harvesting	Mutant	Mutant	Mutant	Mutant		
	Complex)						
	deletion Mutant						
Reactor Bed Mode of Operation.	Chemostat II ¹²	Chemostat II	Single-Bed	Dual-Bed, Single-Bed ¹³	Chemostat II		
		Cell Growth Co	nditions				
Water	Fresh	Fresh	Fresh	Fresh	Fresh		
Temperature (°C)	25-35	25-35	25-35	25-35	25-35		
Final Concentration	0.2	0.2	4.9115	2.8	0.2		
in solution ¹⁴	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)		
Inorganic nutrients	Fertilizer containing: Potassium, Phosphorous, Nitrogen and trace elements						
Daily Rates g/g organism		K: 3.071 x10 ⁻⁶ ,	P: 4.913 x10 ⁻⁵ , N:	6.142 x10 ⁻⁶			
Daily Rates g/m ²		K: 6.14 x10 ⁻⁵	P: 9.83 x10 ⁻⁴ , N: 1	23 x10 ⁻⁴			
Organic nutrient	None	None	None	None	Acetic Acid		
Daily Rate					0.624		
g/g organism	N/A	N/A	N/A	N/A	0.624		
Daily Rate					42 F		
g/m²	N/A	N/A	N/A	N/A	12.5		
Daily CO ₂ Req ¹⁶	0.73	0.73	0.73	0.73	None		
g CO ₂ /g dry mass							
Growth duration	2 day	s initial	4 days	1 day	2 days initial		

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 $^{^{9}}$ We assume an engineered antenna for all organisms. B-1 and B-2 also possess an O_2 tolerant hydrogenase, thus creating a "double mutant". While without precedent in the literature, multiple mutations are necessary to achieve high STH conversion efficiencies.

¹⁰ Based on Synechocystis PCC6803 mutant work of Pin-Ching Maness (NREL)

Analysis does not rely on a specific strain of PNS proteobacterium. Multiple examples of possible organisms are cited in "Photobiological hydrogen production: photochemical efficiency and bioreactor design," Akkerman et. al., Intl. Journal of Hydrogen Energy 27 (2002) 1195-1208.

¹² Chemostat II is a chemostat with simultaneous growth and H₂ production, described in Section 4.1.4

As discussed in Section 3.4, this system utilizes a two day production period, followed by a two day growth period in a single bed. At the end of 180 days of production, the algae grown in a second bed is transferred to the production bed, replacing the spent algae. In this way, it is both a dual-bed and single-bed system

Peak cell concentration in growth bed at end of growth phase, and the target starting concentration for H₂ production. For the Chemostat II systems (B-1, B-2, and B-5), this concentration refers to the final concentration at the end of the initial grown phase i.e. the growth phase used to create the initial colony prior to chemostat operation.

¹⁵ Concentrations higher than 0.2 are needed for B3 and B4 in order to ensure that enough cell mass is accumulated for respiration to keep the system anaerobic

Four times the sustainment amount used for production conditions in this table. Based on private communication with A. Melis. (University of California-Berkeley)

	B-1	B-2	B-3	B-4	B-5			
Hydrogen Production Conditions								
Water	Fresh	Fresh	Fresh	Fresh	Fresh			
Temperature (°C)	25-35	25-35	25-35	25-35	25-35			
Cell Concentration	0.2	0.2	0.85	1.81 ¹⁷	0.2			
in solution	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)	(g/L – Dry Wt)			
Nutrients	Potassium, Phosp	Fertilizer containing horous, and Nitrogen and	Fertilizer containing Potassium, and Nitrogen and trace	Fertilizer containing Potassium, Phosphorous,				
				elements + Low Level of Sulfur	and trace elements + Acetic Acid			
Daily Rates		K: 7.677 x10 ⁻⁷	K: 7.677 x10 ⁻⁷	K: 3.071 x10 ⁻⁶				
g/g organism		P: 1.228 x10 ⁻⁵	N: 1.535 x10 ⁻⁶	P: 4.913 x10 ⁻⁵				
		N: 1.535 x10 ⁻⁶	S: very low levels	Ac acid: 2.1				
Daily Rates		K: 1.54 x10 ⁻⁵ P: 2.46E x10 ⁻⁴	K: 1.54 x10 ⁻⁵ N: 3.07 x10 ⁻⁵	K: 6.14 x10 ⁻⁵ P: 9.83 x10 ⁻⁴				
g/m²		N: 3.07 x10 ⁻⁵	S: very low levels	Ac acid: 42.15				
Daily CO ₂ Req g CO ₂ /g dry mass	0.16 ¹⁸	0.16 ¹⁸	None	None	None None			
Oxygen Tolerance	Aerobic/O ₂ tolerant	Aerobic/O ₂ tolerant	Anaerobic	Anaerobic ¹⁹	Anaerobic			
Deprivations from media	None	None	None	Phosphate deprived, Sulfur limited	Nitrogen deprived			
Production Cycle Duration	Semi-infinite, continuous	Semi-infinite, continuous	3 days H ₂ production, 4 days growth	3 days H ₂ production, 1 day growth for ~180 days total ²⁰	Semi-infinite, continuous			
Gases Produced	H ₂ , O ₂	H ₂ , O ₂	H ₂ , CO ₂	H ₂ , CO ₂	H ₂ , CO ₂			

 $^{^{17}}$ "...the immobilization technique allowed us to increase the cell density about 130-fold compared to a suspension culture" Kosourov, Sergey N. and M. Seibert. Hydrogen Photoproduction by Nutrient-Deprived Chlamydomonas reinhardtii Cells Immobilized within Thin Alginate Films under Aerobic and Anaerobic Conditions. NREL. Colorado. 16 June 2008. p 8. (NREL)

¹⁸ Calculated based on the molar ratios of photosynthesis and the rate of photosynthesis required to support 3% light conversion into biomass.

Operation in aerobic conditions is a possibility but is not postulated for this analysis. "Since this was a critical observation, we further investigated whether alginate-entrapped cells could produce H₂ in the presence of air.... We in fact observed H₂ gas production throughout most of the experiment. However, the final H₂ yields were lower than the yields obtained under an argon atmosphere." Kosourov, Sergey N. and M. Seibert. Hydrogen Photoproduction by Nutrient-Deprived Chlamydomonas reinhardtii Cells Immobilized within Thin Alginate Films under Aerobic and Anaerobic Conditions. NREL, Colorado, 16 June 2008. p 10.

Alternating cycles of 2-days growth/2-days H₂ production with a total film lifetime of 180 days.

	B-1	B-2	B-3	B-4	B-5
	Theoret	ical & Assumed H ₂ P	roduction Paran	neters	
Assumed PAR ²¹	44%	44%	44%	44%	71%
Photons/H ₂ mol	4	4	4	4	11-15
Theoretical Product Ratio	1	nol H ₂ ²² mol O₂	1 m	nol H ₂ nol CO ₂	2 mol H ₂ 1 mol CO ₂
Experimental Product Gas Ratio		ot yet demonstrated		0% H ₂ ²³	0.95 mol H ₂ 0.05 mol CO ₂
Assumed Product Gas Ratio		mol H ₂ mol O ₂	2 mol H_2 0.86 mol CO_2	2 mol H ₂ 0.6 mol CO ₂	2 mol H ₂ 0.05 mol CO ₂
STH ²⁴ Efficiency (Max Theoretical)	12.2%	12.2%	12.2%	3%	6.5%
Solar energy for Coincident Cell Growth ²⁵	3%	3%	N/A	N/A	3%
STH Efficiency (Assumed Upper Bound)	9.2%	9.2%	5.2% (average over growth & production)	2.25% (average over growth & production)	3.5%
STH Efficiency (Near Term Estimate)	2%	2%	1.3%	1.5%	1.5%
Experimental STH Efficiency	H ₂ production r	ot yet demonstrated	H ₂ not demonstrated	0.8% average	2.5% ²⁶
Bed Depth (cm)	10	10	10	10 ²⁷	10
		Reactor Para	meters		
H ₂ Rate (kgH ₂ /day) ²⁸	1,111	1,111	1,176	1,176	1,111
Number of Raceways	20	20	38	90 Production 2 Growth	54
Raceway LxW: Raceway D	1090'x40' x0.33'	1090'x40' x0.33'	1090'x40' x0.33'	1060'x40' x0.33'	1090'x40' x 0.33'
Reactor Area (m²)	80,968	80,968	151,754	352,070	216,228

Email from Pin-Ching Maness. (NREL) 10 October 2008. "...the gas output should be 1 mol O_2 and 2 mol H_2 , with no CO_2 at all."

²¹ PAR: photosynthetically active radiation

While CO_2 must be produced by the reaction, it is dissolved in the aqueous media. Consequently no CO_2 is experimentally observed in the headspace gas. However, in a potential future system, excess CO_2 is expected to exceed the saturation limit and collect as a gas in the reactor bed headspace.

²⁴ STH Efficiency =Solar to Hydrogen conversion efficiency = ratio of hydrogen net energy produced (lower heating value) to total solar energy incident on reactor bed.

This only applies to Chemostat II systems (section 4.1.4), where there is no separate growth stage.

Akkerman, Ida, Marcel Janssen, Jorge Rocha, Rene H. Wijffels. <u>Photobiological hydrogen production: photochemical efficiency and bioreactor design</u>. Intl. Journal of Hydrogen Energy. Vol. 27, p 1195-1208, 2002.

Thinness of film substrate makes this depth unnecessary for photon capture, but it is still necessary for system temperature modulation.

28 Pode and it is a still necessary for photon capture, but it is still necessary for system temperature modulation.

Beds are sized to meet $1000 \text{ kgH}_2/\text{day}$ out of PSA. PSA recovery is determined by input hydrogen + contaminant gases for all beds, some of which are in growth phase. Calculated by PSA spreadsheet model and confirmed by gas separation experts at UOP LLC. H_2 recovery for B1, B2, and B5 estimated at 90%. H_2 recovery for B3 and B4 estimated at 85%.

2.1 *Nutrients*

A wild algal colony reaches a final concentration in the photoautotrophic growth stage of >1 g/L if allowed to grow to stationary phase. Thus, each system must be diluted through algae filtering to achieve a cell density of 0.2 g/L. The bed depth is chosen so that, following transition to the hydrogen production mode, the absorbance achieves the highest yield of hydrogen at this density. For the chemostat systems, a final cell concentration of 0.2g dry weight/L (WT cells) was recommended by NREL before transition to hydrogen production mode²⁹. This concentration can be achieved either by dilution of the stationary phase culture or by earlier commencement of transition to hydrogen producing conditions.

The concentration of algae is important because it determines how several other items are sized in our analysis. It impacts the amount of nutrients and input gases required. Later in the engineering parameters section we will analyze how it can affect pump and valve sizes as well.

2.1.1 Chlamydomonas reinhardtii Nutrients

In most laboratory environments, Chlamydomonas nutrient requirements are fulfilled by the tris-acetate-phosphate (TAP) medium with Hunter Trace Elements or other custom mixes of common lab chemicals. While ideal for a laboratory where these chemicals are readily available and only used in small quantities, on a production scale the costs are extraordinarily expensive. Even in large quantities and at technical grade, the manufacturing that goes into laboratory quality chemicals substantially increases the price. A cost breakdown of the TAP medium can be seen in Figure 2-2. Prices are based on quotes from Spectrum Chemical Corporation and Eastern Chemical Corporation.

²⁹ What we desire is an appropriate matching of organism density and bed depth so that full photon capture is achieved. Full photon capture will lead to maximum hydrogen production. Amos suggests that 0.2g/L is a feasible and practical organism density. Consequently, we have adopted that density and have adjusted bed depth based on the specific organism absorption properties to achieve full photon capture.

Figure 2-2. TAP Medium Costs

Compound	Symbol	Price	Quantity	Concentration	Price	Cost/ Liter			
	TAP Medium								
Tris	(HOCH2)3CNH2	\$13,480.00	907 kg	2.43 g/L	\$14.86/kg	0.03612			
Ammonium Chloride	NH4Cl	\$102.00	23 kg	.4 g/L	\$4.5/kg	0.00180			
Magnesium Sulfate, Heptahydrate	MgSO4.7H2O	\$2,160.00	500 kg	.1 g/L	\$4.32/kg	0.00043			
Calcium Chloride, Dihydrate	CaCl2.2H2O	\$583.00	50 kg	.05 g/L	\$11.66/kg	0.00058			
Potassium Phosphate, Dibasic	K2HPO4	\$216.00	23 kg	.108 g/L	\$9.52/kg	0.00103			
Potassium Phosphate Monobasic	KH2PO4	\$3,300.00	225 kg	.056 g/L	\$14.67/kg	0.00082			
Acetic Acid	СН3СООН	\$558.00	208 L	1. ml/L	\$2.68/L	0.00268			
		Hunter Trace	Elements						
EDTA Disodium Salt	Na2EDTA	\$1,402.74	12 kg	50. g/L	\$116.9/kg	0.00584			
Zinc Sulfate, Heptahydrate	ZnSO4.7H2O	\$709.80	12 kg	22. g/L	\$59.15/kg	0.00130			
Boric Acid	H3BO3	\$531.54	12 kg	11.4 g/L	\$44.3/kg	0.00050			
Manganese Chloride, 4- Hydrate	MnCl2.4H2O	\$1,227.78	12 kg	5.06 g/L	\$102.32/kg	0.00052			
Ferrous Sulfate, Heptahydrate	FeSO4.7H2O	\$865.44	12 kg	4.99 g/L	\$72.12/kg	0.00036			
Cobalt Chloride, Hexahydrate	CoCl2.6H2O	\$2,683.50	12 kg	1.61 g/L	\$223.63/kg	0.00036			
Cupric Sulfate, Pentahydrate	CuSO4.5H2O	\$716.82	12 kg	1.57 g/L	\$59.74/kg	0.00009			
Ammonium Molybdate, Tetrahydrate	(NH4)6Mo7O24.4H2O	\$2,509.13	12 kg	1.1 g/L	\$209.09/kg	0.00023			
Total Cost TAP Medium/ Liter						0.0435			
Total Cost Hunter Elements/Liter						0.0092			
Total Cost/ Liter Solution						0.05267			
Total Cost/ Reactor (B1)						\$427,037.50			
Total Cost/ Year (assuming 12 reactor changes per yr)						\$5,124,450.00			

Due to the prohibitive cost of the TAP medium, we investigated alternative nutrient sources. Fish aquaculture provides an excellent case study for large-scale algae production since algae is the primary food source for most fish, and an effective nutrient source is integral to the success of the culture. The standard source of nutrients for algal based aquaculture is liquid or solid farm fertilizer. The most effective fertilizers are ones that contain all three of the major fertilizer nutrients: Potassium, Phosphorous, and Nitrogen. Commercial fertilizers also come with a wide variety of available trace elements that can be added in any number of custom blends. The prices for commercial fertilizers that would be adequate for effective algae growth are substantially cheaper than those of the TAP medium or other similar media. Information from the US Dept. of Agriculture (USDA) indicates the cost of fertilizers ranges generally between \$150 and \$550 per ton, depending on the type of fertilizer and the quantity being purchased. Some of the more common fertilizers and their prices over the past seven years can be seen Figure 2-3.

Figure 2-3. Fertilizer prices per ton since 2000.

Year	Month	Anhydrous ammonia	Nitrogen solutions (30%)	Urea 45-46% nitrogen	Ammonium nitrate	Sulfate of ammonium	Super-phosphate 44-46% phosphate	Diammonium phosphate (18-46-0)	Potassium chloride 60% potassium
2000	Apr.	\$227	\$131	\$200	\$194	\$167	\$233	\$240	\$165
2001	Apr.	\$399	\$189	\$280	\$260	\$192	\$236	\$244	\$170
2002	Apr.	\$250	\$127	\$191	\$195	\$187	\$221	\$227	\$164
2003	Apr.	\$373	\$161	\$261	\$243	\$195	\$243	\$250	\$165
2004	Apr.	\$379	\$178	\$276	\$263	\$205	\$266	\$276	\$181
2005	Apr	\$416	\$215	\$332	\$292	\$244	\$299	\$303	\$245
2006	Apr	\$521	\$232	\$362	\$366	\$266	\$324	\$337	\$273
2007	Apr	\$523	\$277	\$453	\$382	\$288	\$418	\$442	\$280

According to US Patent #5,567,221 from OMS Investments Inc., the suggested aquaculture algae nutrient rates for the three major fertilizer nutrients is 100 pounds/acre per production cycle for nitrogen, 800 pounds/acre per production cycle for phosphorous, and 50 pounds/acre per production cycle for potassium. Average production cycles vary depending on the species of fish from as much as 18 months to as little as 6 months. If we average that

range to a year, and estimate the algal concentration for these fertilizer quantities we can compute the necessary fertilizer for our application.

The biodiesels industry indicates concentrations of 1g/L to 10 g/L of algae in solution are normally achieved. Taking the average we assume that the nutrient rates suggested by the OMS patent are based on an algae concentration of 5g/L, compared to our colony concentration of 0.2g/L. The bed depth in the OMS patent is 1m compared to our pond depth of 0.1m. The rate of nutrients of interest is g Nutrient/g algae/m²/day. In order to compute this we first convert the rate given to g/m²/day using the conversion factors below.

Conversion Factors		
4046.9	m²/acre	
365	days/yr	
453.592	g/lb	

	Nitrogen	Potassium	Phosphorus
lb/acre/yr	100	50	800
g/m ² /day	0.031	0.015	0.246

Then using the concentration values and bed depths we can compute the g algae/m² for the reference and for our plant.

Conversion Factors		
Volume	1000	L/m³
Bed Depth (Aqua)	1	m
Bed Depth (Photobio)	0.10	m
	Aquaculture	Photobio
g/L g/m ²	5	0.2
g/m ²	5000	20

Lastly, we compute the daily mass ratio of nutrients to algae in the aquaculture then convert to an areal density given the Photobiological algae concentration. This leads us to the values provided in the Biological Parameters table above (Figure 2-1) for colony growth. Naturally, this amount would be less at the start of the colony. However, given the extremely small level of nutrients and the short growth time, we took this nutrient rate as a constant value during the growth phase. During H₂ production the nutrient rates decrease as specified by other sources.

Figure 2-4. Nutrient Rates Computed

	Nutrient>	Nitrogen	Potassium	Phosphorus
Aquaculture	g Nutrient/m²/day	0.031	0.015	0.246
Aquaculture/Photobio	g Nutrient/g algae/day	6.142E-06	3.071E-06	4.913E-05
Photobio	g Nutrient/m²/day	1.228E-04	6.142E-05	9.827E-04

If we average the production cycle range to a year with rates computed, the cost of nutrients drops significantly when compared with the TAP medium. An example of possible nutrient cost for the B-1 system using three different fertilizers, each rich in one of the nutrients, is shown in Figure 2-5. The costs were calculated using the Nitrogen solutions, Super Phosphate, and Potassium Chloride prices from the USDA. While costs may vary and more accurate testing of the adequate fertilizer mix and the appropriate rate still need to be done, these costs are indicative of the cost for using fertilizer as a nutrient source.

Figure 2-5. Sample Fertilizer Costs

Nutrient	Cost/Lb	Lb/Acre/Yr.	Cost/Acre/Yr.	Cost/1 TPD Module/Year
Nitrogen	\$0.14	0.4	\$0.06	\$0.80
Potassium	\$0.14	0.2	\$0.03	\$0.40
Phosphorous	\$0.21	3.2	\$0.67	\$9.63
Total	\$0.49	3.8	\$0.76	\$14.65

It should be noted that this price and nutrient breakdown are merely representative. In hydrogen production mode, a fertilizer without phosphorous would be used for the B-4 system, while in the B-5 system, a fertilizer that is nitrogen deprived would be ideal. Additionally, small amounts of sulfur would be added to the B-4 system in order to maintain the cell during long hydrogen production periods. Since the cost of nutrients is insignificant, more accurate costing of each nutrient system was not necessary for this report.

2.1.2 Bacteria Nutrients

Cyanobacteria (blue-green algae) are a diverse branch of prokaryotic oxygenic photoautotrophs that, like algae, oxidize water as electron donor and fix CO₂ using light. They produce energy during the night by consumption of energy reserves, mainly glycogen, under aerobic conditions (respiration) or anaerobically (fermentation). They differ from algae in using a phycobilin pigment system for antenna. There are many thousands of different genera and strains with vastly different requirements for water, salinity, pH, temperature and nutrients. The native cyanobacterial strain serving as background for the genetic alterations considered above in B-2 is *Synechocystis* PCC6803. This unicellular strain grows in freshwater media similar to that used with *C. reinhardtii*. In our analysis, Cyanobacteria nutrients and nutrient rates are the same as for the *C. reinhardtii*.

2.1.3 PNS Bacteria Nutrients

Purple Non-Sulfur (PNS) photosynthetic bacteria are very different organisms than algae and cyanobacteria and have different nutrient requirements. In previous studies concerning PNS, the primary source of nutrition was a combination of laboratory chemicals; however, organic acids such as acetic acid combined with agricultural fertilizer containing the three major macronutrients are hypothesized for mass production. Acetic acid consumption

during hydrogen production of PNS bacteria has been demonstrated experimentally 30 . Based on the assumed PNS hydrogen production reaction 31 of $C_2H_4O_2 + 2H_2O + Light$ Energy => $2 CO_2 + 4 H_2$, 4 moles of hydrogen gas are formed for each mole of acetic acid. Using this ratio, along with the ratio of acetic acid to PNS cell mass (modeled as $C_5H_8O_2$) needed for the assumed 3% of photons dedicated to growth, we can calculate the overall acetic acid consumption rate shown in Figure 2-6.

Figure 2-6. Acetic acid Consumption by PNS

PNS Acetic Acid Consumption (Based on Theoretical Mass Balance)			
Molar Ratio of Acetic Acid to PNS Mass (Section 3.5)		3	
Molecular Weight of Acetic Acid	g/mol	60.032	
Molecular Weight of PNS Mass	g/mol	100.064	
Mass of PNS Grown (3% of photons)	kg/day	468	
Acetic Acid Needed for Growth	kg/day	842	
Molar Ratio of Acetic Acid to H ₂		0.25	
Molecular Weight of H ₂	g/mol	2.016	
H ₂ Produced	kg/day	1111	
Acetic Acid Needed for H ₂ Production	kg/day	8272	
Total Acetic Acid Needed	kg/day	9113	

According to data from the Chemical Journal (Korea) the international market price for acetic acid is \$0.595/kg³². As an alternative, in an integrated system, the waste product of a fermentor can potentially be used as an organic acid feedstock for the PNS bacteria.

2.1.4 pH of Solution

The pH of the solution in the reactor beds should be maintained near 7 to ensure optimal organism growth. In systems B-3, B-4 and B-5, there will be trapped CO₂ released by the organisms in the process water. In the B-3 and B-4 systems this CO₂ is needed as a feedstock for the algae during the growth stage to return the cell concentration to a level high enough to support the respiration needed to keep the system anaerobic during hydrogen production. Approaches to maintaining targeted pH levels have not been considered in detail within this report. Further investigation of the effects of pH should be considered in future work.

2.1.5 Carbon Dioxide

In addition to fertilizer and acetate, these organisms utilize carbon dioxide to make both structural biomass and energy reserves. The gas rate requirements have been determined using the stoichiometric ratios of photosynthesis. Additional CO₂ will only need to be added to the B-1 and B-2 systems to support the minimal growth required to keep the system alive. Systems B-3 and B-4 will be producing all of the CO₂ necessary for the

³⁰ Barbosa, Maria, Johannes Tramper Jorge Rocha, Rene H. Wijffels. <u>Acetate as a carbon source for hydrogen production by photosynthetic bacteria</u>. Journal of Biotechnology. Vol 85, p 25-33. 2000.

Akkerman, Ida, Marcel Janssen, Jorge Rocha, Rene H. Wijffels. <u>Photobiological hydrogen production:</u> <u>photochemical efficiency and bioreactor design</u>. International Journal of Hydrogen Energy. Vol 27, p 1195-1208. 2002.

³² Lee, Sang Y. <u>Plastic Bacteria? Progress and prospects for polyhydroxyalkanoate production in bacteria</u>. Trends in Biotechnology Vol 14, p 431-438. 1996.

system, and the B-5 system will utilize acetate as its carbon source. The amount of carbon dioxide required was checked against the amount soluble in water. The amount of CO₂ used should be well below saturation to avoid excess CO₂ bubbling out into the H₂ product gas. Using the CRC Handbook of Chemistry and Physics, we obtained the solubility of CO₂ in water. We will maintain a CO₂ partial pressure that will assure adequate CO₂ supply. In the B-3 and B-4 systems the CO₂ produced by the algae will be far above the solubility threshold, and the gaseous CO₂ produced will be filtered out through PSA and added to the system after the dissolved level of CO₂ drops through algae consumption. Since each system consists of numerous beds, their growth and production cycles will be appropriately staggered to ensure that there are always beds in need of the CO₂ that is being filtered by the PSA. A constant slip stream of water will be removed and run through a CO₂ saturation vessel and returned to raceways that are low on CO₂. The only addition of CO₂ necessary for B-3 and B-4 is the initial amount needed at the initial colony growth. B-5 has no CO₂ needs.

The B-1 and B-2 organism needs for normal growth conditions are 31.66mg/L/day and for reduced growth conditions are 146.57 mg/L/day¹⁸. Figure 2-7Figure 2-7. Carbon Dioxide Solubility in Water shows that these CO₂ concentrations are well below the maximum solubility of CO₂ in water at one atmosphere and that the CO₂ input will remain in solution.

The CO_2 needs for sustainment for the entire system amounts to only $257 \text{kgCO}_2/\text{day}$ (17,560ft³/day at 1atm). The CO_2 can be readily provided by maintaining a CO_2 partial pressure of 0.5psia. This partial pressure will also minimize the CO_2 dilution of the product H_2 in the headspace of the reactor.

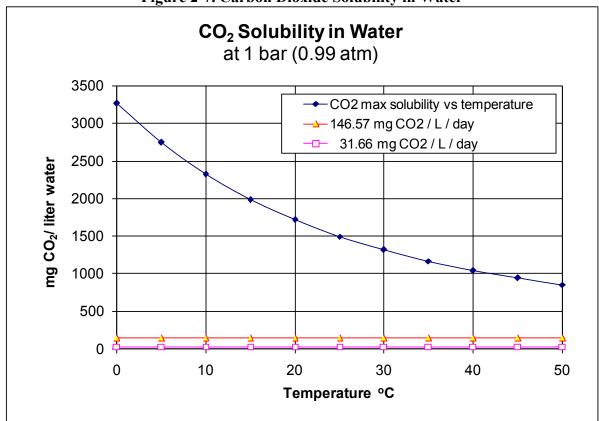


Figure 2-7. Carbon Dioxide Solubility in Water

2.2 *O*₂-tolerant Hydrogenase (B-1 & B-2)

The B-1 and B-2 systems utilize organism mutants that are O₂-tolerant, with B-1 using the algae strain C. *reinhardtii* and the B-2 system using the cyanobacterium *Synechocystis* PCC6803. The O₂-tolerant hydrogenase pathway in both organisms is comprised of theoretical mutants with truncated Ch1 antennae (Light Harvesting Complex, or LHC, mutants) to minimize excess absorption of solar energy beyond what is needed for maximal H₂ production. Two research groups have reported mutants in C. *reinhardtii* that have reduced Ch1 content associated with truncated antenna complexes.³³, ³⁴ In both cases, the cells exhibit a reduced optical cross section and a higher growth rate at full solar light intensity. Factors of two have been reported. However, in both cases, reports on hydrogen production from these mutants have not been published, since research is ongoing.

A number of oxygen tolerant hydrogenases have been identified in bacteria as potential enzymes in algal hosts; bioengineering has yet to produce a mutant that exhibits stable H_2 output over extended periods.

³³ Melis, A. (2007) <u>Photosynthetic H-2 metabolism in Chlamydomonas reinhardtii (unicellular green algae),</u> *Planta 226*, 1075-1086.

Mussgnug, J. H., Thomas-Hall, S., Rupprecht, J., Foo, A., Klassen, V., McDowall, A., Schenk, P. M., Kruse, O., and Hankamer, B. (2007) <u>Engineering photosynthetic light capture: impacts on improved solar energy to biomass conversion</u>, *Plant Biotechnology Journal* 5, 802-814.

The current best solar-to-hydrogen (STH) energy conversion efficiency of non-tolerant C. *reinhardtii* is ca. 0.8% for immobilized cells³⁵. The theoretical prediction for algae assuming 100% flux of photoelectrons going solely into H₂ production and without any loss or competition with other processes predicts an STH of ~12.2%. However, a certain amount of energy must be diverted for homeostasis, the regulation of the general health and functioning of the cell, regardless of the outside environment. Allowing for energy losses required for homeostasis, but assuming no competition with other pathways for utilization of light energy, our analysis assumes that hypothetical mutant B-1 algae will produce hydrogen at 9.2% STH efficiency, while growing at approximately ½ of the normal growth-only doubling rate (i.e. the doubling rate of algae that is not producing H₂). Because the growth rate during production is assumed to be ½, the carbon dioxide and nutrients during this condition is also assumed to be ½.

For the B-2 system, Cyanobacteria do not produce significant levels of hydrogen upon illumination, even those strains which possess a native hydrogenase. However, hydrogenase-containing strains can produce hydrogen upon incubation under dark anaerobic conditions which induces autofermentation. In order to produce significant levels of photohydrogen with cyanobacteria, an engineered strain will need to be derived in which the native [NiFe]-hydrogenase is replaced with one capable of utilizing the same photoreductant produced in algae, ferredoxin. Though deemed possible, no such bacteria have been reported to date in the literature. Therefore, extrapolations made herein are based on predictions provided by the NREL staff. The algae assumptions of a theoretically possible 12.2% STH for the B-1 pathway are also applied to the B-2 pathway.

Pathways B-1 and B-2 are expected to produce hydrogen indefinitely unless the colony is spoiled by external factors. Since these mutants are still in a research stage, our analysis will assume that the amount of energy spent on hydrogen production can be regulated somewhat by controlling CO₂ or ferredoxins (controlling how much energy goes to cell maintenance and cell growth). Although the organism is different for photobiological system B-1 and B-2, we assume their growth rates and calculated parameters to be identical in Figure 2-1, as the systems are future projections of yet undeveloped strains. Cyanobacteria may have an advantage to algae as their native hydrogenase is less sensitive to oxygen⁷. However, as noted above they produce H₂ most efficiently in the dark and would require an algal-like hydrogenase if photohydrogen was the primary goal. As more data become available for these systems, the STH performance can be modified to assess the impact on hydrogen production capabilities and system costs.

Photobiological Systems B-1 and B-2 are modeled by the following reactions:

H₂ Production: $2 \text{ H}_2\text{O} + \text{Light Energy} \Rightarrow 2\text{H}_2 + \text{O}_2$ Respiration: $6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6 \Rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

Photosynthesis/Growth: $6CO_2 + 6H_2O + Light Energy \rightarrow C_6H_{12}O_6 + 6O_2$

The inputs and outputs of the system are depicted in Figure 2-8.

3 4

Kosourov, Sergey N. and Michael Seibert. <u>Hydrogen Photoproduction by Nutrient-Deprived Chlamydomonas reinhardtii Cell Immobilized within Thin Alginate Films under Aerobic and Anaerobic Conditions</u>. Basic Sciences Center, NREL, Golden Colorado. 16 June 2008.

³⁶ Telecom. <u>09JUL08 Mtg Minutes</u>. Technoeconomic Analysis of Bio-Hydrogen Program. NREL Contract # AFH-8-88601-01. Revision 10 July 2008.

Nutrients

Outputs
66% H₂ by mol,
34% O₂ by mol

Water

Water+Algae

Waste Algae

LEGEND

GASES
SOLIDS
LIQUIDS

Figure 2-8. Oxygen-Tolerant Hydrogenase Process

The product gases from this system are hydrogen and oxygen. In certain ratios, those gases can be a highly combustive mixture. The gas mixture would be located above the reactor bed. The engineering analysis portion of this report addresses ways to separate this mixture to obtain the pure product hydrogen.

2.3 Sulfate-permease Green Algae (B-3)

Like the B-1 pathway the sulfate-permease pathway utilizes algae mutants with truncated antennae. However, the algae in this pathway lack the mutated O₂-tolerant hydrogenase of B-1. Hydrogen production is controlled through genetic mutation of the chloroplast sulfur uptake mechanism, reducing the rate of oxygenic photosynthesis. Sulfur is necessary for the regeneration of proteins damaged by photo-oxidation. Over time, the build-up of damaged photosynthetic proteins in the chloroplast will lead to a reduction in oxygen evolution. As the rate of oxygen evolution falls below the rate of oxidative respiration, the system will become anaerobic, leading to the induction of the hydrogenase pathway and continuous hydrogen production. The level of respiration needed to eliminate the high levels of oxygen produced by the water splitting hydrogen production reaction will necessitate a large amount of starch that must be produced by the cells prior to hydrogen production. Therefore, this organism is operated in a cyclic manner, with: (1) a growth/regeneration leading to starch buildup and (2) a hydrogen production phase which is anaerobic. In order to achieve the required level of starch mass, the starting concentration of the cells at the end of the hydrogen production phase will be 0.85g/l and will increase rapidly over the course of the regeneration phase to ensure enough mass exists to keep the system anaerobic when subsequently producing the necessary volume of hydrogen gas. Over time, however, the lack of starch production and the loss of cell mass due to respiration keeping the system

anaerobic will inhibit cellular function, necessitating the regeneration phase where the system is bubbled with CO_2 and air. For phase transition, adding small amounts of air to the system will shut down the hydrogenase enzyme, ceasing H_2 production and directing photosynthesis towards algae mass production.

During the production phase, the carbon dioxide production from respiration will rapidly saturate the process water and be released into the headspace. This CO₂ will be removed from of the product gasses using a PSA and then returned to other beds in the system that are in growth phase, and thus need CO₂ (the individual raceways will be staggered so that not all of them will be in the same phase of the cycle at once). Data has indicated that a system like this can engage in continuous hydrogen production for 80-100 hours. Experimental data are lacking for hydrogen production rates since research is ongoing and data has yet to be published. Theoretically, while in hydrogen production mode, the sulfate permease mutant could convert 100% of photoelectrons into H₂ production without any loss or competition with other processes. However, the maximal 12.2% STH efficiency of the photohydrogen production must be averaged over both phases, and thus is reduced by a factor of 3/7, given the need for a 3-day hydrogen production period followed by a 4-day recovery and regeneration period.

Photobiological System B-3 is modeled by the following reactions:

H₂ Production Phase

H₂ Production Reaction: $2 \text{ H}_2\text{O} + \text{Light Energy} \Rightarrow 2\text{H}_2 + \text{O}_2$ Respiration Reaction: $6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6 \Rightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}$

Growth/Regeneration Phase:

Photosynthesis Reaction: $6CO_2 + 6H_2O + Light Energy \rightarrow C_6H_{12}O_6 + 6O_2$

Respiration Reaction: $6O_2 + C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O$

The inputs and outputs of the system for both production and growth phase are depicted in Figure 2-9.

Figure 2-9. Sulfate Permease Process Hydrogen Production Phase Inputs Outputs Water H₂ and CO₂ Sulfate Permease B-3 LEGEND GASES **Growth Phase** Inputs **Outputs** Air O_2 **Nutrients** Sulfate Permease Water B-3 CO_2 Water

2.4 Immobilized sulfate-deprived green algae (B-4)

In this photobiological pathway the basic system concept utilizes mutant, truncated-antenna *Chlamydomonas reinhardtii* algae. It involves use of a designated bed for algal growth followed by immobilization of the algae by attachment to a thin film in the growth bed. The film with immobilized algae is transferred to a production bed for the H₂ production mode, which is initiated by sulfur deprivation. Sulfur deprivation leads to the gradual and reversible reduction of O₂ evolution in algae. As the rate of O₂ evolution falls below the rate of oxidative respiration, the system goes anaerobic, leading to H₂ production. The benefit of thin film immobilization is a substantial increase in duration of the H₂ production mode as compared to non-immobilized sulfate-deprived algae systems due to the reduced energy requirements of the cells for movement and increased cell density. Unlike the B-1 and B-2 pathways, the immobilized system has been successfully tested in a laboratory environment.

Data for the immobilized, sulfate-deprived green algae are based on an NREL study by Kosourov and Seibert³⁷. The NREL study utilized a thin alginate film as the immobilization substrate; however other types of films have also been used in analogous applications. For example, nitrogen-fixing blue-green algae have been attached using their heterocyst cells to cellulose sheets and to spunbond and meltblown polypropylene web sheets for use in stimulating agricultural plant growth³⁸. In order to improve the affinity of the algae to the polypropylene film, the film surface energy will probably need to be increased to a level of 40 dynes/cm using corona treatment, or an alternative material having higher inherent surface energy, such as polyester can be used. With any man-made polymer, it is ultra-important to steam clean or otherwise treat the material to eliminate the manufacturing process substances that would be deleterious to the algae.

In other research work, cyanobacteria have been immobilized on polyurethane foam sheets (as well as alginate) for hydrogen production purposes at King's College in London³⁹. As noted therein, polyurethane foam was also used to immobilize the algae *Chlorella vulgaris*.

In this report, we have chosen to use meltblown polypropylene web sheets for minimum cost immobilization. The Kosourov report uses an alginate/plastic screen configuration. This alginate has advantages if the immobilized algae are later used in a fermentation process, since the alginate film will also ferment. However, the higher cost of the screen along with the cost associated with impregnating the screen with alginate increases the levelized hydrogen cost of the B-4 system. Conversations with NREL have also indicated that on substrates other than alginate, hydrogen production periods of up to six months can be maintained with the addition of minimal amounts of sulfur⁴⁰. This increase in hydrogen production time will reduce the labor requirement for film replacement.

As with the B-3 system, there will be a hydrogen production phase followed by a growth/regeneration phase in which the concentration and mass of algae will increase enough to allow adequate starch for the respiration necessary to keep the system anaerobic during the production phase. This growth/regeneration phase will be triggered by the addition of sulfur to the nutrient medium. Sulfur deprivation will then be used to trigger the hydrogen production phase. At the end of a two day hydrogen production phase, the concentration of algae will be at 1.81/L, the concentration needed for the necessary mass growth to allow enough respiration for anaerobic hydrogen production. Also like the B-3 system, the beds will be staggered to allow excess CO₂ separated through PSA to be added to a slip stream of water removed from raceways during the regeneration phase. After 180 days of cycling between growth and production, the algae films will need replacement from mats being created in the two designated growth beds.

Kosourov, Sergey N. and Michael Seibert. <u>Hydrogen Photoproduction by Nutrient-Deprived Chlamydomonas reinhardtii Cell Immobilized within Thin Alginate Films under Aerobic and Anaerobic Conditions. Basic Sciences Center NREL Golden Coloredo. 16 June 2008</u>

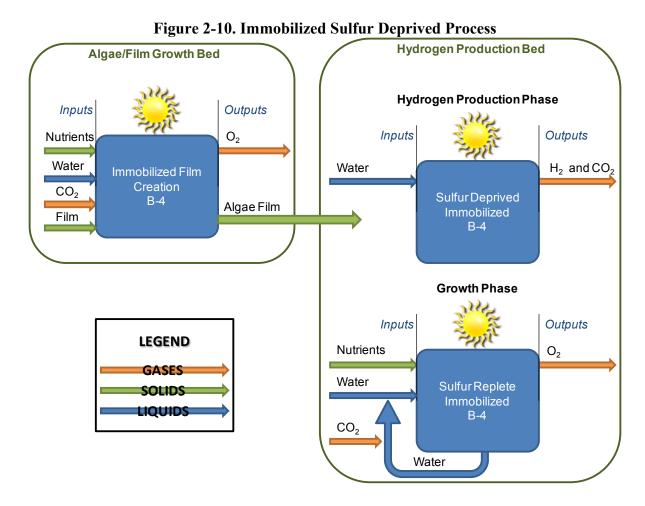
Conditions. Basic Sciences Center, NREL, Golden Colorado. 16 June 2008.

38 U.S. Patent 4,879,232, Nov 7, 1989, "Multilayered Structure Containing Immobilized Blue-Green Algae".

 $^{^{39}}$ Muallem, Bruce, and Hall, "Photoproduction of H_2 and NADPH $_2$ by Polyurethane Immobilized Cyanobacteria", King's College, London.

⁴⁰ Private communication with Dr. Mike Seibert of NREL, 29 May 2009.

Theoretically, the algae can be separated from the binder and rejuvenated but, since the algae growth costs are low, it is not worth the complexity of the separation system. Figure 2-10 shows the growth and production modes of this pathway.



In this system we assume the same growth rate as other Chlamydomonas systems. To ensure that the growth beds are fully utilized, we will use two algae film/growth beds to produce algae for the 68 production beds. The H₂ production cycles of each bed will be staggered appropriately, so that each day the growth beds will be utilized to replenish a spent production bed.

Compared to O₂-tolerant algal systems (B-1, B-2), cellular maintenance energy requirements are substantially lower due to the immobilization of the algae on thin films. The theoretical STH efficiency is 3%; however, the laboratory tests have only achieved 0.8% STH efficiency³⁷. Since this is an actual data point, it is not reasonable to compare it to other systems that only have theoretical values. For comparison purposes we will use the STH efficiency of the assumed reactor operation of 2.25%, due to the one day of production for every three days of growth.

Photobiological System B-4 is modeled by the following reactions:

H₂ Production Phase

H₂ Production Reaction: $2 \text{ H}_2\text{O} + \text{Light Energy} \Rightarrow 2\text{H}_2 + \text{O}_2$ Respiration Reaction: $6\text{O}_2 + \text{C}_6\text{H}_{12}\text{O}_6 \Rightarrow 6\text{CO}_2 + 6\text{H}_{2}\text{O}$

Growth Phase:

Photosynthesis Reaction: $6CO_2 + 6H_2O + Light Energy \rightarrow C_6H_{12}O_6 + 6O_2$

Respiration Reaction: $6O_2 + C_6H_{12}O_6 \rightarrow 6CO_2 + 6H_2O$

2.5 Purple non-sulfur bacteria (B-5)

Unlike the carbon-fixing organisms in the previous systems, these bacteria are photoheterotrophic, nitrogen-fixing organisms. Under anaerobic conditions and using simple organic acids or glycerol as an electron donor, these bacteria produce hydrogen gas from the light driven, ATP-dependent reduction of protons to H_2 in the absence of nitrogen⁴¹. In this mode they require removal of N_2 and O_2 and require a supply of organic acids. The photosynthetically active radiation, or PAR, for purple bacteria is 400 - 950 nm, compared to 400 - 700 nm for green algae. However, the PNS organism requires 11 to 15 photons (depending on wavelength) per hydrogen molecule rather than the 4 photons required in the algal systems. As a result of the wavelength energy span and the required photon ratio, the maximum solar-to-hydrogen conversion efficiency is 6.5%. Due to the 3% of photons needed for cell maintenance, the assumed reactor STH is 3.5%.

Since the PAR wavelength of PNS is shifted relative to algae, there is an opportunity to capture a fuller spectrum of light energy by "stacking" an algae system on top of a PNS system. This concept will be further described in Part IV (System Integration).

Photobiological System B-5 is modeled by the following reactions:

H₂ Production Reaction: $C_2H_4O_2 + 2H_2O + Light Energy \rightarrow 2CO_2 + 4H_2$ Fermentation Reaction⁴²: $2C_6H_{12}O_6 + 2H_2O \rightarrow 5C_2H_4O_2 + 2CO_2 + 4H_2$

Growth Reaction⁴³: $3C_2H_4O_2 \rightarrow (C_5H_8O_2)_n + CO_2 + 2H_2O$

The inputs and outputs of the system are depicted in Figure 2-11.

_

Akkerman, Ida, Marcel Janssen, Jorge Rocha, Rene H. Wijffels. <u>Photobiological hydrogen production:</u> <u>photochemical efficiency and bioreactor design</u>. International Journal of Hydrogen Energy. Vol 27, p 1195-1208. 2002.

⁴² The fermentation reaction produces additional hydrogen as well as organic acids (here modeled as acetate). However, it doesn't produce these in appreciable quantities and is thus ignored in this analysis.

The actual PNS growth reaction is complex and involves ammonia (NH₃) and multiple intermediaries. For simplicity and clarity, we base our analysis on the displayed simplified net reaction. This photosynthesic growth reaction produces a variety of organic products, including the glucose utilized in fermentation. Ashing analysis (from Van Gemerden H. 1968. Utilization of reducing power in growing cultures of Chromatium. Arch. Mikrobiol. 64:111) shows that the molecular ratio is represented as $(C_5H_8O_2)_n$.

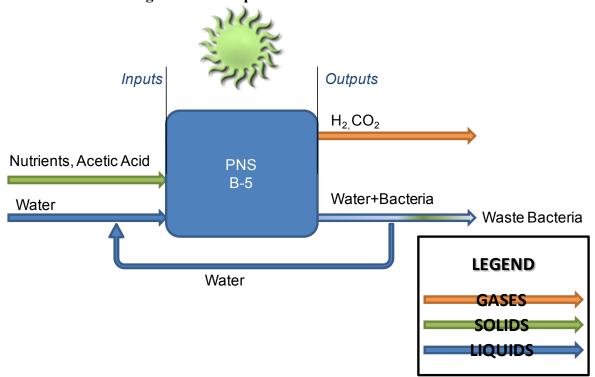


Figure 2-11. Purple Non-Sulfur Bacteria Process

3. Engineering Parameters

The production plant has been divided into the Photobiological Reactor Bed and 4 auxiliary or balance of plant (BOP) subassemblies, namely,

- Organism Feed Subassembly,
- Recycle Subassembly,
- Gas Capture Subassembly, and
- Control System Subassembly

The interfaces between the primary system and its BOP subassemblies are shown in Figure 3-1. Each subassembly is depicted in a different color. The Photo Bio Reactor Bed can take on several forms. The subassemblies have several components that will be identified in later sections of this document.

Hydrogen **Pipeline** LEGEND Reactor Bed Primary System **Gas Capture** Organism Feed Subassembly Subassembly Gas Capture Subassembly Recycle Subassembly Control System Subassembly **Photo Bio Reactor Bed** Recycle **Primary** Subassembly System **Organism Feed** Subassembly Power Source PC **Control System** Subassembly

Figure 3-1. Simplified Photobiological Hydrogen Production Plant

A modular design philosophy was used in the design of the production plant. Each function that needs to be performed in the plant is treated as an independent subassembly and is sized appropriately so that multiple systems can be arranged in parallel within a production plant. The subassemblies are designed such that a single module produces 1,000kgH₂/day at the boundary limits of the production facility. As will be discussed in the results section, the baseline cost estimates correspond to a 10 tonne/day plant consisting of ten 1,000kgH₂/day modules.

3.1 Photo Bio Reactor Bed (Primary System)

Several designs for reactors beds have been developed to enhance performance of these photobiological systems. Each system has both strengths and weaknesses. Our study reviewed four different forms for reactor beds. Each form was then applied to a specific organism to determine which was more or less suitable for the different algae and bacteria. The reactor bed form was selected based on the author's initial judgment of cost effectiveness and because an analysis of all five pathways with all bed form options was beyond the scope of the project.

3.1.1 Single Reactor Bed

The simplest form for a bed is the single reactor. In this bed there is one pond where all photobiological processes occur. The processes occur sequentially, not simultaneously. Thus, if algae are in the growth phase they cannot produce hydrogen and vice versa. The strengths and weaknesses of this system are listed in Figure 3-2.

Figure 3-2. Strengths and Weaknesses of Single Bed Reactors

Single Bed Reactor Design	
Strengths	Weaknesses
Organisms are working at their most efficient point during each process.	Batch process
Single pond; less area, lower cost	Time split between production and growth not most efficient.
	Requires more area for a given hydrogen production

A conceptual design of the single reactor bed is shown in Figure 3-3. The blue box represents the reactor bed. The dotted line separates the different processes that occur in the same bed but at different times. The organisms transition from one photobiological process to another by a manipulation of the inputs and climate conditions. Sunlight is required during both photobiological phases.

Figure 3-3. Conceptual Design: Single Bed Reactors



Duration: Phase 2 = Phase 1

Single Bed Reactor

3.1.2 Dual Reactor Bed

The next form for a bed is the dual reactor. In this reactor there are two ponds; one where all photobiological growth occurs and another where photobiological hydrogen production occurs. Because there are separate beds for each process, growth and production can occur simultaneously. The strengths and weaknesses of this system are listed in Figure 3–4.

Figure 3-4. Strengths and Weaknesses of Dual Bed Reactors

Dual Bed Reactor Design	
Strengths	Weaknesses
Simultaneous growth and production	Cost of two reactor beds
Growth and production bed sizes can be optimized for maximum utilization	Batch process
No mixing of nutrients or gases from production and growth stages	Large flow pumps required under intermittent operation (transfer process)

A conceptual design of the dual reactor bed is shown in Figure 3-5. The blue boxes represent the reactor beds. The organisms are transferred from the growth reactor bed to the production bed when the colony reaches a given concentration. Although growth and production occur simultaneously this is still essentially a batch process. Sunlight is required during both photobiological phases. This dual bed concept is useful when growth and production conditions are different, such as when growth can occur aerobically but production cannot.

Figure 3-5. Conceptual Design of Dual Bed Reactors



Water + Organism

Batch

Dual Bed Reactor

3.1.3 Chemostat Reactor Bed

A chemostat system requires two reactor beds. Like the dual bed reactor, there is one pond where all photobiological growth occurs and another where photobiological hydrogen production occurs. Because there are separate beds for each process, growth and production occurs simultaneously. A chemostat system seeks to maintain a constant volume in the reactor bed. This is accomplished by a continuous slip stream of volume being removed while simultaneously being replenished from the growth reactor bed. The volume of slip stream is computed such that the hydrogen production is constant. Because of the constant volume criteria, chemostat reactors continuously grow algae and produce hydrogen (as long as sunlight is available). The strengths and weaknesses of this system are listed in Figure 3-6.

Figure 3-6. Strengths and Weaknesses of Chemostat Bed Reactors

Weaknesses
Large slip stream volumes of up to 25% /day
No means of selectively separating algae such that slip stream contains waste algae

A conceptual design of the chemostat reactor bed is shown in Figure 3-7. Conceptually, the chemostat form looks identical to the dual reactor bed however the water + organism flow between the two reactors is continuous rather than intermittent. Sunlight is required during both photobiological phases.

Figure 3-7. Conceptual Design of Chemostat Bed Reactors



Water + Organism

Continuous

Chemostat Bed Reactor

3.1.4 Chemostat II Reactor Bed

The Chemostat II's chief characteristic is a single reactor bed that, after the initial growth of the colony, is used simultaneously for both growth and production. The system operates similarly to a chemostat system however it does so in a single reactor bed. During initial growth no production occurs. The bed is filled with the appropriate nutrients required for algae colony to achieve a target algal concentration. Afterwards, climate conditions are adjusted such that algae grow at a ½ of their normal rate and maintain cell functions while producing hydrogen.

In H₂ production mode, the organisms use a limited amount of their energy to complete cell maintenance functions and the remainder of the energy is spent producing hydrogen. By simultaneously doing growth and production, the Chemostat II system allows for continuous hydrogen production without having to stop and replenish algae. The strengths and weaknesses of this system are listed in Figure 3-8.

Figure 3-8. Strengths and Weakness of Chemostat II Bed Reactors

Chemostat II Bed Reactor Design	
Strengths	Weaknesses
Single pond; less area, lower cost	Continuous supply of nutrient may result in diluted product stream
Lower nutrient requirement	

A conceptual design of the Chemostat II reactor bed is shown in Figure 3-9. The Chemostat II looks similar to the single bed reactor, however growth and production occur simultaneously and continuously. Sunlight is required during both the growth and reduced growth with production processes.

Figure 3-9. Conceptual Design of Chemostat II Bed Reactors



Duration: Phase 2 >> Phase 1

Chemostat II Bed Reactor

For this system to be feasible the number of days spent growing the culture must be insignificant when compared to the number of hydrogen production days. The colony concentration will increase slightly every hour and therefore a slip stream of the algal solution will be removed from the bed on a continuous basis. As that stream is being drawn, the reactor bed will be dosed with additional water and nutrients to maintain the colony at constant concentration, size, and pH levels.

3.1.5 Reactor Bed Embodiment

The reactors forms were mapped against the biological parameters of each photobiological system and the best form was selected for each process. The forms selected are listed in Figure 2-1. A complete bill of materials for each pathway is provided in section 4 of this report. Here is included a lengthy description of the physical embodiment of these reactor beds. The components of the reactor bed are described and materials selected for the bed are listed in this section.

A reactor bed could be open or closed to the environment. While an open pond would provide direct access to sunlight, it also leaves our algae colony susceptible to contamination and provides no means of collecting the production hydrogen. A closed pond with a translucent cover allows light to penetrate while protecting the algae from weather conditions (wind, temperature) that may harm them. It also contains any gases produced by the algae. For these reasons all reactor beds in this analysis will be of the closed pond variety.

The reactor bed serves 4 basic functions: fluid containment, product gas containment, access to sunlight, and algal mixing (to avoid stratification). The bed can be a single monolithic structure, such as a pond, or several smaller beds, such as raceways, connected by a piping system. Since typical reactor bed areas are quite large (~20-87 acres for a 1,000kgH₂/day), a modular concept was chosen where the reactor bed is comprised of smaller raceways. This facilitates ease of access, ease of maintenance, isolation of any contaminants, and economies of scale in equipment purchases. The reactor bed is sketched in Figure 3-10 and the components are listed in Figure 3-11.

The reactor bed we have chosen is comprised of several raceways, each measuring between 1060' and 1090' in length, 40' in width, and 10cm in depth. Raceways are designed in an oval shape so that a system of paddlewheels creates a flow in the bed to evenly disperse nutrients and prevent cell coagulation. Each raceway has inlet and outlet ports for the slurry and a separate outlet port for the product gases. Raceway widths are limited by the translucent film dimensions. The film is attached to a frame to maintain a gas-tight seal in the system. Driveways are interspersed between the raceways to provide vehicular access. The quantity of raceways is driven by daily hydrogen production rate and STH of the organism. For our systems there will be between 20 and 90 raceways.

In concept B-4, immobilized organisms are grown on an inert mat which floats upon the surface of the raceway. Circulation of the water/nutrient mixture via paddlewheels is not needed nor is it feasible. Consequently, an oval reactor bed is not needed, and a "runway" configuration is instead used. A "runway" is merely a single side of the oval raceway, without the paddlewheels and without fluid connection between the two sides.

TOP VIEW Raceways **Driveways** To Gas **Gas Outlet Ports** Capture To Gas Capture Algal Colony To Recycle **Photo Bio Reactor Bed** Primary Paddlewheels **Pond Area** From Algae Inlet & Outlet Ports: To Recycle Makeup Water & **Nutrients** From Algae Feed **Gas Tight Frame** Transparent Film Film Attachment Points Driveway Paddlewheel Inlet Ports: Makeup Shallow Éarth

Figure 3-10. Reactor Bed Design

Figure 3-11. Reactor Bed Components

FRONT VIEW

Trough

Bed Depth

Pond Liner

Raceways

Reactor Bed Components
Transparent Film
Pond Lining
Pond Edging
Paddlewheel & Motor
Gas Valves
Gas Ports (Flanges)
Water Valves
Water Ports (Flanges)

3.1.5.1 Films, Edging, and Lining

Earthen Berms

Water & Nutrients

In the Front View one can see that the bed itself is not made with any solid materials but rather shaped from earthen berms and lined with a suitable pond liner material that will keep the system gas tight. Pond liner material is available in roll sizes of 50' x 100' on www.justliners.com. To achieve the necessary pond dimensions the material will be heat-sealed to itself, which is a common practice when creating any kind of retention pond.

Above the raceways a low density polyethylene (LDPE) transparent film (6 mm) is used to allow sunlight in and keep the product hydrogen gas from escaping. A presentation from Daniel Blake at NREL concerning Hydrogen reactor development indicates that the hydrogen permeability coefficient for polyethylene is fairly low (near 200 cm³•mm/m²•atm•day)⁴⁴. Based on our calculations, show in Figure 3-12, the volume of hydrogen lost through the film is negligible.

Figure 3-12. Polyethylene Hydrogen Losses

Polyethylene Hydrogen Losses						
	Units B1/B2 B3 B4 B5					
Hydrogen Permeability Coefficient	cm³•mm/m²• atm•day	200	200	200	200	
Total Area	m ²	80,968	151,035	352,070	216,228	
Film Thickness	mm	6	6	6	6	
Partial Pressure Differential	atm	0.67	1.00	1.00	0.95	
kg/cm³ Hydrogen		0.00000009	0.00000009	0.00000009	0.00000009	
H ₂ lost	kg/day	0.16	0.45	1.06	0.61	
% H ₂ lost from system	%	0.016%	0.045%	0.106%	0.061%	

According to conversations with Berry Plastics, the LDPE film allows 90% of available light through. It is available in rolls 56' wide and more than 1000' long and, therefore, a single continuous roll is able to stretch over an entire raceway 45. The film attaches to a frame structure along the edges of the raceway so that a gas tight compartment is formed. Notice that the film is not taught over the top of the berms, but rather is slack. This is to allow for variations in hydrogen production rate which is expected with varying solar insolation. The number of raceways for a given reactor bed will depend on hydrogen production rate. Thus far it appears that the limiting factor is the width of the transparent roll sizes. We do not want to bond multiple sheets of LDPE as it will only provide additional leakage points for our product gas.

The Pond Edging envisioned would be a mechanical fixture that would seal the transparent film to the pond lining as shown in Figure 3-13.

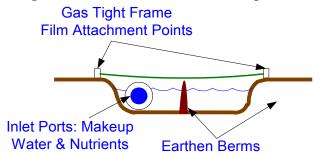
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⁴⁴ Blake, Daniel M. "Hydrogen Reactor Development and Design for Photofermentation and Photolytic Processes". NREL Project PD19. May 23-26, 2005.

⁴⁵ Agriculture Films by Berry Plastics.

http://www.covalenceplastics.com/site/content/agricultural/agricultural.asp#gh. Date Accessed 18 July 2008.

Figure 3-13. Film-Frame interface point



3.1.5.2 Paddlewheel Mixers

Two paddlewheels and a center berm are located in each raceway to provide circulation of the algae solution for proper mixing. The paddlewheel mixer would look similar to a water wheel at a mill. Our analysis for the amount of mixing necessary is based on typical mixing parameters for algal growth in the biodiesel industry. Using that data and resizing to our raceway configuration, we obtained comparable parameters which are listed in Figure 3-14. Paddlewheels with higher flow rates of up to 60cm/s and larger may be necessary to assist in the thermal control of the pond. The B-4 system consists of immobilized mats of algae, and, therefore, will not need paddlewheels for mixing. The nutrients will be provided through a perforated PVC tube that travels the length of the raceway to ensure adequate nutrient dispersal.

Figure 3-14. Paddlewheel Electrical Requirements

Biodiesel Equipment for Algal Growth			
Algae Concentration	1%	volume of pond	
Flowrate	20	cm/s	
Pond Size	1000	m ²	
Paddle Wheel (single)	1.23	kWh/day	

Source: http://www.bioking.lv/algae cultivated in raceway ponds.html

Reactor Raceway			
Algae Concentration	0.02	volume of pond	
Flowrate	20	cm/s	
Pond Size	4050	m ²	
Size Factor	4.05		
Paddle Wheel (two)	2.46	kWh/day	

3.1.5.3 Ports and Valves

In the Top View of Figure 3-10 one can see that the bed is made up of several raceways, each with an inlet and two outlet ports. At each of these ports are manual valves to isolate individual raceways or regulate the flow to or from each raceway. From our research it is possible for the daily water level drop due to evaporation to be as much as 6.2mm for a

⁴⁶ R. Vitale. Waterwheel Factory Inc. Telephone Interview. 08 October 2008.

1,000m² pond.⁴⁷ This would translate into makeup water requirements of 28.8m³/day in our raceway without including the slip stream flow rates that are part of the Chemostat II and Chemostat reactor bed forms. In this subassembly we only consider the costs of the flanges and valves. All piping runs are accounted for in the subassemblies they support.

3.1.5.4 *Capital Costs*

The materials selected and unit costs of the components are listed in Figure 3-15. The plant is anticipated to operate for 20 years. However, the transparent film is susceptible to UV damage which causes the film to haze and thereby become non-transparent. Thus the costs of that material shown below are only for the initial material. Replacements costs of the film are considered an operational expense. In our cost analysis (to be described) we will assume the polyethylene is good for 5 years. All other components of this subassembly are anticipated to last the entire plant life.

-

⁴⁷ http://www.bioking.lv/algae_cultivated_in_raceway_ponds.html. Date Accessed 08 October 2008.

Figure 3-15. Capital Costs of Reactor Bed Components

Reactor Bed	Material Chosen	Unit Pricing
System		+ 2
Transparent Film	Tufflite Brand Products , available up to 56' wide, Polyethylene, 4-6mil	\$ 0.54/m ²
	Source: Berry Plastics	
	(http://www.covalenceplastics.com/site/content/ag	ricultural/agricultu
	ral.asp#gh)	
Pond Lining	Either Butyl rubber, PVC, or LDPE (low density	\$0.47/m ²
	polyethylene), 30 – 40 mil	
	Source:	
Pond Edging	Hard Plastic	\$ 7/m
	Source: DTI Estimate	
Paddlewheel Mixer	14 blades (6' long x 6" wide), ¾ hp motor, capable	\$ 5000 ea.
with Motor	of 1ft/s flow	
	Source: Waterwheel Factory, Inc.	
Manual Gas Valve	IPEX VKD series PVC Ball Valve Part# VKDBV108,	\$ 67.23
	EPDM/Teflon Seals 2"	
	Source: http://www.valvestore.com	
Manual Water Valve	IPEX VKD series PVC Ball Valve Part# VKDBV108,	\$ 43.46
	EPDM/Teflon Seals 2"	
	Source: http://www.valvestore.com	
Water Port	ISO-QF flange, Schedule 80 Polyvinyl Chloride, Ref	\$8
	#PVC50-SF	
	Source: http://www.ancorp.com/line.aspx?id=819	
Gas Port	ISO-QF flange, Schedule 80 Polyvinyl Chloride, Ref	\$8
	#PVC50-SF	
	Source: http://www.ancorp.com/line.aspx?id=819	
Excavation/Installation	Based on 5 day excavation, 6 workers, medium	\$26,083/raceway
	sized equipment and no dirt removal.	
	Source: Dept of Labor, Davis Bacon Wage Determin	nations (CA Labor
	Rates) & The Blue Book of Building & Construction	

3.1.5.5 *Heat Exchangers*

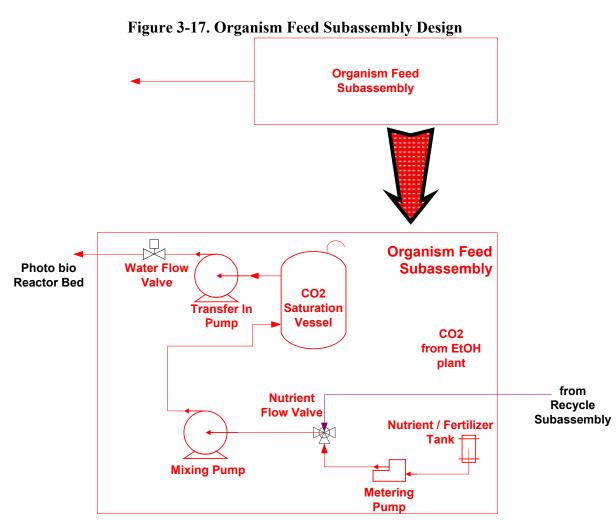
The covered reactor area in direct sunlight could increase bed temperatures significantly. Heat exchangers would require large electricity and/or water requirements. In order to keep costs low we are assuming that the earth will provide a sufficient heat sink for this system so no heat exchangers would be required.

3.2 Organism Feed Subassembly

The organism feed subassembly provides the necessary nutrients, medium and gases to grow and maintain a hydrogen producing algal or bacteria colony. The components of this subassembly are listed in Figure 3-16 and shown in Figure 3-17. The components of the subassembly can be further specified for a given organism and reactor bed form. A variation of this system will be required in the B-4 pathway, where algae growth beds and hydrogen production beds require different nutrients simultaneously.

Figure 3-16. Organism Feed Components

Organism Feed Subassembly	Organism Feed Subassembly
Components	Consumables
Nutrient/Fertilizer Tank	CO_2
Metering Pump	Nutrients/Fertilizer
Mixing Pump	Water (Initial Fill)
CO ₂ Cylinder	
CO ₂ Saturation Vessel	
Transfer In Pump	
Piping	



3.2.1 Flow Valves

The flow valves are shown in this flow diagram because they are located within the area of the organism feed subassembly. However because they will be monitored and operated remotely, their costs are accounted for in the control system subassembly. For further description of what types of valves are selected refer to that section of the document.

3.2.2 Vessels and Tanks

There are three vessels in this subassembly. The CO₂ Cylinder is a standard off the shelf item from one of the gas producer such as Air Products which supplies to industrial plants. The fertilizer is envisioned to be in aqueous form. The fertilizer will arrive at the facility pre-mixed for our application. The tank can be a stationary item on its own concrete pad that is refilled as necessary. The alternative would be a trailer provided by the fertilizer supplier which is dropped off when the trailer on site is dry.

3.2.3 Pumps

This subassembly has several pumps. After further research, centrifugal pumps were considered the most cost effective and appropriate pumps for our application. The pumps are sized based on the flow rates required to operate the reactor. Thus given a fixed hydrogen production rate of 1,000kgH₂/day, pump size will vary depending on the form of the reactor bed.

3.2.4 Capital Costs

The capital costs associated with this subassembly have been identified in Figure 3-18. A distinction is made between the consumables needed to establish the initial colony (which are included in capital costs of the Organism Feed Subassembly) and consumables needed for subsequent operation of the production plant (which will be included as feedstock costs under plant operation expenses). In a Chemostat II reactor bed, we postulate that CO₂ gas will be necessary during the initial growth stage of the algae and, thus, are included in the plant capital costs. The costs of CO₂ required during the reduced growth stage will be accounted for in plant operational expenses. The fertilizer will need to be continually fed to the colony during hydrogen production. Transporting liquids into and out of the reactor bed will require piping which is considered part of this subassembly. Pump sizes are a representative average in Figure 3-18. Actual sizes are in the Bill of Materials in section 4.

Figure 3-18. Capital Cost of Organism Feed Components

Material Chosen

Uni

Organism Feed	Material Chosen	Unit Pricing
Subassembly	Components	
Nutrient Metering	1468 gph	\$2,594
Pump	Source: Perry's Chemical Handbook, Plant Des	ign and
	Economics/Peters and Timmerhaus	
Transfer In Pump	316 SS centrifugal pump 7.5KW Motor,	\$10,252
	150 gpm capacity	
	Source: Perry's Chemical Handbook, Plant Des	ign and
	Economics/Peters and Timmerhaus	
Mixing Pump	316 SS centrifugal pump 7.5KW Motor,	\$10,252
	150 gpm capacity	
	Source: Perry's Chemical Handbook, Plant Des	ign and
	Economics/Peters and Timmerhaus	
CO₂ Cylinder	Aluminum 6061-T6 alloy, 1800 psi Service	\$ 360
	Pressure, 50 lb. Capacity Part #6125	e e e e e e e e e e e e e e e e e e e
	Source: http://kegman.net/carbon.htm#alum	
CO ₂ Saturation Vessel	S.S. field erected, 14,760 gal capacity	\$30,000
	Source:	
Nutrient Tank	10 gallon Cylindrical Process Tank, Part	\$ 30
	#0275-085	
	Source: http://www.watertanks.com/product	· · · · · · · · · · · · · · · · · · ·
Raceway Slurry	1" diameter, plastic	\$1.00/ft
Collection Piping	Source: PVC Plastic Corp (http://www.usplast	
Main Slurry Collection	2" diameter, plastic	\$2.12/ft
Piping (B1/B2)	Source: PVC Plastic Corp (http://www.usplast	ic.com/)
Main Slurry Collection	3" diameter, plastic	\$4.31/ft
Piping (B5)	Source: PVC Plastic Corp (http://www.usplast	ic.com/)
Main Slurry Collection	4" diameter, plastic	\$6.18/ft
Piping (B3)	Source: PVC Plastic Corp (http://www.usplast	ic.com/)
Recycle-Feed Transfer	3" diameter, plastic	\$4.31/ft
Piping (B1/B2)	Source: PVC Plastic Corp (http://www.usplast	ic.com/)
Recycle-Feed Transfer	4" diameter, plastic	\$6.18/ft
Piping (B5)	Source: PVC Plastic Corp (http://www.usplast	
Recycle-Feed Transfer	5.5	\$8.51/ft
Piping (B3)	" diameter, plastic	
	Source: PVC Plastic Corp (http://www.usplast	ic.com/)
	Consumables	
Nutrient, Initial Colony	3 lb/Acre/yr	~\$ 0.49/lb
Growth	Source: USDA	
CO ₂ Gas	50 lb cylinder refill at distributor facility	\$ 35
	Source: NFC Company, Chicago, IL (800) 734	1515
Water	Standard Process Water, not Salt Water	\$0.001665/gal
	Source: H2A Feedstock Costs, 2008	. 3

3.3 Recycle Subassembly

The purpose of the recycle subassembly is to separate waste organisms from water so that the water can be reused in the reactor bed. The components of this subassembly in general terms are listed in Figure 3-19 and shown in Figure 3-20.

Figure 3-19. Recycle Components

Recycle Subassembly Components
Transfer Out Pump
Algal Separation Unit
Piping

In this subassembly the organism solution is pumped to a device capable of separating the organism from the water. This is envisioned as a rotary drum filter. However, several other systems were considered. The organism-water separator will result in both organism and water outflows. The water outflow is recycled and combined with new water to make up for the amount that has evaporated, consumed in the production of hydrogen, or could not be separated from the organism. That water is sent back to the Organism Feed Subassembly to be combined with nutrients prior to being re-injected into the Photo-bio reactor bed. The subassembly components are all shown in Figure 3-20.

Figure 3-20. Recycle Subassembly Design Recycle Subassembly Wet Spent Algae Algae Feed < Subassembly Recycle Subassembly Photo bio **Reactor Bed Transfer Out Pump Algal Separation** to Algae Feed Subassembly **Wet Spent** Algae Makeup Water

3.3.1 Organism Separation Concepts

In order to maintain a constant volume of living organisms in the system, it will be necessary to remove both dead and excess living organisms stemming from the continual growth of the culture. It is also imperative to separate the organisms from the water to allow for maximum water recycling. Two different concepts for organism separation were examined: industrial centrifuges and rotary drum filters. In the end, rotary drum filters are the most economically and technically viable option, due to their lower capital cost and much higher rate of water return.

3.3.1.1 *Centrifuges*

In most of the research concerning photobiological production of hydrogen using algae or bacteria, a laboratory centrifuge is used to separate the organisms from the nutrient medium. Owing to this precedent, we initially investigated industrial sized centrifuges as a means of algae separation. Consultation with many centrifuge manufacturers including Alfa Laval, Westphalia, US Centrifuge, and Centrifuge Experts International indicated that while centrifuges are able to handle large flow rates, the extremely low concentration of organisms in the mixture would prove difficult to separate well. Capital costs for this system would also be fairly expensive since many machines running at flow rates far below their rated capacity would be necessary to effectively separate the organisms.

After consultation, the two kinds of industrial centrifuges considered were vertically spun and decanter centrifuges. Conversations with representatives from the aforementioned companies all suggested that vertically spun centrifuges would be more adept at algae/bacteria separation than decanter. The decanter centrifuges generally offered higher flow rates, but extremely poor separation performance. Dialogue with representatives from Centrifuge Experts International indicated that in order to get an appreciable percentage of water return from a vertically spun centrifuge, the machines would have to be run at 15% of rated capacity, necessitating multiple machines. One potential avenue for increasing the flow rate while maintaining a high water recovery percentage would be through the use of chemical flocculants. The drawback of this method is the contamination of the water, a solution to which is still being developed. At nearly \$400,000 each, with the necessity for a minimum of four machines, the capital costs for this system are fairly high, especially given the water recovery rate of only 90%. Westphalia centrifuges yielded similar results with slightly higher capital costs. Details about the various types of centrifuges can be seen in Figure 3-21.

Figure 3-21. Types of Centrifuges

Algae Separation							
Company	Type of Filtration	Flow Rate (GPH)	Motor Required	Туре	Cost	Quantity needed	Drawbacks
Centrifuge Experts International	Vertically Spun	24, 000	50 HP	Seital SE 10	\$400, 000	2-4	Unable to run at full flow rate
Westphalia	Vertically Spun	15, 600	75 KW	HSB 400	550, 000	2-4	Unable to run at full flow rate
US Centrifuge	Decanter	22, 500	150HP/ 25HP	Model CQ 7	\$400, 000	1	Not able to separate algae well
Alfa Laval	Decanter	30, 000	250HP/ 50HP	Aldec G2	\$750, 000-\$800, 000	1	Not able to separate algae well

3.3.1.2 Rotary Drum Filters

Considering the limitations of conventional centrifuge separation, research was done into the aquaculture industry, which deals heavily with algae and algae separation. Discussions with Advanced Aquaculture Systems Inc. and information from www.phyco.org indicated that rotary drum filters are far superior to centrifuges for organism separation. In rotary drum separation the input water from the pond is pumped into the filter. The organisms catch on the inside of a <10 micron screen in the rotating drum and the clean water passes through the screen as a backwash system rinses the solids of the screen into a sludge trough. A diagram of a drum filter can be seen in Figure 3-22. Expected water return from such a system is greater than 99%. The capital costs are also lower. Three Hydrotech drum filters will be needed to handle the flow rate of one B-1 module, but are only \$87,000 per drum, substantially lower than the centrifuges.

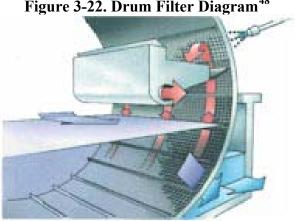


Figure 3-22. Drum Filter Diagram⁴⁸

3.3.2 Pumps

This subassembly has a single pump. A centrifugal pump was considered the most cost effective and appropriate for our application. The pump is sized based on the flow rates Thus given a fixed hydrogen production rate of required to operate the reactor. 1,000kgH₂/day, pump size will be different depending on the form of the reactor bed. The materials selected and unit costs of the components needed for this subassembly are listed in Figure 3–23

⁴⁸ Email from Dana Kent. (Advanced Aquaculture Inc.) 19 August 2008.

Figure 3-23. Capital Costs of Recycle Components

Recycle Subassembly	Material Chosen	Unit Pricing		
Rotary Drum filter	Hydrotech Drum Filter - 3750 gph	\$87,000 ea.		
	Source: Advanced Aquaculture Inc.			
Transfer Out Pump	316 SS centrifugal pump 7.5KW Motor, 150 gpm capacity	\$10,252		
	Source: Perry's Chemical Handbook, Plant Design and Economics/Peters			
	and Timmerhaus			
Main Slurry Feed Piping	2" diameter, plastic	\$2.12/ft		
(B1/B2)	Source: PVC Plastic Corp (http://www.usplastic.com/)			
Main Slurry Feed Piping	3" diameter, plastic	\$4.31/ft		
(B5)	Source: PVC Plastic Corp (http://www.usplastic.com/)			
Main Slurry Feed Piping	4" diameter, plastic	\$6.18/ft		
(B3)	Source: PVC Plastic Corp (http://www.usplastic.com/)			
Raceway Slurry Feed	1" diameter, plastic	\$1.00/ft		
Piping	Source: PVC Plastic Corp (http://www.usplastic.com/)			

3.4 Gas Capture Subassembly

The function of gas capture subassembly is to compress and separate our product hydrogen and deliver it to the production facility limits. The components of this subassembly in general terms are listed in Figure 3-24.

Figure 3-24. Gas Capture Components

Gas Capture Subassembly Components
Compressor
Gas Separation
Piping

The outlet pressure of hydrogen at the plant gate is 300psi. This pressure was selected to provide a system comparable to other DOE H2A Production Plants. Those cases have been normalized to an outlet pressure of 300psi. The hydrogen is at atmospheric pressure when released by the organisms. The Hydrogen Flow Meter is located at this subassembly but it is accounted for in the control system subassembly. Between these two points in the subassembly there is minimally a compressor and a gas separation unit. The compressor will need to bring the gas mixture to the pressures required for separation and transport to the plant gate. Pressure losses are possible in the gas separation unit and the pipeline runs so compression may be higher than 300psi. The subassembly components are all shown in Figure 3-25.

Figure 3-25. Gas Capture Subassembly Design Hydrogen **Pipeline Gas Capture Subassembly** Gas Capture Subassembly Hydrogen **Pipeline** from Hydrogen Gas Photo bio Compressor Separation **Flow Meter Reactor Bed**

3.4.1 H₂-O₂ Gas Mixture Safety

Since the organisms create hydrogen via water splitting, oxygen is necessarily created as a byproduct of hydrogen production. For the systems that must maintain anaerobic conditions for hydrogen production (B3, B4, and B5), a separate reaction (i.e. respiration) occurs to virtually instantaneously consume the oxygen, so that O_2 levels are maintained at very low levels. However, the B1 and B2 pathways use oxygen tolerant organisms that can carry out water splitting without a separate respiration reaction to absorb the O_2 , and thus they generate substantial O_2 , at a stoichiometric ratio with the produced hydrogen. This 2:1 molar ratio of hydrogen to oxygen is a flammability concern and therefore precautions must be taken to eliminate any potential ignition source. H_2 safety precautions are important to all the systems, however, the issue particularly affects the B-1 and B-2 pathways where a stoichiometric H_2/O_2 mixture is stored, i.e., in raceways, headspaces, and gas processing systems. For this analysis, the requisite safety sensors and controls are used to assure safe plant operation with this gas mixture. These kinds of safety measures are also routinely dealt with in other industrial systems using H_2 .

3.4.2 Compressors

Conversations with Norwalk Compressors of Norwalk CT suggest that an oil-free, balanced-opposed, 3-stage piston compressor can be used to safely compress the hydrogen or hydrogen/oxygen gas stream prior (or after) gas separation. Particular care must be taken when compressing flammable gas mixtures to avoid sparking or exceeding temperature

limits. However, compression of flammable mixtures is a routine industrial process conducted safely every day.

Pursuant to the modular concept, the compression system is scaled for the gas flows of a 1,000kgH₂/day module. The compression module is sized for the average hydrogen production for the longest day of the year: the summer solstice (June 21st). At all other times, the compressor is operated at reduced capacity. Power for the compressor is based on mass flow rate and compression ratio⁴⁹ which are both modest by industrial standards. Consequently, compressor power is moderate: approximately 78-123 kW depending on system. However, due to the low hydrogen pressure generated above the raceways (1atm), compressor piston diameter for the first stage will be quite large. For this reason, diaphragm compressors, which would normally be attractive for their longer life and non-leak attributes, are not viewed as viable candidates.

Since the biohydrogen compressors are similar in type (piston compressors) and compression ratio (~20) to the compressors used in the DOE's H2A forecourt analyses⁵⁰, we have adopted the H2A compressor cost algorithm of \$4,580/ (kgH₂/h). However, since this algorithm is based on hydrogen compression and the biohydrogen systems produce a mixture of gases, we convert the costing algorithm to a molar basis: \$9,233/ (kgmol/h).

3.4.3 Gas Separation Concepts

There are several commercial means available for separating hydrogen gas from a gas mixture. In this analysis we have focused our attention on pressure swing adsorption (PSA), temperature swing adsorption (TSA), membranes, electrochemical pumps and combinations of these methods.

3.4.3.1 Pressure Swing Adsorption

A pressure swing adsorption (PSA) system is preliminarily selected as the H₂ separation system. PSA technology takes advantage of a materials affinity to preferentially adsorb a particular gas species at high gas pressure. PSA systems are commonly used in the petroleum industry to purify a variety of gases. Separation of hydrogen gas from steam methane reforming (SMR) product gases (H₂, CO, CO₂, H₂O, CH₄) is common. We propose to use PSA to separate hydrogen from a H₂, O₂, H₂O mixture, a much less frequently encountered application. Dialogue with Adsorption Research, Inc. indicated that it was feasible to use PSA to separate such a mixture.⁵¹

PSA operate by flowing a pressurized stream of gases across a multi-component adsorbent bed (commonly layers of activated carbon, zeolite, silica gel, etc.) to preferentially capture an undesired gaseous species on the surface of the adsorbent. By careful selection of adsorbent materials, all undesirable species may be captured in the bed so that only high purity gas (often greater than 5 nines purity) exits the bed. PSA systems are inherently cyclic with a series of bed (typically 4, 6, 8 or 12) operating out of phase. After a bed is

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⁴⁹ Compression ratio is 300psi/14.7psi = 20.4.

⁵⁰ The standard DOE H2A forecourt analysis assumes a 4-stage, piston compressor, 300psi inlet, 6250psi outlet, and approximate 1500kgH2/day flow rate.

⁵¹ Knaebel, Kent. Phone conversation. 20 Oct 2008

"full" (i.e. the adsorbent material no longer has open sites on which to further adsorb contaminant gases), the bed goes into a "vent' cycle where pressure is decreased (typically to 1atm but sometimes < 1atm) to desorb the contaminants. This vent gas stream is typically vented to the atmosphere or fed to a burner if it contains fuel value. After venting, the bed is purged with pure gas stream reserve flowed i.e. fed from the exit of the bed to drive any residual containment gas back towards the inlet. After purging, the bed enters an "equalization" cycle where gas pressure is raised to full operating pressure in preparation for the resumption of contaminant gas flow.

Hydrogen recovery is a key metric of PSA performance. Hydrogen recovery is defined as the fraction of inlet gas hydrogen that is captured in the pure gas stream. There are two main sources of hydrogen loss. The first is hydrogen that is contained in the bed at the beginning of the vent cycle. As the bed is depressurized, this hydrogen is expelled and lost to recovery. The second source of loss is during the purge cycle when pure hydrogen is used to actively vent the system of impurities. By summing these two losses, an accurate measure of hydrogen recovery can be attained.

To determine H_2 recovery for an H_2/O_2 mixed gas system, we have ascertained the packing density and adsorption performance of carbon (for O_2 adsorption) and silica gel (for water adsorption). These parameters are listed in Figure 47. By carefully modeling the desired flow rates and calculating the hydrogen contained in the bed during the various cycles, the hydrogen recovery is calculated.

Key parameters of the PSA system are shown in Figure 3-26. Parameters are listed for the adsorption of water, methane, carbon dioxide, carbon monoxide, nitrogen, and oxygen. Although oxygen is the primary species for adsorption, the other gases are included both because they were used in validation of the modeling approach and may be present in low quantities due to the decomposition of algae. For each adsorbent there are two values of interest; the amount of gas that adheres to the adsorbent at high pressure, and the amount of gas that adheres to the absorbent at low pressure. It is the difference in adsorption levels between the two pressures that is of interest. Although not necessarily linear, we have assumed that the adsorption data varies linearly between the two data points listed.

Capital costs for the individual PSA systems are estimated based on both the performance model described above and on a scaling factor approach. The performance model is used to calculate the approximate bed size of the PSA vessels for the particular flow rates and gas compositions of each system. Once this PSA bed size is determined, a scaling factor approach is used to ratio the cost relative to a H2A model PSA system. A 0.5 scaling factor is assumed resulting in the following equation:

$$NewCost = BaseCost * \sqrt{\frac{NewBedSize}{BaseBedSize}}$$

The base PSA system cost assumed is based on an H2A 1500kgH₂/day SMR PSA having 6,065L of total absorbent and a \$100,000 total price.

Figure 3-26. Possible PSA Parameters

	Figure 3-26. Possible PSA Parameters					
Silica Gel (for Water Absorption)						
Bed Void Fraction	%	36%				
Bed Usage Fraction (1/LUB)	%	50%				
Adsorp. Fraction at Specified Pressure	g H20/ g adsorbent	30%				
Specified Pressure for Adsorbent Data	psi	250				
Adsorp. Fraction at Specified Purge Pressure	g H20/ g adsorbent	0.2				
Specified Purge Pressure	psi	14.7				
Estimated adsorbent O2 Update Fraction	g H2O/ g adsorbent	0.12039949				
Bulk Density	g/L	500				
	9 . –					
Carbon (for Methane)						
Bed Void Fraction	%	0.36				
Bed Usage Fraction (1/LUB)	%	0.8				
Update Fraction at Specified Pressure	g CH4/ g adsorbent	0.0448				
Specified Pressure for Adsorbent Data	psi	250				
Adsorp. Fraction at Specified Purge Pressure	g CH4/ g adsorbent	0.016				
Specified Purge Pressure	psi	14.7				
Estimated adsorbent O2 Update Fraction	g CH4/ g adsorbent	0.034675053				
Bulk Density	g/L	515				
0.1(5000)						
Carbon (for CO2)						
Bed Void Fraction	%	0.36				
Bed Usage Fraction (1/LUB)	%	0.714285714				
Update Fraction at Specified Pressure	g CO2/ g adsorbent	0.1694				
Specified Pressure for Adsorbent Data	psi	250				
Adsorp. Fraction at Specified Purge Pressure	g CO2/ g adsorbent	0.044				
Specified Purge Pressure	psi	14.7				
Estimated adsorbent O2 Update Fraction	g CO2/ g adsorbent	0.15098096				
Bulk Density	g/L	515				
Zeolite (for CO)						
Bed Void Fraction	%	0.36				
Bed Usage Fraction (1/LUB)	%	0.714285714				
Update Fraction at Specified Pressure	g CO/ g adsorbent	0.042				
Specified Pressure for Adsorbent Data	psi	250				
Adsorp. Fraction at Specified Purge Pressure	g CO/ g adsorbent	0.0364				
Specified Purge Pressure	psi	14.7				
Estimated adsorbent O2 Update Fraction	g CO/ g adsorbent	0.006742371				
Bulk Density	g/L	515				
	9. –					
Zeolite (for N2)						
Bed Void Fraction	%	0.36				
	%	0.3				
Bed Usage Fraction (1/LUB)	% g N2/ g adsorbent	0.3 0.04725				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure	g N2/ g adsorbent	0.04725				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data	g N2/ g adsorbent psi	0.04725 250				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent	0.04725 250 0.0406				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi	0.04725 250 0.0406 14.7				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent	0.04725 250 0.0406 14.7 0.008006566				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi	0.04725 250 0.0406 14.7				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent	0.04725 250 0.0406 14.7 0.008006566				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2)	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L	0.04725 250 0.0406 14.7 0.008006566 515				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L	0.04725 250 0.0406 14.7 0.008006566 515				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB)	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L %	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L % % g O2/ g adsorbent	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L % % g O2/ g adsorbent psi	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032 250				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L % % g O2/ g adsorbent psi g O2/ g adsorbent	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032 250 0				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L % % g O2/ g adsorbent psi g O2/ g adsorbent psi	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032 250 0				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent gsi g N2/ g adsorbent g/L	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032 250 0 0.001				
Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure Specified Purge Pressure Estimated adsorbent O2 Update Fraction Bulk Density Zeolite (for O2) Bed Void Fraction Bed Usage Fraction (1/LUB) Update Fraction at Specified Pressure Specified Pressure for Adsorbent Data Adsorp. Fraction at Specified Purge Pressure Specified Purge Pressure	g N2/ g adsorbent psi g N2/ g adsorbent psi g N2/ g adsorbent g/L % % g O2/ g adsorbent psi g O2/ g adsorbent psi	0.04725 250 0.0406 14.7 0.008006566 515 0.36 0.769230769 0.032 250 0				

Where

Bed Void Fraction = interstitial void fraction between adsorbent particles

Bed Usage Fraction = 1/(Length of Unused Bed) = Fraction of bed used for adsorbent calcs where the remained is buffer against contaminant breakthrough.

3.4.3.2 Temperature Swing Adsorption

Temperature swing adsorption (TSA) systems are analogous to PSA systems except they use differences in temperature rather than pressure to preferentially adsorb and desorb contaminant species. While used industrially, TSA systems are not as prevalent in process plants as PSA systems. The main advantage of a TSA system is that it would not require compression of the H_2 -rich gas thereby avoiding the safety concerns of compressing H_2/O_2

gas mixtures and potentially lowering electrical requirements. However, separation of H₂ and O₂ via TSA requires a significant temperature swing with a refrigeration system required to achieve the lower temperature bound. Was "waste" cooling or heating available from an adjacent process, TSA would be an attractive option. However, as currently configured such "waste" thermal energy is not readily available and thus the refrigeration system would be a substantial energy and cost element. Additionally, conversations with Kent Knaebel from Adsorption Research Incorporated, a gas separation consulting company, indicated that PSA was a far superior option, given its vastly reduced cycle time. The cycle for a TSA system would be measured in hours, as opposed to minutes for PSA, necessitating a much larger bed size in order to separate the same amount of gas. This increased capital cost of the beds and cooling system makes TSA less economically practical than PSA. Consequently, we have not pursued further TSA system analysis for any of the bio-hydrogen systems.

3.4.3.3 *Membrane Separation*

Membrane separation units are of two main types: metallic membranes and nano-porous membranes. Metallic membranes typically use palladium (Pd), Pd-alloys, or layered Pd/alloy to allow the diffusion of H+ ions through the membrane. Pd membranes are characterized by very high hydrogen selectivity (typically <10,000), high cost (due to the inherent Pd material cost), and moderate hydrogen permeability that is primarily a function of temperature and membrane thickness. Hydrogen flux through the membrane follows Boyds Law and is proportional to the difference of the square root of the reformate (upstream) hydrogen partial pressure and the square root of the permeate (downstream) hydrogen partial pressure. Consequently, Pd-membrane systems work best with highly pressurized inlet streams and low pressure H₂ product streams. While a few small scale Pd-membrane commercial products are on the market (e.g. IdaTech), large scale Pd-membrane hydrogen purification systems are not employed industrially due to performance and cost concerns. Based on membrane system modeling for a bio-hydrogen system with 60% H₂ at 20atm (300psi) and a latm permeate (pure H₂) outlet pressure, hydrogen recoveries in excess of 90% are theoretically possible.

Drawbacks of Pd-membrane separation systems include:

- the necessity to heat the membrane (and hydrogen) to 250-350°C to ensure adequate hydrogen permeability
- the requirement to compress the H₂-rich feedstream to high pressure thereby raising safety concerns related to H₂/O₂ compression
- the low pressure of the pure H₂ product stream thereby requiring additional H₂ compression to achieve a pipeline transport pressure
- uncertainty of using Pd membrane with H₂/O₂ gas mixtures (the Pd may oxidize or be an H₂/O₂ combustion catalyst)
- the general immaturity of the technology.

For these reasons, Pd-membranes are not selected for further analysis.

The other broad class of membrane separation systems is based on nano-porous materials. Nano-porous materials function as molecular sieves and use pore size to preferentially pass

molecular hydrogen. As reproduced in Figure 3-27, Phair and Badwal⁵² have surveyed the range of nano-porous membrane options. Of these, we judge polymeric membrane to be most applicable to bio-hydrogen gas separation due to their low temperature of operation. However, polymer membranes are not highly selective and thus would require additional downstream purification. Additionally, hydrogen flow is driven by differences in hydrogen partial pressure across the membrane. Consequently, compression of the unseparated gas is required once again raising safety concern for H₂/O₂ gas mixtures. A detailed analysis beyond the scope of this project is required to optimize pressure level, permeate purity, and recover H₂. For these reasons, polymer membranes don't appear to offer substantially superior benefits over PSA systems. Consequently, polymer membranes are not selected for further analysis.

Figure 3-27. Nano-porous Membranes

	Polymeric	Carbon	Glass	Aluminosilicate	Oxides	Metal
Pore size ^a	Meso-macro	Micro-meso	Meso-macro	Micro-meso	Micro-meso	Meso-macro
Surface area/porosity	Low>0.6	High 0.3-0.6	Low 0.3-0.6	High 0.3-0.7	Medium 0.3-0.6	Low 0.1-0.7
Permeability	Low-medium	Low-medium	High	Low	Low-medium	High
Strength	Medium	Low	Strong	Weak	Weak-medium	Strong
Thermal stability	Low	High	Good	Medium-high	Medium-high	High
Chemical stability	Low-medium	High	High	High	Very high	High
Costs	Low	High	High	Low-medium	Medium	Medium
Life	Short	Long	Long	Medium-long	Long	Long

^aMicoporous = pore radius <1 nm, mesoporous = 1 nm <pore radius <25 nm, macroporous = pore radius >25 nm.

3.4.3.4 *Electrochemical Pumps*

Electrochemical purification of hydrogen is possible using an applied voltage to drive hydrogen across a separation membrane. Such systems have been demonstrated at small scale but are not currently in industrial use. In addition to the gas separation function, electrochemical pumps can be used to pressure the hydrogen stream thereby eliminating or reducing the need for mechanical H_2 gas compression. In theory, a mixed gas stream could enter the electrochemical pump at 1atm and a high H_2 purity gas stream could exit at pressure (10-100atm).

Conversations with Glen Eiseman of Hydrogen Pump LLC preliminarily explored the use of electrochemical pumps for biohydrogen purification. Current products from Hydrogen Pumps use a PBI membrane, operate at ~160°C, employ a Pt catalyst, compress the H₂ stream to several atmospheres, and contain a supplementary gas cleanup system since only 98% pure H₂ is passed across the membrane. Since exposure of a H₂/O₂ gas mixture to Pt would result in catalyst combustion of the gases, such a combination is unacceptable. Development of alternate non-Pt catalyst is theoretically possible, but the authors know of no such development efforts.

Phair, S.P.S. Badwal, (CSIRO Manufacturing and Infrastructure Technology, Victoria, Australia) Science and Technology of Advanced Materials 7 (2006) 792–805.

^{52.} Materials for separation membranes in hydrogen and oxygen production and future power generation", J.W.

Electrochemical pumps could be used for separation of non-O₂ containing gas mixtures. However, the systems would incur the following disadvantages:

- the necessity to heat the membrane (and hydrogen) to 160°C
- the need for a secondary gas cleanup system (such as PSA) to further purify the H₂ product gas to five 9's purity
- the electrical consumption to power the device

For these reasons, electrochemical pumps are not selected for further analysis.

3.4.4 Capital Costs

The components of the subassembly can be further specified for a given organism and reactor bed form. However we have included in Figure 3-28 materials selected and unit costs of components.

Figure 3-28. Capital Cost of Gas Capture Components

Gas Capture Subassembly	Material Chosen	Unit Pricing	
Compressor	142kgH ₂ /hr size for 1000kgH ₂ /day plant	\$9233/kgmol/hr	
	Source: Using H2A Cost guidelines		
Gas Separation	Pressure Swing Adsorption	\$30,542 - \$119,408	
	Source: Using H2A Cost guidelines and scaling f	actors	
Gas Capture Collection	5.5" diameter, plastic, 100ft/s velocity,	\$8.51/ft	
Piping	Source: PVC Plastic Corp (http://www.usplastic.com/)		
Gas Capture Collection	4.5" diameter, plastic, 100ft/s velocity,	\$6.18/ft	
Piping	Source: PVC Plastic Corp (http://www.usplastic	<u>.com/</u>)	
Main Collection Piping	4" diameter, plastic, 100ft/s velocity,	\$6.18/ft	
	Source: PVC Plastic Corp (http://www.usplastic	.com/)	
Main Collection Piping	3" diameter, plastic, 100ft/s velocity,	\$4.31/ft	
	Source: PVC Plastic Corp (http://www.usplastic	.com/)	
Raceway Collection	1.5" diameter, plastic, 100ft/s velocity,	\$1.57/ft	
Piping	Source: PVC Plastic Corp (http://www.usplastic	.com/)	
Raceway Collection	1" diameter, plastic, 100ft/s velocity,	\$1.00/ft	
Piping	Source: PVC Plastic Corp (http://www.usplastic	.com/)	

3.4.5 Piping

Transporting gases out of the reactor bed and the product hydrogen to the facility limits will require several hundred feet of piping which are included as part of the subassemblies cost. For the B-3 and B-4 systems, the piping lengths needed must be doubled to account for the piping needed to bring CO₂ to the CO₂ saturation vessel. There is no drum filter for these systems.

3.4.6 Additional Gas Capture Subassembly Components

It is possible for the product gas to have water saturation. In this case, a dryer may be needed to remove water from the gas mixture. A slight vacuum might be required to draw the gas mixture out of the pond network and into the gas capture subassembly. These components are not part of the system yet but as we finalize our analysis we'll be able to determine if these components are necessary.

3.5 Control System Subassembly

Plant control systems serve many functions including local and remote monitoring, alarming and controlling of plant equipment and functions. The more functions the system performs, the more costly and complex the system becomes. A very simple system may provide only local indication or monitoring of equipment operation. A complex system would include all three functions for each piece of equipment from a remote facility and some logic for how to operate each piece under a given set of conditions. Automating plant operations can increase the cost of the control system. These costs need to be evaluated against the operational labor savings.

3.5.1 Components

For this subassembly the design approach was to create a very basic system which is practical enough to provide some savings in operational labor. Because of the reactor bed's large area requirements remote capabilities are essential. This will require electrical conduit and wiring to be laid out between the plant components and the primary control area. Monitoring of only the most primary indicators will be included. Alarming capabilities of only the most hazardous conditions will be required. Control will only be available for flow valves. No automation is assumed thus a PLC will not be included. For the basic control system described the components and instrumentation for each function are listed in Figure 3-29.

Figure 3-29. Control System Components

Control System Subassembly						
Components						
Control Room						
Control Room Wiring Panel						
Raceway Wiring Panel	Raceway Wiring Panel					
Computer, Monitor, Labview software						
Electrical Conduit (power and	instrumentation)					
Instrumentation Wiring	Instrumentation Wiring					
Instrumentation						
Monitor	Alarm	Control				
Level Indicators	Pressure Sensors	Nutrient Flow Valve				
Hydrogen Aı	rea Sensors	Water Flow Valve				
Air Temperature Indicator	Oxygen Area Sensors					
Water Temperature Indicator						
Hydrogen Flow Meter						
pH level indicator						
Consumables						
Electricity						

While the control system is relatively simple, the subassembly is complicated by the sheer size of the reactor beds and the modular nature of the raceways. Each raceway must be individually monitored and controlled, leading to a large number of replicated sensors. Additionally, the instruments are dispersed over this area, ~20-66 acres in size, leading to very long runs of wiring and conduit. Signal boosting may be required. To simplify the system all instrumentation will operate on electricity rather than instrument air, so that an air compressor is not required. There is no power transformer considered here, rather electricity will be treated as a plant operating expense and bought off the grid at the typical \$/kWh for the region.

3.5.2 Wiring and Conduit

Because of the large size of our plant there is significant amount of wiring involved with conveying power to each raceway for the paddlewheels and instrumentation as well as bringing back signal wiring for instrumentation. Figure 3-30 shows a possible layout of the production facility where growth and production are carried out in a single bed. Some key dimensions are identified so that approximate lengths of wiring and conduit can be computed. The number of wires required to each raceway panel is shown in the Raceway Wiring Panel. All panels are assumed to be at the near end of each raceway and subassembly center for conceptual design calculations. The hydrogen flow meter has a single signal and power wire. The flow valves have 1 power wire but need 2 signal wires; 1 for actuating valve and 1 for status of valve. The remaining equipment at each subassembly has power wires but no signal wires. Since this is a simple control system other equipment (pumps, compressor, and algal separation unit) will only have local control and monitoring. All monitoring and sensor instrumentation has a single power and a single signal wire with the exception of the hydrogen area sensor. It requires two signal wires for monitoring

hydrogen and alarming at certain conditions. Water flow control into and out of each individual raceway will be done with manual valves so they do not factor into the control system. The additional power wires are for the paddlewheel motors. There is no signal indicating the operation of these motors to the control room. Based on the other signals the operator should be able to infer the operating status of the paddlewheels.

RACEWAY R A C E W A Y RACEWAY RACEWAY RACEWAY R A C E W A Y RACEWAY RACEWAY R A C E W A Y RACEWAY 10 9 5 4 3 2 X2 =100' Gas Capture Subassembly Algae Feed Subassembly Recycle Subassembly Water Flow Valve Wiring Panel Hydrogen Flow Meter Nutrient Flow Valve R A C E W A Y RACEWAY RACEWAY RACEWAY R A C E W A Y R A C E W A Y RACEWAY RACEWAY RACEWAY 17 20 18 15 14 13 12 11 10 X1 = 60'

Figure 3-30. Control System Subassembly Design

For the B-1 and B-2 systems, a plant layout like this yields the lengths of conduit and wiring shown in Figure 3-31. Signal and power wiring will be run in separate conduits. This is done to ensure that there is no interference in the signal data from voltage associated with the power wiring. In the diagram above one can see there are two main horizontal conduits runs (above and below the subassemblies). That route will be used for both power and signal wiring. Each individual raceway will have its own conduit run along the length of the raceway for the raceway wiring panel located at the near end of the raceway. Each subassembly will have its own conduit run off the main horizontal conduit lines for its wiring.

Figure 3-31. Control System Wiring and Conduit Quantities for B-1, B-2

Components	Signal Wiring Qty (ft)	Power Wiring Qty (ft)	Conduit Qty (ft)
Raceways	67,200	84,000	4,560
Organism Feed	900	450	100
Subassembly			
Recycle	540	270	100
Subassembly			
Gas Capture	630	630	100
Subassembly			
Totals	69,270	85,350	4,860

The raceways category in Figure 3-31 above is a summation of all the wiring required for each of the 20 raceway wiring panels needed in the B-1 and B-2 systems. The flow valve and flow meter wiring requirements are included in the appropriate subassembly line. The additional power wiring in those subassembly lines are for the other equipment (pumps, compressors, etc) that require power but are not monitored and operated remotely. The control system wiring could have been done overhead with cable trays, however, since some level of excavation will already take place to create raceways, this analysis assumes underground lines. The installation costs of buried conduit in this case will be lower because it is included in the excavation of the raceways.

3.5.3 Capital Costs

The analysis above provides a fairly extensive bill of materials for a typical control system. All of the instrumentation, wiring and conduit is assumed to be commercially on the shelf and readily available. The costs of those components are summarized in Figure 3-32.

Figure 3-32. Capital Costs of Control System Components

Control System Subassembly	Material Chosen	Unit Pricing
Control Room	8' x 20' trailer	\$50/ft²
	Source:	
	http://www.buyerzone.com/industrial/modular	buildings/prefab_guide.html
Control Room	Customized to wire count	\$3000
Wiring Panel		
	Source: Consultation with Innomation Systems In	c.
Raceway	Termination panel. Features transmit and,	\$146
Wiring Panel	adjustable input/output levels. Available as PC	
	board only or in a case. +6 to 15 mA Tx.	
	Source: Information from Tessco Technologies In	C.
Computer &	Standard Desktop, Vostro 420 or similar	\$1500
Monitor	Source: Dell	
Labview	Labview 8.6 Professional Edition	\$4299
Software	Source: National Instruments	

Control System Subassembly	Material Chosen	Unit Pricing
Level Indicators	Flanged, Float level, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Omega Engineering Inc.	\$714
Pressure Sensors	Solid State Pressure Transducer and meter, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Omega Engineering Inc.	\$345
Hydrogen Area Sensors	Thermal Conductivity Gas Analyzer, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Lesman Instrument Company	\$7,600
Air Temperature Indicator	Thermistor, 316 SST components, 4 to 20 ma output, standard process connection Source: Omega Engineering Inc.	\$38
Air Temperature Meter	Panel Meter, single width, up to 24 inputs Source: Omega Engineering Inc.	\$599
Water Temperature Indicator	Comes with pH sensor Source: Information from Emerson Process Management	\$0
pH level Indicator	CPVC components, displays, 4 to 20 ma output, standard process connection Source: Omega Engineering Inc.	\$435
Oxygen Area Sensors	Comes with Hydrogen Sensor Source: Omega Engineering Inc.	\$0
Nutrient Flow Valve	6" vortex type, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Information from Emerson Process Management	\$5,500
Water Flow Valve	6" vortex type, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Information from Emerson Process Management	\$5,500
Hydrogen Flow Meter	6" vortex type, 316 SST components, displays, 4 to 20 ma output, standard process connection Source: Information from Emerson Process Management	\$5,500
Instrument Wiring	22 GA Copper wire UL1007/UL1569 Source: Waytek Inc. at www.waytekwire.com @ 500' qty	\$0.02/ft
Power Wiring	22 GA Copper wire UL1007/UL1569 Source: Waytek Inc. at www.waytekwire.com @ 500' qty	\$0.02/ft
Conduit	½", 100' pack, Highly flexible black PVC tubing, resistant to oil, water, and corrosion Source: Waytek Inc. at www.waytekwire.com @ 550' qty	\$0.58/ft

4. Bill of Materials for Pathways

While most of the photobiological work has been done in a laboratory scaled environment under conditions uneconomical for large-scale production, the food industry has some experience at growing these organisms at larger scales. Looking at both sources, we have determined that the most practical means of hydrogen production with a photobiological system for each of the 5 photobiological pathways.

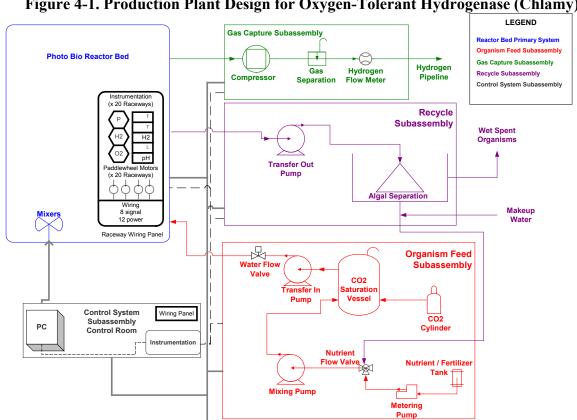
4.1 *B-1 Pathway Production Plant*

The B-1 Pathway is a Chemostat II photobiological reactor system using a mutant-antenna *Chlamydomonas reinhardtii* oxygen-tolerant variant as the H₂ production microorganism. As a Chemostat II, the initial algal colony is grown at the normal cell growth rate until final colony concentration is reached, and then the process is switched over to steady-state mode where simultaneous growth and hydrogen production occur in the reactor beds. This is achieved by manipulating the nutrients and carbon dioxide provided. H₂ production is projected at 9.2% solar-to-hydrogen efficiency and corresponds to a future optimized organism. Sufficient cellular activity to keep the micro-organism during H₂ production healthy is assumed to occur with new cell growth taking place at a reduced rate compared to wild-type organisms (20% per day vs. ~80% per day).

Twenty racetrack raceways of approximately 40ft width by 1090ft length are used to produce an average of 1,000kgH₂/day throughout the year. The raceways have a liquid depth of 10cm to correspond to full photon capture at a cell concentration of 0.2g/L. Paddlewheels circulate the water/*Chlamydomonas reinhardtii* slurry. A slip stream of water/micro-organisms slurry is drawn off continuously to maintain the 0.2g/L micro-organism concentration. Micro-organisms are removed from the recycle stream by a rotary drum filter. The slip stream volume removed is carefully matched to the growth rate to maintain a constant organism mass within the system (assuming a constant concentration of algae within the bed). The removed micro-organisms are taken to a land-fill, used in a subsequent fermentor, or otherwise disposed. Nutrients in the form of commercial grade fertilizer are mixed with the returning water to provide required nourishment to the micro-organisms. CO₂ is bubbled into a reservoir tank of the returning water to dissolve CO₂ into the water for use by the micro-organisms. Only a very low amount of CO₂ is needed to maintain cell health; thus CO₂ does not appreciably accumulate in the headspace of the reactor beds.

The *Chlamydomonas reinhardtii* micro-organism produces a net product gas of 33.33% O₂ and 66.66% H₂ (plus water vapor). A piston compressor is used to compress the gas mixture to 300psi prior to separation. A pressure swing adsorption (PSA) system is used to purify the hydrogen gas stream.

Further details of the B-1 pathway are specified in Figure 2-1. The subassemblies of this pathway are shown in Figure 4-1. The complete bill of materials and capital costs of this production plant are shown in Figure 4-2. The total system cost is \$2,164,488.



Power

Figure 4-1. Production Plant Design for Oxygen-Tolerant Hydrogenase (Chlamy)

Figure 4-2. Bill of Materials for B-1 Pathway

Description	Size Req'd Units	Unit Size	Units		Unit cost	Qty Req'd	Total Cos		Material / Part Description
Photo Bio Reactor Bed Subassembly									
Transparent Film	87,080 m2	1	m2	\$	0.54	87,080			olyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	93,998 m2	1	m2	\$	0.47	93,998			utyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	13,982 m	1	m	\$	7.00	13,982			Init Cost is engineering estimate at \$7/m
Installation of Ponds		1	raceway	\$	26,083.00	20	\$ 521,6	60 B	ased on California labor rates.
Paddlewheel Mixers		1	each	\$	5,000.00	40	\$ 200,0	00 E	st. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in	1	each	\$	43.46	20	\$ 8	69 P	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in	1	each	\$	43.46	20	\$ 8	69 PI	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Gas Valve	1.0 in	1	each	\$	67.23	20	\$ 1.3	45 Pi	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Flanges	0.5 in	1	each	\$	8.00	60			rice from http://www.ancorp.com/line.aspx?id=819
Gas Capture Subassembly									
Compressor	66 kgmol/hi	- 66	kgmol/hr	¢	9.233.00	1	\$ 606.3	07 11	Ising H2A Unit cost
PSA	oo ngmoym	00	кылол/п	\$	119,407.39	1			Ising H2A scaling
Raceway Collection Pipe	40 ft	1	ft	\$	1.57	40			ized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Main Collection Pipe	1080 ft	1	ft	\$	6.18	1080			ized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Gas Capture Pipe	50 ft	1	ft	\$	6.18	50			ized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Organism Feed Subassembly	150 gp	150	anm	Ś	10.252	2	ć 20.F	02 -	st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Transfer In Pump	150 gpm		gpm	\$		1			
Nutrient Metering Pumps	1468 gph	1	each		2,594				st. Based on Perry's Chemical Handbook, Plant Design and Economics. Pumps nutrients into return flow
Mixing Pump	150 gpm	150	gpm	\$	10,252	2			st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
CO2 Cylinder	50 lb	50	lb	\$	360	1			luminum 6061-T6 alloy, 1800 psi Service Pressure, 50 lb. Capacity Part #6125 (http://kegman.net/carbon.htm)
CO2 Saturation Vessel	15000 gal	15000	gal	\$	30,000	1		00 Fi	ield erected Stainless Steel tank from Perry's chemical Handbook, Plant Design and Economics
Nutrient Tank	8 gal	10	gal	\$	30.00	1	\$	30 1	0 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe	40 ft	1	ft	\$	1.00	40	\$	40 P	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	1080 ft	1	ft	\$	2.12	1080	\$ 2,2	90 P	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft	1	ft	\$	4.31	180	\$ 7	76 P	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle Subassembly									
Rotary Drum filter	9639 gph	3750	anh	\$	87,000.00	3	¢ 261.0	00 10	nformation from Dana Kent at Advanced Aquaculture Inc. on Hydrotech Drum Filter
Transfer Out Pump	150 gpm	150	gph	\$	10.252	2			st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
			gpm						
Main Slurry Feed Pipe Raceway Slurry Feed Pipe	1080 ft 40 ft	1	ft ft	\$	2.12 1.00	1080 40			ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Consumables									
Initial CO2	5241 lb	50	lb	\$	35.00	105		75 c	ost based on average fertilizer use for Aquaculture and average fertilizer costs from the USDA
Initial Nutrients	0.42 lb	1	lb	\$	0.20	0	\$	0 N	IFC Company, Chicago, IL (800) 734 4515
Initial Water	2,142,278 gal	1	gal	\$	0.0017	2,142,278	\$ 3,5	67 н	12A Feedstock Costs
Control System									
Control Room	160 ft2	1	ft2	\$	50.00	160	\$ 8,0	00 c	omes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.html
Control Room Wiring Panel		1		\$	3,000.00	1	\$ 3,000	00 c	ionsultation with Innomation Systems Inc.
Raceway wiring Panel		1		\$	146.00	20			nformation from Tessco Technologies Inc.
Computer and Monitor		1		\$	1,500.00	1			nformation from Emerson Process Management
Labview Software		1		Ś	4,299,00	1			nformation from Emerson Process Management
Level Indicators		1		\$	714.00	20			Imega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors		1		\$	345.00				Imega Engineering Inc. LVKS1 Liquid Level Float Transmitter + DPI32 Weter Omega Engineering Inc. PX209 Pressure Trnasducer + DPI32 Meter
		1		\$	7.600.00				Imega Engineering Inc. PX2U9 Pressure Tmasducer + DPI32 Meter Ioneywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt_hwhydrogengas.htm)
Hydrogen Area Sensors					,				
Air Temperature Meter		1		\$	599.00	1			Omega DP81T Meter
Air Temperature Indicator		1		\$	38.00	20			Omega TH-10-44000 Thermistor Probe
Water Temperature Indicator		1		\$		20			omes with the PH sensor
pH level Indicator		1		\$	435.00	20			mega Engineering Inc. PHE - 6510 PH electrode + DP24 -PH Meter
Oxygen Area Sensors		1		\$	-	20	\$	C	omes with H2 Sensor
Nutrient Flow Valve		1		\$	5,500.00	1	\$ 5,500	00 In	nformation from Emerson Process Management
Water Flow Valve		1		\$	5,500.00	1	\$ 5,500	00 In	nformation from Emerson Process Management
Hydrogen Flow Meter		1		\$	5,500.00	1	\$ 5,500	00 In	nformation from Emerson Process Management
Instrument Wiring	69270 ft	1	ft	\$	0.02	69270			nformation from Waytek inc. at waytekwire.com
Power Wiring	85350 ft	1	ft	Ś	0.02	85350			nformation from Waytek Inc. at waytekwire.com
Conduit	4860 ft	1	ft	\$	0.58	4860			nformation from Waytek Inc. at waytekwire.com
	-1000 11			Y		m Initial Cost			

4.2 B-2 Pathway Production Plant

The B-2 pathway is a Chemostat II photobiological reactor system using a mutant-antenna cyanobacteria (often called blue-green algae) oxygen-tolerant variant as the H₂ production microorganism. As a Chemostat II, the initial bacteria colony is grown at the normal cell growth rate until final colony concentration is reached, and then the process is switched over to steady-state mode where simultaneous growth and hydrogen production occur in the reactor beds. This is achieved by manipulating the nutrients and carbon dioxide provided. H₂ production is projected at 9.2% solar-to-hydrogen efficiency and corresponds to a future optimized organism. Sufficient cellular activity to keep the micro-organism healthy during H₂ production is assumed to occur with new cell growth taking place at a reduced rate compared to wild-type organisms (20% per day vs. ~80% per day). The B-2 pathway is very similar to the B-1 pathway with the primary difference being type of micro-organism.

Twenty racetrack raceways of approximately 40ft width by 1090ft length are used to produce an average of 1,000kgH₂/day over the year. The raceways have a liquid depth of 10cm to correspond to full photon capture at a cell concentration of 0.2g/L. Paddlewheels circulate the water/bacteria slurry. A slip stream of water/micro-organisms slurry is drawn off continuously to maintain the 0.2g/L micro-organism concentration. Micro-organisms

are removed from the recycle stream by a rotary drum filter. The slip stream volume removed is carefully matched to the growth rate to maintain a constant organism mass within the system (assuming a constant concentration of algae within the bed). The removed micro-organisms are taken to a land-fill, used in a subsequent fermentor, or otherwise disposed. Nutrients in the form of commercial grade fertilizer are mixed with the returning water to provide required nourishment to the micro-organisms. CO_2 is bubbled into a reservoir tank of the returning water to dissolve CO_2 into the water for use by the micro-organisms. Only a very low amount of CO_2 is needed to maintain cell health; thus CO_2 does not appreciably accumulate in the headspace of the reactor beds.

The cyanobacteria micro-organisms produce a net product gas of 33.33% O₂ and 66.66% H₂ (plus water vapor). A piston compressor is used to compress the gas mixture to 300psi prior to separation. A pressure swing adsorption (PSA) system is used to purify the hydrogen gas stream.

Further details of the B-2 pathway are specified in Figure 2-1. The subassemblies of this pathway are shown in Figure 4-3. The complete bill of materials and capital costs of this production plant are shown in Figure 4-4. The total system cost is \$2,164,488.

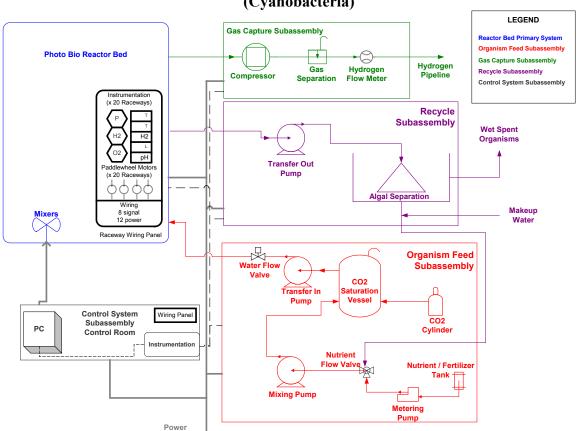


Figure 4-3. Production Plant Design for Oxygen-Tolerant Hydrogenase (Cyanobacteria)

Source

Figure 4-4. Bill of Materials for B-2 Pathway

Description	Size Req'd Units	Unit Size	Units		Unit cost	Qty Req'd	Total Cos		Material / Part Description
Photo Bio Reactor Bed Subassembly									·
Transparent Film	87,080 m2	1	m2	\$	0.54	87,080		71 Po	olyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	93,998 m2	1	m2	\$	0.47	93,998		12 Bu	utyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	13,982 m	1	m	\$	7.00	13,982	\$ 97,8	876 Unit Cost is engineering estimate at \$7/m	
Installation of Ponds		1	raceway	\$	26,083.00	20	\$ 521,6	660 Based on California labor rates.	
Paddlewheel Mixers		1	each	\$	5,000.00	40	\$ 200,0	00 Est	st. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in	1	each	\$	43.46	20	\$ 8	69 Pri	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in	1	each	\$	43.46	20	\$ 8	69 Pri	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Gas Valve	1.0 in	1	each	Ś	67.23	20	Š 1.3	45 Pri	rice from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Flanges	0.5 in	1	each	\$	8.00	60	\$ 4	BO Pri	rice from http://www.ancorp.com/line.aspx?id=819
Gas Capture Subassembly									
Compressor	66 kgmol/hr	66	kgmol/hr	\$	9.233.00	1	\$ 606.2	07 Usi	sing H2A Unit cost
PSA			0 .,	\$	119,407.39	1			sing H2A scaling
Raceway Collection Pipe	40 ft	1	ft	\$	1.57	40			zed for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Main Collection Pipe	1080 ft	1	ft	\$	6.18	1080			zed for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Gas Capture Pipe	50 ft	1	ft	\$	6.18	50			zed for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Organism Food Subassambly									
Organism Feed Subassembly Transfer In Pump	150 gpm	150	gnm	Ś	10,252	2	ć 30 i	no e	st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
		150	gpm	\$	2,594	1			st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmernaus st. Based on Perry's Chemical Handbook, Plant Design and Economics. Pumps nutrients into return flow
Nutrient Metering Pumps	1468 gph		each						
Mixing Pump	150 gpm	150	gpm	\$	10,252	2			st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
CO2 Cylinder	50 lb	50	lb _.	\$	360	1			luminum 6061-T6 alloy, 1800 psi Service Pressure, 50 lb. Capacity Part #6125 (http://kegman.net/carbon.htm)
CO2 Saturation Vessel	15000 gal	15000	gal	\$	30,000	1			eld erected Stainless Steel tank from Perry's chemical Handbook, Plant Design and Economics
Nutrient Tank	8 gal	10	gal	\$	30.00	1			0 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe	40 ft	1	ft	\$	1.00	40			ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	1080 ft	1	ft	\$	2.12	1080	\$ 2,2	90 Pri	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft	1	ft	\$	4.31	180	\$ 7	76 Pri	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle Subassembly									
Rotary Drum filter	9639 gph	3750	gph	\$	87,000.00	3	\$ 261,0	00 Inf	formation from Dana Kent at Advanced Aquaculture Inc. on Hydrotech Drum Filter
Transfer Out Pump	150 gpm	150	gpm	\$	10,252	2	\$ 20,5	03 Est	st. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Main Slurry Feed Pipe	1080 ft	1	ft	\$	2.12	1080	\$ 2,2	90 Pri	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Raceway Slurry Feed Pipe	40 ft	1	ft	\$	1.00	40		40 Pri	ricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Consumables									
Initial CO2	5241 lb	50	lb	Ś	35.00	105	\$ 36	75 co	ost based on average fertilizer use for Aquaculture and average fertilizer costs from the USDA
Initial Nutrients	0.42 lb	1	lb	\$	0.20	0			FC Company, Chicago, IL (800) 734 4515
Initial Water	2,142,278 gal	1	gal	\$	0.0017	2,142,278			2A Feedstock Costs
Control System									
Control Room	160 ft2	1	ft2	Ś	50.00	160	c 01	nn	omes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.html
Control Room Wiring Panel	100 112	1	112	\$	3,000.00	1			onsultation with Innomation Systems Inc.
Raceway wiring Panel		1		Ś	146.00	20			formation from Tessco Technologies Inc.
		1		Ś					
Computer and Monitor		_			1,500.00	1			formation from Emerson Process Management
Labview Software		1		\$	4,299.00	1			formation from Emerson Process Management
Level Indicators		1		\$	714.00	20			mega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors		1		\$	345.00	20			mega Engineering Inc. PX209 Pressure Trnasducer + DPi32 Meter
Hydrogen Area Sensors		1		\$	7,600.00				oneywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt_hwhydrogengas.htm)
Air Temperature Meter		1		\$	599.00	1			mega DP81T Meter
Air Temperature Indicator		1		\$	38.00	20			mega TH-10-44000 Thermistor Probe
Water Temperature Indicator		1		\$	-	20			omes with the PH sensor
pH level Indicator		1		\$	435.00	20			mega Engineering Inc. PHE - 6510 PH electrode + DP24 -PH Meter
Oxygen Area Sensors		1		\$	-	20		Co	omes with H2 Sensor
Nutrient Flow Valve		1		\$	5,500.00	1	\$ 5,500	00 Inf	formation from Emerson Process Management
Water Flow Valve		1		\$	5,500.00	1	\$ 5,500	00 Inf	formation from Emerson Process Management
Hydrogen Flow Meter		1		\$	5,500.00	1			formation from Emerson Process Management
Instrument Wiring	69270 ft	1	ft	\$	0.02	69270			formation from Waytek Inc. at waytekwire.com
Power Wiring	85350 ft	1	ft	\$	0.02	85350			formation from Waytek Inc. at waytekwire.com
Conduit	4860 ft	1	ft	\$	0.58	4860			formation from Waytek Inc. at waytekwire.com
				-		m Initial Cost			·

4.3 B-3 Pathway Production Plant

The B-3 pathway is a single-bed photobiological reactor system using a mutant-antenna *Chlamydomonas reinhardtii* sulfate permease variant as the H₂ production micro-organism. As a single bed reactor, the initial algal colony is grown at the normal cell growth rate until final colony concentration is reached. After sealing the system, the oxygen evolution rate, reduced due to the mutation in the sulfate permease proteins, falls below the rate of oxidative respiration, leading to an anaerobic system that produces hydrogen for a period of roughly 3 days. When the organism's capability to produce hydrogen under these conditions has diminished, the system undergoes a 4-day regeneration/growth phase wherein O₂ is given to the micro-organisms, halting H₂ production through hydrogenase inhibition and encouraging cellular growth. This is followed by another 3-day H₂ production phase under anaerobic conditions, when the outside O₂ addition is stopped. H₂ production is projected at 5.2% average solar-to-hydrogen efficiency and corresponds to a future optimized organism.

Thirty-eight raceways of approximately 40ft width by 1090ft length are used to produce an average of 1,000kgH₂/day throughout the year. The raceways have a liquid depth of 10cm to correspond to full photon capture at a cell concentration of 0.2g/L. In order to allow

enough growth during the regeneration phase, however, the concentration will be higher during reactor operation. Paddlewheels circulate the water/*Chlamydomonas reinhardtii* slurry. Nutrients in the form of commercial grade fertilizer are mixed with make-up water stream to provide required nourishment to the microorganisms.

The *Chlamydomonas reinhardtii* sulfate permease mutant will produce a large amount of carbon dioxide that will quickly saturate the process water and begin filling the headspace. A piston compressor is used to compress the hydrogen to 300psi. A pressure swing adsorption (PSA) system is used to purify the hydrogen gas stream to five nines purity and return the CO₂ to the CO₂ saturation vessel where it will be mixed with a slipstream of water that has been removed from raceways low in saturated CO₂ during their regeneration phase. During the regeneration phase all product gases will be vented.

Further details of the B-3 pathway are specified in Figure 2-1. The subassemblies of this pathway are shown in Figure 4-5. The complete bill of materials and capital costs of this production plant are shown in Figure 4-6. The total system cost is \$3,562,117.

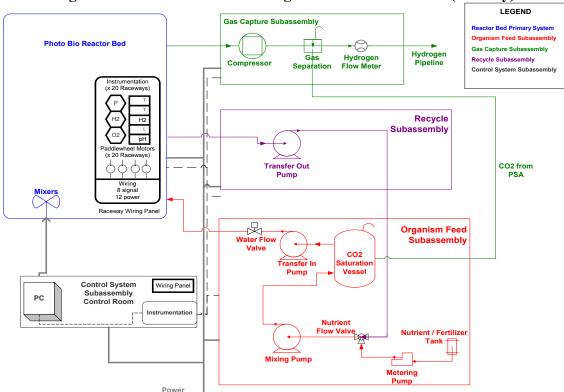


Figure 4-6. Bill of Materials for B-3 Pathway

Description	Size Req'd Units	Unit Size	Units		Unit cost	Qty Req'd	Total Cos	t Material / Part Description
Photo Bio Reactor Bed Subassembly								
Transparent Film	165,452 m2	1	m2	\$	0.54	165,452 \$	89,0	954 Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	178,597 m2	1	m2	\$	0.47	178,597 \$	84,	Butyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	26,566 m	1	m	\$	7.00	26,566 \$	185,9	O65 Unit Cost is engineering estimate at \$7/m
Installation of Ponds		1	raceway	\$	26,083.00	38 \$	991,	L54 Based on California labor rates.
Paddlewheel Mixers		1	each	\$	5,000.00	76 \$	380.0	000 Est. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in	1	each	\$	43.46	38 \$	1.0	551 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in	1	each	Ś	43.46	38 \$		551 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Gas Valve	1.0 in	1	each	Ś	67.23	38 S		555 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Flanges	0.5 in	1	each	Ś	8.00	114 S		312 Price from http://www.ancorp.com/line.aspx?id=819
rialiges	0.5 III	1	eacii	۶	8.00	114 3		12 Fine non-nep.//www.ancorp.com/mie.aspx:nu=619
Gas Capture Subassembly								
Compressor	65 kgmol/hr	65	kgmol/hr	\$	9,233.00	1 \$		582 Using H2A Unit cost
PSA				\$	80,034.78	1 \$		O35 Using H2A scaling
Raceway Collection Pipe	76 ft	1	ft	\$	2.80	76 \$		13 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Main Collection Pipe	2160 ft	1	ft	\$	6.18	2160 \$	13,	349 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Gas Capture Pipe	350 ft	1	ft	\$	6.18	350 \$	2,	63 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Organism Feed Subassembly								
Transfer In Pump	150 gpm	150	anm	\$	10,252	16 \$	164	127 Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
			gpm			16 \$ 1 \$		
Nutrient Metering Pumps	1468 gph	1	each	\$	2,594			594 Est. Based on Perry's Chemical Handbook, Plant Design and Economics. Pumps nutrients into return flow
Mixing Pump	150 gpm	150	gpm	\$	10,252	16 \$		227 Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
CO2 Cylinder	50 lb	50	lb	\$	360	1 \$		Aluminum 6061-T6 alloy, 1800 psi Service Pressure, 50 lb. Capacity Part #6125 (http://kegman.net/carbon.htm)
CO2 Saturation Vessel	15000 gal	15000	gal	\$	30,000	10 \$		100 Field erected Stainless Steel tank from Perry's chemical Handbook, Plant Design and Economics
Nutrient Tank	15 gal	10	gal	\$	30.00	2 \$		60 10 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe	76 ft	1	ft	\$	2.12	76 \$		61 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	2160 ft	1	ft	\$	8.51	2160 \$	18,	182 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft	1	ft	\$	8.51	180 \$	1,	Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle Subassembly								
Transfer Out Pump	150	150		\$	10,252	16 \$	104)27 Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
	150 gpm		gpm					
Raceway Slurry Collection Pipe	76 ft	1	ft	\$	8.51	76 \$		547 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	2160 ft	1	ft	\$	8.51	2160 \$	18,	182 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Consumables								
Initial CO2	41629 lb	50	lb	\$	35.00	833 Ś	29.	.55 Cost based on average fertilizer use for Aquaculture and average fertilizer costs from the USDA
Initial Nutrients	0.78 lb	1	lb	\$	0.20	1 \$		O NFC Company, Chicago, IL (800) 734 4515
Initial Water	3,997,674 gal	1	gal	Ś	0.0017	3.997.674 S		i56 H2A Feedstock Costs
mittal water	3,337,074 gai	-	gai	,	0.0017	3,337,074 3	0,	JO TENT COMOR COM
Control System								
Control Room	160 ft2	1	ft2	\$	50.00	160 \$	-,	000 comes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.htm
Control Room Wiring Panel		1		\$	3,000.00	1 \$.00 Consultation with Innomation Systems Inc.
Raceway wiring Panel		1		\$	146.00	38 \$	5,	48 Information from Tessco Technologies Inc.
Computer and Monitor		1		\$	1,500.00	1 \$	1,500	.00 Information from Emerson Process Management
Labview Software		1		\$	4,299.00	1 \$	4,299	.00 Information from Emerson Process Management
Level Indicators		1		\$	714.00	38 \$.00 Omega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors		1		Ś	345.00	38 \$.00 Omega Engineering Inc. PX209 Pressure Trnasducer + DPi32 Meter
Hydrogen Area Sensors		1		Ś	7,600.00	19 \$.00 Honeywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt_hwhydrogengas.htm)
Air Temperature Meter		1		ŝ	599.00	15 \$.00 Omega DP81T Meter
		-		Ś				
Air Temperature Indicator		1			38.00	38 \$,	.00 Omega TH-10-44000 Thermistor Probe
Water Temperature Indicator		1		\$		38 \$		Comes with the PH sensor
pH level Indicator		1		\$	435.00	38 \$.00 Omega Engineering Inc. PHE - 6510 PH electrode + DP24 -PH Meter
Oxygen Area Sensors		1		\$	-	38 \$		Comes with H2 Sensor
Nutrient Flow Valve		1		\$	5,500.00	1 \$	5,500	.00 Information from Emerson Process Management
Water Flow Valve		1		\$	5,500.00	1 \$	5,500	.00 Information from Emerson Process Management
Hydrogen Flow Meter		1		Ś	5,500.00	1 \$.00 Information from Emerson Process Management
Instrument Wiring	213180 ft	1	ft	Ś	0.02	213180 \$.69 Information from Waytek Inc. at waytekwire.com
Power Wiring	264360 ft	1	ft	Ś	0.02	264360 \$.58 Information from Waytek Inc. at waytekwire.com
	204300 IL			-	0.02			
Conduit	8820 ft	1	ft	Ś	0.58	8820 Ś		.84 Information from Waytek Inc. at waytekwire.com

4.4 B-4 Immobilized Photobiological System

The B-4 pathway is a dual-bed photobiological reactor system using a sulfur-deprived, immobilized, mutant-antenna *Chlamydomonas reinhardtii* as the H₂ production microorganism. H₂ production is projected at 3% solar-to-hydrogen conversion efficiency, corresponding to a future optimized organism. However, laboratory testing has only yielded 0.8% conversion efficiency.

The dual-bed system consists of 2 growth reactors and 90 H₂ production reactors. Each reactor is approximately 40ft wide by 1060ft long. Reactors are large rectangular beds without a middle divider because there is no need to direct circular flow. Unlike reactor systems which use paddlewheels for circulation, these reactors will use a perforated pipeline system and central pump to distribute nutrients and provide mixing. The entire system is scaled to produce an average of 1,000kgH₂/day over the year. All reactors have a liquid depth of 10cm⁵³ to ensure full photon capture, moderate temperature swings by adding heat capacity to the system, and allow for sufficient circulation of nutrients. A thriving algal

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⁵³ 10cm depth at 1g/L is not needed for full photon capture. However, the bed is made this deep to provide commonality with the other pathways studied, to provide temperature moderation, and to relax construction tolerances on the bed itself.

culture is maintained in the growth reactors at an enhanced concentration of >1g/L. Two porous, fibrous substrates (2mil spin-molded polypropylene sheets) each 20ft wide and the length of the reactor are floated in the growth reactor for 2 days. During this time, the newly grown algae attach to the substrate and grow, forming an immobilized biofilm⁵⁴. Commercial fertilizer and CO_2 are fed to the growth reactors to ensure micro-organism health and growth. After 2 days, the film substrate is transferred to the H_2 production reactors.

The substrate then begins to cycle between two days of hydrogen production and two days of regenerative growth to keep the culture alive for an extended period of time and to allow enough biomass to accumulate as substrate for the respiration needed to keep the system anaerobic during hydrogen production. Sulfur deprivation will lead to H₂ production, and adding sulfur will begin the regeneration phase. During the growth stage, all product gases will be vented to the outside.

The H_2 production phase is ~180 days in duration before the film needs replacing. Like in the growth beds, the biofilm containing immobilized algae floats to the top of the 10cm reactor liquid layer. A custom blend of commercial fertilizer nutrients with a minimal amount of sulfur is added to the reactors via a water recirculation system. Sulfur deprivation will trigger hydrogen production. As in the growth reactors, a central pump and pipeline system circulates nutrients.

The biofilm substrate from the growth reactors are rolled up and then unrolled into the H_2 production reactors using an industrial unwind machine that is attached to the front end of a forklift truck. The unwind machine, as quoted by Powell Engineering, costs around \$37,000 and winds the film onto a one foot diameter aluminum core. The Forklift is an \$18,571 Caterpillar C3000 lift. By using the forklift to transport the unwind machine, a single device can be used for all biofilm transfers. At the end of the 180-day production cycle, the biofilm substrate is discarded. The forklift mounted wind machine is again used to collect the substrate.

The *Chlamydomonas reinhardtii* micro-organism in sulfur-deprived mode produces a nominally pure hydrogen product gas (plus water vapor). A piston compressor is used to compress the hydrogen to 300psi. A small pressure swing adsorption (PSA) system is used to polish the hydrogen gas stream to five nines purity and return the CO₂ to the CO₂ saturation vessel where it will be mixed with a slipstream of water that has been removed from raceways low in saturated CO₂ during their regeneration phase. During the regeneration phase all product gases will be vented.

Further details of the B-4 pathway are specified in Figure 2-1. The subassemblies of this pathway are shown in Figure 4-7. The complete bill of materials and capital costs of this production plant are shown in Figure 4-8. The total system cost is \$4,843,599.

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⁵⁴ While a biofilm is "grown" on the substrate, the algae are actually a combination of the free-floating algae that clings to the substrate and new algae that blooms during the 2 days of incubation.

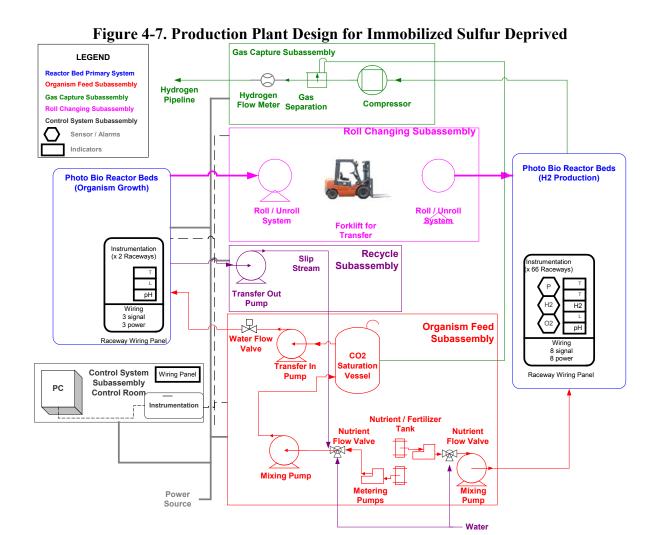


Figure 4-8. Bill of Materials for B-4 Pathway

Description	Size Req'd Units	Unit Size	Units		Unit cost	Qty Req'd	Total Cost	Material / Part Description
Photo Bio Reactor Bed Subassembly	204 0752		2	,	0.51	204.075 *	205	Debuglished and the second of the Second Sec
Transparent Film	381,075 m2	1	m2	\$	0.54	381,075 \$		Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	411,355 m2	1	m2	\$	0.47	411,355 \$		Butyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	61,258 m	1	m	\$	7.00	61,258 \$		Unit Cost is engineering estimate at \$7/m
Installation of Ponds		1	raceway	\$	26,083.00	92 \$	2,399,636	Based on California labor rates.
Inlet Water Valve	0.5 in	1	each	\$	43.46	90 \$	3,911	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in	1	each	\$	43.46	90 \$	3,911	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Gas Valve	1.0 in	1	each	Ś	67.23	90 S	6.051	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Flanges	0.5 in	1	each	\$	8.00	270 \$		Price from http://www.ancorp.com/line.aspx?id=819
				*		+	_,	
Gas Capture Subassembly								
Compressor	56 kgmol/hr	56	kgmol/hr	\$	9,233.00	1 \$	521,146	Using H2A Unit cost
PSA				\$	60,970.48	1 \$		Using H2A scaling
Raceway Collection Pipe	180 ft	1	ft	\$	1.00	180 \$	180	Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Main Collection Pipe	5280 ft	1	ft	\$	6.18	5280 \$	32,630	Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Gas Capture Pipe	460 ft	1	ft	\$	6.18	460 \$	2,843	Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Organism Feed Subassembly								
	450	450		,	40.353	1 \$	40.000	For Board or Board of Charles I Househood Blood Board of Control of Charles of Tours
Transfer In Pump	150 gpm	150	gpm	\$	10,252			Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Nutrient Metering Pumps	1468 gph	1	each	\$	2,594	1 \$		Est. Based on Perry's Chemical Handbook, Plant Design and Economics. Pumps nutrients into return flow
Mixing Pump	150 gpm	150	gpm	\$	10,252	1 \$		Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
CO2 Cylinder	50 lb	50	lb	\$	360	1 \$	360	Aluminum 6061-T6 alloy, 1800 psi Service Pressure, 50 lb. Capacity Part #6125 (http://kegman.net/carbon.htm)
CO2 Saturation Vessel	15000 gal	15000	gal	\$	30,000	1 \$	30,000	Field erected Stainless Steel tank from Perry's chemical Handbook, Plant Design and Economics
Nutrient Tank	35 gal	10	gal	\$	30.00	4 \$	120	10 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Nutrient Piping	90000 ft	1	ft	\$	0.58	90000 \$	52,200	
Raceway Slurry Collection Pipe	180 ft	1	ft	Ś	0.52	180 Ś		Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	5280 ft	1	ft	\$	2.12	5280 \$		Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft	1	ft	Ś	2.80	180 S		Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
kecycle-reed transfer ripe	100 10	1	11	۶	2.00	160 \$	304	Pricing based on or estimates from PVC Plastic Corp. Assumes to hysecolid flow late and bensity or 1g/mi
Roll Changing Subassembly								
Roll-Unroll System	20 ft	1	Roller		\$37,000	1 \$	37.000	Information from conversations with Powell Engineering. \$29,500 for base, \$4,000 for motor, and \$3,500 for Core
Polypropylene Film	352070 m2	1	m2	Ś	0.12	352070 S	42,248	
Forklift	332070 1112	1	Forklift	Ś		1 \$		Price Quote from Atlantic Lift Truck Inc.
Recycle Subassembly								
Transfer Out Pump	150 gpm	150	gpm	\$	10,252	1 \$	10,252	Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Main Slurry Feed Pipe	5280 ft	1	ft	\$	2.12	5280 \$	11,194	Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Raceway Slurry Feed Pipe	180 ft	1	ft	\$	0.52	180 \$		Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
L								
Consumables				Ś				
Initial CO2	206180 lb	50	lb	-	35.00	4124 \$		Cost based on average fertilizer use for Aquaculture and average fertilizer costs from the USDA
Initial Nutrients	1.81 lb	1	lb	\$	0.20	2 \$		NFC Company, Chicago, IL (800) 734 4515
Initial Water	9,324,121 gal	1	gal	\$	0.0017	9,324,121 \$	15,525	H2A Feedstock Costs
Control System								
Control Room	160 ft2	1	ft2	Ś	50.00	160 \$	8.000	comes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.html
Control Room Wiring Panel		1		\$	3,000.00	1 Ś		Consultation with Innomation Systems Inc.
Raceway wiring Panel		1		Ś	146.00	90 S		Information from Tessco Technologies Inc.
		1		ś	1,500.00	1 \$		Information from Emerson Process Management
Computer and Monitor		_						
Labview Software		1		\$	4,299.00	1 \$		Information from Emerson Process Management
Level Indicators		1		\$	714.00	90 \$		Omega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors				\$	345.00	90 \$		Omega Engineering Inc. PX209 Pressure Trnasducer + DPi32 Meter
		1					242 000	The second state of the se
Hydrogen Area Sensors		1		\$	7,600.00	45 \$	342,000	Honeywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt_hwhydrogengas.htm)
		_		\$	7,600.00 599.00	45 \$ 1 \$		Omega DP81T Meter
Hydrogen Area Sensors		1					599	
Hydrogen Area Sensors Air Temperature Meter		1		\$	599.00	1 \$	599	Omega DP81T Meter
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator		1 1 1		\$	599.00 38.00	1 \$ 90 \$ 90 \$	599 3,420	Omega DP81T Meter Omega TH-10-44000 Thermistor Probe Comes with the PH sensor
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator pH level Indicator		1 1 1 1		\$ \$	599.00	1 \$ 90 \$ 90 \$ 90 \$	599 3,420 - 39,150	Omega DP81T Meter Omega TH-10-44001 Thermistor Probe Comes with the PH sensor Omega Engineering Inc. PHE - 6510 PH electrode + DP24 -PH Meter
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator pH level Indicator Oxygen Area Sensors		1 1 1 1 1		\$ \$	599.00 38.00 435.00	1 \$ 90 \$ 90 \$ 90 \$	599 3,420 - 39,150	Onego DREIT Meter Onego Thi-10-Met000 Thermistor Probe Comes with the PH sessor Onego Engineering Inc. PHE -6510 PH electrode + DP24-PH Meter Comes with 10-Metor Comes with 10-Sessor
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator pH level Indicator Oxygen Area Sensors Nutrient Flow Valve		1 1 1 1 1 1		\$ \$ \$ \$ \$	599.00 38.00 - 435.00 - 5,500.00	1 \$ 90 \$ 90 \$ 90 \$ 90 \$ 1 \$	599 3,420 - 39,150 - 5,500	Omega DP81T Meter Omega TH-10-44000 Thermistor Probe Comes with the PH stessor Omega Engineering Inc. PHE - 65.10 PH electrode + 0P24 - PH Meter Comes with Nt 2 Sessor Information From Emerson Process Management
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator Ple level Indicator Orygen Area Sensors Nutrient Flow Valve Water Flow Valve		1 1 1 1 1 1 1		\$ \$ \$ \$ \$	599.00 38.00 435.00 5,500.00 5,500.00	1 \$ 90 \$ 90 \$ 90 \$ 90 \$ 1 \$ 1 \$	599 3,420 - 39,150 - 5,500 5,500	Omega DP-81 Meter Omega Th-10 A4000 Thermistor Probe Comes with the PH sensor Omega Enjoneering Inc. PHE - 6510 PH electrode + DP24 -PH Meter Comes with 12 Sensor Process Management Information from Emerson Process Management
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator Phi level Indicator Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve Hydrogen Flow Meter		1 1 1 1 1 1 1 1 1		\$ \$ \$ \$ \$	599.00 38.00 - 435.00 - 5,500.00 5,500.00 5,500.00	1 \$ 90 \$ 90 \$ 90 \$ 90 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$	599 3,420 - 39,150 - 5,500 5,500 5,500	Omega DR41 Meter Omega TH4-044000 Thermistor Probe Comes with the PH sensor Omega Engineering Inc. PHE - 6510 PH electrode + DP24-PH Meter Comes with 12 Sensor or Information from Emerson Process Management Information from Emerson Process Management Information from Emerson Process Management
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator Ple Ievel Indicator Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve	1065720 ft	1 1 1 1 1 1 1 1 1 1	ft	\$ \$ \$ \$ \$ \$	599.00 38.00 	1 \$ 90 \$ 90 \$ 90 \$ 1 \$ 1 \$ 1 \$ 1065720 \$	599 3,420 - 39,150 - 5,500 5,500 5,500 20,675	Omega DP41 Meter Omega Th4 10-44000 Thermistor Probe Comes with the 9H sensor Omega Regionering Inc. PHE - 6510 PH electrode + 0P24 -PH Meter Comes with 112-5ensor Information from Innerson Process Management Information from University Innerson Process Management Information Innerson Process Management Innerson Innerson Process Management Innerson Inn
Hydrogen Area Sensors Air Temperature Meter Air Temperature Indicator Water Temperature Indicator Phi level Indicator Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve Hydrogen Flow Meter	1065720 ft 1327500 ft 20260 ft	1 1 1 1 1 1 1 1 1	ft ft	\$ \$ \$ \$ \$	599.00 38.00 - 435.00 - 5,500.00 5,500.00 5,500.00	1 \$ 90 \$ 90 \$ 90 \$ 90 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$ 1 \$	599 3,420 - 39,150 - 5,500 5,500 5,500 20,675 25,754	Omega DR41 Meter Omega TH4-044000 Thermistor Probe Comes with the PH sensor Omega Engineering Inc. PHE - 6510 PH electrode + DP24 - PH Meter Comes with 12 Sensor or Information from Emerson Process Management Information from Emerson Process Management Information from Emerson Process Management

4.5 B-5 Pathway Production Plant

The B-5 pathway is a Chemostat II photobiological reactor system using a mutant-antenna purple-non-Sulfur (PNS) proteobacteria as the H_2 production micro-organism. As a Chemostat II, the initial bacterial culture is grown at the normal cell growth rate until final colony concentration is reached, and then the process is switched over to steady-state mode where simultaneous growth and hydrogen production occur in the reactor beds. This is achieved by manipulating the nutrients. H_2 production is projected at 3.5% solar-to-hydrogen efficiency and corresponds to a future optimized organism. Current PNS systems have been demonstrated at only 2.5% conversion efficiency in the laboratory. Sufficient cellular activity to keep the micro-organism healthy is assumed to occur during H_2 production with new cell growth taking place at a reduced rate compared to wild-type organisms (20% per day vs. \sim 80% per day). Since the system functions as a Chemostat II with 20% daily organism renewal, an effectively infinite H_2 production phase duration is achieved.

Fifty-four raceways of approximately 40ft width by 1090ft length are used to produce an average of 1,000kgH₂/day throughout the year. The raceways have a liquid depth of 10cm to correspond to full photon capture at a cell concentration of 0.2g/L. Paddlewheels circulate the water/PNS slurry. A slip stream of water/micro-organism slurry is drawn off

continuously to maintain the 0.2g/L micro-organism concentration. Micro-organisms are removed from the recycle stream by a rotary drum filter. The micro-organism mass removed is carefully matched to the growth rate to maintain a constant organism mass within the system. The removed micro-organisms are taken to a land-fill, used in a subsequent fermentor, or otherwise disposed. Nutrients in the form of acetate are mixed with the returning water to provide required nourishment to the micro-organisms and as a substrate in the hydrogen production reaction.

The PNS micro-organisms produce a net product gas of 95% H₂ and 5% CO₂ (plus water vapor). A piston compressor is used to compress the gas mixture to 300psi prior to separation. A pressure swing adsorption (PSA) system is used to purify the hydrogen gas steam.

Further details of the B-5 pathway are specified in Figure 2-1. The subassemblies of this pathway are shown in Figure 4-9. The complete bill of materials and capital costs of this production plant are shown in Figure 4-10. The total system cost is \$4,034,192.

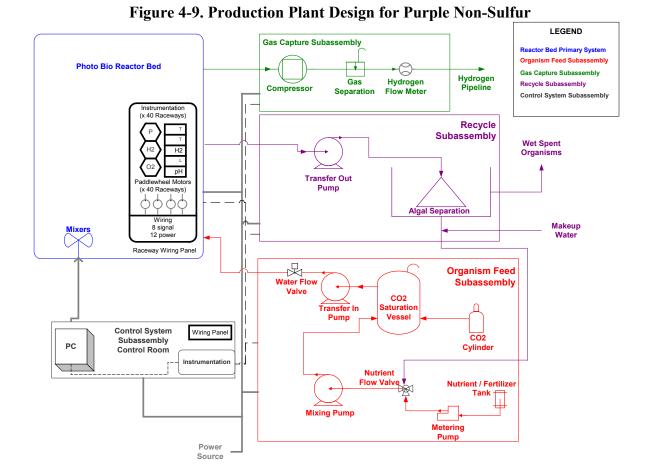


Figure 4-10. Bill of Materials for B-5 Pathway

Description	Size Req'd	Units	Unit Size	Units		Unit cost	Qty Req'd	Total Co	st	Material / Part Description
Photo Bio Reactor Bed Subassembly										
Transparent Film	235116 m2		1	m2	\$	0.54	235,116 \$			Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	253795 m2		1	m2	\$	0.47	253,795 \$			Butyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	37752 m		1	m	\$	7.00	37,752 \$	264,	266	Unit Cost is engineering estimate at \$7/m
Installation of Ponds			1	raceway	\$	26,083.00	54 \$	1,408,	482	Based on California labor rates.
Paddlewheel Mixers			1	each	\$	5,000.00	108 \$	540,	000	Est. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in		1	each	\$	43.46	54 \$	2,	347	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in		1	each	\$	43.46	54 \$	2,	347	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Gas Valve	1.0 in		1	each	\$	67.23	54 \$	3,	630	Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Flanges	0.5 in		1	each	\$	8.00	162 \$			Price from http://www.ancorp.com/line.aspx?id=819
Gas Capture Subassembly										
Compressor	45 kgn	nol/hr	45	kgmol/hr	\$	9,233.00	1 \$	414	241	Using H2A Unit cost
PSA	43 KBII	1101/111	45	Kgillol/III	Ś	30,541.73	1 \$			Using H2A scaling
Raceway Collection Pipe	108 ft		1	ft	Ś	1.00	108 S			Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
										Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Main Collection Pipe	3120 ft		1	ft	\$	6.18	3120 \$			
Gas Capture Pipe	50 ft		1	ft	\$	6.18	50 \$		309	Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Organism Feed Subassembly										
Transfer In Pump	150 gpn	m	150	gpm	\$	10,252	3 \$	30,	755	Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Nutrient Metering Pumps	1468 gph	1	1	each	\$	2,594	1 \$	2,	594	Est. Based on Perry's Chemical Handbook, Plant Design and Economics. Pumps nutrients into return flow
Mixing Pump	150 gpn	m	150	gpm	\$	10.252	3 \$	30.	755	Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Nutrient Tank	21 gal		10	gal	Ś	30.00	3 \$		90	10 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe	108 ft		1	ft	Ś	1.00	108 \$			Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	3120 ft		1	ft	ś	4.31	3120 \$			Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft		1	ft	\$	6.18	180 \$			Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle Subassembly					_		- 4			
Rotary Drum filter	25741 gph		3750	gph	\$	87,000.00	7 \$			Information from Dana Kent at Advanced Aquaculture Inc. on Hydrotech Drum Filter
Transfer Out Pump	150 gpn	n	150	gpm	\$	10,252	3 \$			Est. Based on Perry's Chemical Handbook, Plant Design and Economics/Peters and Timmerhaus
Main Slurry Feed Pipe	3120 ft		1	ft	\$	4.31	3120 \$			Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Raceway Slurry Feed Pipe	108 ft		1	ft	\$	1.00	108 \$		108	Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Consumables										
Initial Nutrients	1.11 lb		1	lb	\$	0.20	1 \$		0	NFC Company, Chicago, IL (800) 734 4515
Initial Water	5,720,312 gal		1	gal	\$	0.0017	5,720,312 \$	9,	524	H2A Feedstock Costs
Initial Acetate	7,793 kg		1	kg	\$	0.5950	7,793 \$	4,	637	Chemical Journal of Korea. Assumes consumption to be four times more to account for full growth conditions.
Control System										
Control Room	160 ft2		1	ft2	Ś	50.00	160 S	8.	000	comes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular buildings/prefab guide.html
Control Room Wiring Panel			1		Ś	3,000.00	1 \$			Consultation with Innomation Systems Inc.
Raceway wiring Panel			1		Ś	146.00	54 \$			Information from Tessco Technologies Inc.
Computer and Monitor			1		Ś	1,500.00	1 \$			Information from Emerson Process Management
			1		Ś	4,299.00	1 \$			Information from Emerson Process Management
Labview Software										
Level Indicators			1		\$	714.00	54 \$			Omega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors			1		\$	345.00	54 \$			Omega Engineering Inc. PX209 Pressure Trnasducer + DPi32 Meter
Hydrogen Area Sensors			1		\$	7,600.00	27 \$			Honeywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt hwhydrogengas.htm)
Air Temperature Meter			1		\$	599.00	1 \$			Omega DP81T Meter
Air Temperature Indicator			1		\$	38.00	54 \$		2.00	Omega TH-10-44000 Thermistor Probe
Water Temperature Indicator			1		\$	-	54 \$		-	Comes with the PH sensor
pH level Indicator			1		\$	435.00	54 \$	23,490	0.00	Omega Engineering Inc. PHE - 6510 PH electrode + DP24 -PH Meter
Oxygen Area Sensors			1		\$	-	54 \$		-	Comes with H2 Sensor
Nutrient Flow Valve			1		Ś	5.500.00	1 \$			Information from Emerson Process Management
Water Flow Valve			1		Ś	5,500.00	1 \$			Information from Emerson Process Management
Hydrogen Flow Meter			1		Ś	5,500.00	1 \$			Information from Emerson Process Management
Instrument Wiring	406380 ft		1	ft	Ś	0.02	406380 S			Information from Waytek Inc. at waytekwire.com
			1	ft	Ś	0.02		,		
Power Wiring	505080 ft						505080 \$			Information from Waytek Inc. at waytekwire.com
Conduit	12340 ft		1	ft	\$	0.58	12340 \$	7,154	1.73	Information from Waytek Inc. at waytekwire.com

System Initial Cost \$ 4,034,192

5. Capital Cost Assumptions and Calculations

Thus far in the report we have discussed the basic science that applies to photobiological systems as well as the biological parameters of micro-organisms and the engineering design conditions which were used in the analysis. This section of the document is dedicated to financial and engineering assumptions that have been made in order to evaluate the economics of each of the bio-hydrogen solutions under review. The assumptions have been divided between those necessary to develop capital costs and those essential to determining levelized hydrogen costs. That is followed by computation of the levelized hydrogen costs and a discussion of the results and how they may be improved.

5.1 Capital Cost Assumptions

A bill of materials for each pathway outlining the capital costs associated with the construction and components of that photobiological hydrogen production facility is provided in the previous section. That section characterized the basic operation and configuration assumptions but many other assumptions relating to the capital cost were not defined. This section outlines and defines the other underlying assumptions used in determining the capital costs associated with the individual cost components.

5.1.1 Material Margins

When calculating the size of the Low Density Polyethylene (LDPE) film needed to cover the top of the raceways, it was necessary to add an extra margin to account for ease of assembly and the potential for misalignment as the film is unrolled. We assumed an additional one foot would be more than sufficient to cover the pond edging and leave extra material for sealing against the edging. In addition, we calculate that an additional six inches on either side and on either end will be necessary to give room for the accumulation of gas at times of day when production of gas exceeds removal. Excess gas accumulation is covered in Section 5.2.3.

5.1.2 Bed Dimensions

In choosing the dimensions of the raceways, polyethylene manufacturers were consulted to determine the manufacturing constraints of polyethylene film production. Since the LDPE is intended as an impermeable hydrogen gas barrier, it is desirable to avoid seams between sheets as those are at higher risk for leakage. While sealing on the edges of the raceways is unavoidable, the difficulty of sealing against hydrogen loss led us to size the raceways based on the largest single sheet of LDPE that could be produced. Conversations with Berry Plastics indicated that the maximum width for a roll of LDPE film is 56 feet. However, we recognized the constraints of transporting such a large roll, and assumed a maximum width that could fit onto a truck to be roughly 50 feet. To allow for the overage mentioned in the previous section, we assume a roll width of 43 feet, leaving a 40 foot wide raceway. Berry Plastics also indicated that roll lengths of over 1000 feet are feasible. impermeability to hydrogen, Berry Plastics recommended 6mm thick film. We desired an even number of raceways to make material cost calculations and system design easier. Therefore, to determine the length of raceways for each system, we chose a round number of feet near 1000 that, with a 40 foot active width, would cover the necessary production area with an even number of raceways. For all systems, raceway length is between 1060 and 1090ft. In addition to these physical dimension parameters, the LDPE also impacts bed dimension because it is a barrier to the full solar insolation reaching the algae. Data from manufacturer indicates that the transmission of sunlight is 90% across the film. That has been taken into consideration in sizing the raceways.

5.1.3 Gas Capture Sizing

Due to yearly variation in insolation, it is necessary to size the elements of the gas capture subassembly for the projected peak day of production, June 21. Sizing for the average would lead to extreme H₂ accumulation of during the days where insolation is higher than the average (March 21 to September 21). Thus, the gas capture subassembly will be operating below rated capacity for most of the year.

5.1.4 Pipe Sizing

Pipe sizing was achieved through the use of the continuity equation $\dot{m} = \rho Av$. For gas piping, we assumed a maximum gas velocity of 100 ft/second to limit pressure loss due to pipe flow. For water piping, we assumed a maximum velocity of 15 ft/second. The exact physical layout of the piping systems is needed to accurately assess the velocity and pressure drop relationship. Since a detailed piping layout is beyond the scope of this project, the specific velocity cannot be known. Consequently, the number computed is used as a surrogate for more detailed analysis and we judge it to be adequate given the low costs

associated with small changes in PVC pipe diameter. We rounded our pipe diameter calculated to the nearest nominal size for cost analysis purpose.

There were three different pipe sizes calculated for the various stages of liquid removal and recycling. The pipes that transfer the water out to and back from the individual raceways are sized for individual raceway requirements. Each of these individual raceway pipes comes from or combines with a collection manifold sized for half of the overall volume, since the raceways are placed in two even rows with the recycle and algae feed subassemblies in the middle. Finally, one pipe combines flow from the two collection manifolds and feeds it to the recycle subassembly and out of the algae feed subassembly. This manifold must be sized to contain the entire flow volume. The pipe sizes for each system are given in Figure 5-1. Similarly, gas piping was sized both for individual outlets on each raceway, and then the main collection lines that lead to the Gas Capture Subassembly.

Figure 5-1. Piping sizes for B-1 through B-5

	Algal O2- tolerant Hydrogenase	Cyanobacterium O2-tolerant Hydrogenase	Algal Sulfate Permease	Immobilized Algal, Sulfur deprived	PNS bacteria
	B-1	B-2	B-3	B-4	B-5
		Gas Piping			
Raceway Collection Pipe	1.5"	1.5"	1"	1"	1"
Main Collection Pipe	4"	4"	4"	3.5"	3.5"
Gas Capture Collection Pipe	5.5"	5.5"	5.5"	5.0"	4.5"
		Slurry Piping			
Raceway Slurry Collection	1"	1"	2"	0.5"	1"
Main Slurry Collection	2"	2"	7"	2"	3"
Recycle-Feed Transfer Pipe	3"	3"	10"	2.5"	4.5"
Main Slurry Feed Pipe	2"	2"	7"	2"	3"
Raceway Slurry Feed Pipe	1"	1"	2"	0.5"	1"

5.1.5 Equipment Duty Cycles

Given that the biological production of hydrogen gas can only occur during sunlight, it was originally assumed that the operation cycles of the gas capture subassembly equipment would match the production cycle. However this would necessitate sizing the compressor and the PSA for the maximum gas production rate. Considering the substantial capital and operation costs associated with the compressor and the PSA, it is more cost effective to size the compressor and the PSA for average daily gas production and have it run 24 hours a day so the last of the product gases are removed from the bed as a new production day begins.

The organisms require nutrients even though they may not be producing hydrogen. Because of this the replenishment supply and slip stream removal must be continuous. Thus the pumps and drum filters are also expected to operate 24 hours a day and sized as such. Paddlewheel operation is not continuous because the mixing of the micro-organisms is only required during sunlight hours.

5.1.6 Operational Cycle

While ideally the hydrogen production bioreactor would operate all days of the year, it will be necessary to shut down the reactor at times for maintenance or to flush out and restart individual raceway colonies in case of culture contamination. With these considerations in mind, we have assumed a plant operation time of 90%.

In a given day, the production cycle will be entirely determined by the duration of sunlight, which varies throughout the year. To simplify the equipment sizing procedure we have assumed that on average, there will be 12 hours of sunlight per day throughout the year.

5.2 Calculations Explained

Many of the calculations used for the sizing of elements in the raceway are explained in the following sections. They are based on assumptions stated in the previous section or elsewhere in this report.

5.2.1 Quantity of Raceways

As mentioned in Section 1.1.2 the dimensions of the raceways are determined largely by the constraints of the LDPE film production and practical considerations such as ease of truck transport. We slightly tweaked the length in order to obtain an even number of raceways. However, with these numbers relatively constrained, the determining factor for quantity of raceways is the area of bed required to produce 1,000kg of usable hydrogen gas per day. According to PSA modeling and conversations with PSA manufacturer UOP, PSA systems operating on H₂/O₂ gas mixtures can achieve approximately 90% hydrogen recovery. As mentioned earlier, the LDPE film is only 90% transparent as well. Thus we must oversize the reactor bed in order to account for both this photon loss and PSA hydrogen losses and achieve the target net 1,000kgH₂/day. Based on the efficiency assumptions of the particular system involved, the average insolation data referenced earlier, and the assumed conversion efficiency of photons to hydrogen also mentioned earlier, we integrated the hourly H₂ production to get a daily gH₂/m² rate. This, combined with our desired H₂ production level, allowed us to calculate the total production area required. Knowing the constraints of our raceway size mentioned earlier, we determined the quantity of raceways by dividing the total area needed by the size of an individual raceway.

5.2.2 Water Slip Stream Volume or Rates

Although organisms in hydrogen production mode generally grow at a reduced rate, there is some continual growth occurring. In order to maintain a constant concentration of organisms within the bed it is necessary to draw off a specific volume of water/organism solution to filter out the excess organisms. The specific slip stream volume required is based on the average doubling rate of our organisms. Using hourly solar intensity data and the corresponding organism growth rate, an iterative process determines that a removal rate

of 0.45%/hour of the total bed aqueous volume is needed to ensure that concentration is constant throughout the day. Each system has a different total reactor volume depending on the assumed efficiency of hydrogen production in the system. Making use of 0.45% of the overall volume of the system as the hourly removal mass fraction, the hourly slip stream volume is computed. This volume value is employed to size pumps, pipes, and saturation vessels. In the B-3 and B-4 system a slip stream of water will be pumped to the CO₂ saturation vessel for CO₂ addition necessary for the growth and regeneration phase. The volume of water drawn off was calculated by determining how much water is needed each day of the regeneration phase to fully absorb all the CO₂ that was bubbled into the headspace during the hydrogen production phase based on the CO₂ saturation rate of 1.4g/L.

5.2.3 Product gas storage under Film

As mentioned in Section 1.1.4, to keep compressor and PSA size down, the rate of gas drawn off of the raceways will not necessarily match the rate of gas production. As a consequence, excess gas will accumulate underneath the LDPE film. This accumulation will necessitate a surplus headspace volume above the liquid level of the bed and below the LDPE film. The LDPE film above the bed will rise as the gas accumulates during the day and fall as the gas is drawn out during the night. An excess of film material is needed to accommodate this film motion and avoid stretching of the film. In order to calculate the amount of extra film necessary, we used data from the NREL SOLPOS model combined with data from the NASA Atmospheric Data Center to calculate the amount of hydrogen gas being produced at 15 minute intervals during the month of June where insolation and corresponding hydrogen production will be at its peak^{55, 56}. Based on the molar ratios of each system, we calculated the amount of total gas produced for each 15 minute interval. Knowing the density and the molar ratios of the gas we calculated the volume. Using the volume of gas and the area of the raceway, we computed the total height required of the film to achieve that volume. Lastly, by subtracting a specific rate of gas every 15 minutes, we determined the minimum rate of gas removal that will leave no gas accumulated by the following dawn. According to our calculations, approximately 6cm of headspace is required to account for gas accumulation. The resulting gas removal rate is then used in PSA sizing.

5.2.4 Electricity Consumption

The power consumption of the system primarily comes from the Gas Capture Subassembly, with slight contributions elsewhere. The items consuming power are the compressor, PSA, pumps, nutrient metering pumps, rotary drum filters, paddlewheels and the control room. PSA power is minimal as it is only needed for air compression to actuate pneumatic valves. The power consumption of the pumps, nutrient metering pumps, rotary drum filters and paddlewheels all come from quotes we have received concerning these items and have been documented previously in this report. The gas compressor is assumed to be a 2-stage piston compressor (N=2) with interstage cooling. Its power was calculated by assuming isentropic compression from 20° C ambient temperature with efficiency, η , of 75%. Overall pressure ratio was 20.4 for an outlet pressure of 300psi.

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⁵⁵ NREL MIDS SOLPOS (Solar Position) model.

⁵⁶ NASA Atmospheric Data Center, Langley ASDC User Services, Surface meteorology and Solar Energy (SSE) data base (release 6.0).

$$P = \frac{dm}{dt} Cp T N \frac{1}{\eta} \left(\frac{P2^{\frac{\gamma-1}{\gamma N}}}{P1} - 1 \right)$$

Lastly, the power consumption of the control room was calculated by taking 5% of the overall power consumption of the plant. Given the relatively low power consumption of the control room and the ambiguity of all the different power consuming devices it might contain, this fairly conservative estimate is adequate. Figure 5-2 lists the electricity usage anticipated for each of the components previously described and provides a total consumption value to be used in further analysis. The previously mentioned duty cycles and operational cycle have been taken into account in these computations.

B1 В2 В3 **B4 B5** Compressor kW 123 123 78 78 83 PSA kW 1 1 1 1 1 Pumps (3) kW 18 18 96.0 9 27 Nutrient Pump kW 1.5 1.5 1.5 1.5 1.5 Control Room 9.8 kW 9.8 13.5 4.5 12.7 Rotary Drum Filters kW 3.9 3.9 0.0 0 9 1 Paddlewheels kW 49.2 49.2 93.5 0 132.8 otal kW 206.4 206.4 283.7 94.2 267.0 1,581,043 kWh/yr 2,041,916 1,433,023 1,433,023 742,765 Jsage Rate kWh/kg H₂ 4.36 4.36 6.22 2.26 4.81 \$/yr \$70,957 \$70,957 \$101,106 \$36,778 \$78,286 \$/kg H₂ Cost \$0.20 \$0.20 \$0.28 \$0.10 \$0.22

Figure 5-2. Electricity Consumption per Pathway⁵⁷

5.2.5 Excavation of Land for Reactor Bed Placement

Because of the considerable size of the raceways, detailed attention was given to calculating an accurate cost for the construction of the reactor ponds. Consultation with Mark Dormsteader from Metro Earth Works, a company that focuses solely on earth moving projects, suggested that our project would require a loader, a dozer, and a roller. He said that medium sized equipment would be adequate for such a shallow pool depth. The project would also require a foreman and two laborers on foot. No dump truck for dirt removal will be necessary since all dirt excavated will be used in construction of the side and central berms. Assuming a standard 8 hour work day, it was estimated to take 5 days to construct one raceway. Since multiple teams of workers would be working simultaneously to build all the raceways necessary for a plant, the time per raceway constructed would be significantly reduced, however, the overall cost per raceway would remain the same, since increased workforce brings increased cost.

To calculate the wages of the workers, we used the Department of Labor's Davis-Bacon Wage Determinations for 2008, as referenced in the US Department of Agriculture's "Cost Estimating Guide for Road Construction", which provide a state by state breakdown of

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⁵⁷ Equipment consumptions rates are based on producing of $1,111kgH_2/day$. Yearly Consumption is based on all equipment operating 360days/yr, 24hrs/day, with the exception of paddlewheels, which operate only 12hrs/day. Consumption Rate/Hydrogen Product is based on final product of $1,000kgH_2/day$ over previously stated 360 days.

average wages for various jobs⁵⁸. We also used equipment rental costs referenced by this report taken from The Blue Book of Building and Construction. The cost for equipment rental and the wages vary widely, causing substantial variability in the construction price depending on location. Figure 5-3 shows some examples of wages and rental costs in the American Southwest. We chose the numbers corresponding to Californian wages and rental rates. Given the fact that the organisms involved in biohydrogen production are sensitive to temperature, we decided that a location with more moderate temperatures, yet still high levels of sunlight would be ideal. Thus, southern California, which has more moderate temperatures due to its proximity to the ocean, would be more ideal than desert areas in Arizona or Nevada. Although not considered in our analysis, the proximity to the ocean could also provide an added benefit: an endless supply of water for the system⁵⁹. Figure 5-4 shows the cost estimation for the B-1 system, which requires 20 raceways. Were the plant built in some other state, such as New Mexico, there would be up to a 50% reduction in construction costs.

Figure 5-3. Davis-Bacon Wage Determinations and Blue Book Rental Costs

TABLE 1 - HOURLY WAGE RATES

JOB CLASSIFICATION	AZ	CA	CO		ID		KS	NE	NE NV	
ZONE			1	2	1	2			LV	CAR-
										SON
										CITY
Foreman	44.44	78.84	43.87	45.46	45.73	47.91	23.89	23.84	71.06	63.33
General Laborer	25.69	49.97	22.15	28.63	39.75	41.93	13.76	13.06	50.89	38.71
Chainsaw Operator	26.05	52.97	25.98	29.69	40.26	42.44	15.20	17.63	51.28	39.09
Powderman	28.71	52.97	40.88	40.65	40.04	42.23	17.74	18.26	51.48	39.46
Wagon Drill Operator	40.02	69.43	40.88	41.10	43.55	45.74	17.01	18.26	51.35	39.09
Asphalt Spreader Operator	41.57	67.40	40.65	40.65	43.06	45.24	19.55	19.44	62.10	56.12
Backhoe Operator	40.80	69.51	29.00	29.00	43.42	45.61	18.10	15.50	66.45	57.48
Dozer Operator (1)	35.33	71.38	40.65	40.65	43.51	45.69	18.10	18.26	66.95	56.23
Dozer Operator (2)	40.02	71.38	40.65	40.65	43.51	45.69	18.10	20.15	66.95	58.55
Front End Loader Operator (1)	40.02	71.38	40.65	40.65	43.06	45.24	18.10	17.94	66.45	58.01
Front End Loader Operator (2)	41.57	73.50	40.88	40.88	43.31	45.49	18.10	19.04	67.13	58.65
Grader Operator	41.57	75.77	28.73	40.88	43.51	45.69	19.55	18.93	67.10	58.29
Heavy Duty Mechanic/Welder	35.56	71.38	29.25	41.10	43.51	45.69	21.00	20.38	68.60	57.48
Hydraulic Excavator Operator	41.57	75.77	40.88	40.88	44.09	46.28	19.55	19.75	67.38	61.11
Truck Driver (1)	31.94	56.92	25.01	27.62	41.13	43.31	17.38	15.19	54.29	34.67
Truck Driver (2)	32.83	57.38	25.01	28.12	41.39	43.57	18.10	17.08	55.26	40.48
Roller Operator Compaction	35.33	68.31	40.65	40.65	42.61	44.79	17.38	15.19	54.29	34.67

LOADERS:

Crawler type, diesel powered, with EROPS:

Model	Bucket Size	Hourly Rate (\$)					
	Cubic Yards	AZ,NM,UT	CO,ID,KS,NE,NV	CA,SD,WY			
Caterpillar 933C	1.30	41.72	43.33	45.42			
Deere 555G	1.50	51.52	53.56	56.21			
Caterpillar 953C	2.42	84.96	88.76	93.68			
Caterpillar 963C	3.20	110.46	115.20	121.34			
Caterpillar 973C	4.19	161.25	168.29	177.42			

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Moll, Jeff, Marjorie Apodaca, Ken Goddard, Jon Stites, Andrea Glover. Cost Estimating Guide for Road Construction. US Forest Service, USDA, Washington DC. April 2008.

While some organism may flourish in sales.

⁵⁹ While some organism may flourish in saltwater, we assume fresh water for all of the biohydrogen systems under analysis. Consequently, a desalination plant would be necessary to achieve unlimited water from the ocean.

Figure 5-4. Excavation Cost Estimate for B-1 System using California Costs

Excavation Cost Estima	tion fo	r California
Equipment Cost- Loader		93.68 \$/hr
Equipment Cost- Dozer		94.25 \$/hr
Equipment Cost- Roller		74.3 \$/hr
Operator Cost- Loader		71.38 \$/hr
Operator Cost- Dozer		71.38 \$/hr
Operator Cost- Roller		68.31 \$/hr
Laborer Cost		49.97 \$/hr
Foreman Cost		78.84 \$/hr
Number of Laborers		2
Number of Operators		3
Total Cost/ day	\$	5,217
Total Cost/ pool	\$	26,083
Total Cost/ system	\$	521,664

The excavation costs calculated concern only the construction of the raceways and the berms. The installation costs of the other components in the system are computed using the H2A methodology.

6. <u>Levelized Costs Assumptions & Calculations (H2A)</u>

Thus far, this report has discussed the capital cost and expenditures associated with building a photobiological-to-hydrogen plant. While this is critical and valuable information, the build decision is ultimately based on the financial and economic benefits of these capital expenditures. The investment is quite large and cannot be properly evaluated without some knowledge of the expected return on that investment. In order to evaluate the return, DTI performed a discounted cash flow (DCF) analysis using the H2A Production Model, Version 2.0.

The H2A model provides a structured format for a user to enter in parameters which impact cash inflows and outflows associated with the construction and operation of the plant. There are H2A Default values for several of the parameters which can be selected as part of the analysis. Additionally, there are plant specific parameters which the analyst must enter.

Once all parameters have been entered the H2A model computes the levelized cost of hydrogen in \$/kgH₂.⁶⁰

6.1 Standard H2A parameters

In order to develop levelized costs, several parameters must be defined. Because this analysis focuses on a plant which is still in its conceptual stage, many of the values for these parameters must be assumed. The assumptions are documented in this section. These are meant to represent a baseline system and analysis. Later in the discussion portion of this report, the assumed values can be altered for sensitivity analyses.

Standard H2A financial values and assumptions shown in Figure 6-1 apply to all biohydrogen pathways. This list does not encompass all parameters which must be defined in order to run the analysis; just those were there is an H2A Default value which has been accepted for this analysis. The remaining parameters are defined later in this section. Some of those parameters are common to all biohydrogen pathways and others are pathway specific. No dispensing parameters are listed here because the biohydrogen plants are central type plants and thus dispensing is not factored into the analysis.

⁶⁰ For further description of the H2A Model reference, D. Steward, T. Ramsden, and J. Zuboy. H2A Production Model, Version 2 User Guide. NREL/TP-560-43983. Golden, CO. September 2008.

fault Values and Assumptions used for all Richydrogen Pathways 61

gure 6-1. H2A Default Values and Assumptions used for all Biohydrogen Pathways ⁶¹					
Parameter	Assumptions				
Analysis Period	20 years				
Burdened Labor Rate for Staff	\$50/hour				
CO2 Capture Credit	Not included in base cases (default				
-	value = 0)				
CO2 Production Taxes	Not included in base cases (default value = 0)				
Construction Period and Cash Flow	1 year				
Co-produced and Cogenerated Electricity Price	\$30/MWh				
Decommissioning	10% of initial capital				
Depreciation Type and Schedule for Initial	MACRS: 20 years for central model				
Depreciable Capital Cost	•				
Facility Life	20 years				
G&A Rate	20% of the staff labor costs				
Hydrogen Pressure at Central Gate	300 psig				
Hydrogen Purity ⁶²	98% minimum; CO < 10 ppm, sulfur <				
	10 ppm				
Income Taxes	35% federal; 6% state; 38.9% effective				
Inflation Rate	1.9%, but with resultant price of				
	hydrogen in reference year constant				
	dollars				
Installation Cost Factor	1.3				
Land Cost	\$5,000/acre purchased				
Licensing, Permits and fees	\$1000				
O2 Credit	Not included in base cases				
Production Maintenance & Repairs	½% of direct capital cost				
Property Taxes and Business Insurance	2%/year of the total initial capital cost				
Reference Financial Structure	100% equity with 10% IRR; includes				
	levelized hydrogen price plot for 0%-				
	25% IRR; model allows debt financing				
Sales Tax	Not included on basis that facilities and				
	related purchases are wholesale and				
	through a general contractor entity				
Salvage Value	10% of initial capital				
Working Capital Rate	15% of the annual change in total				
	operating costs				

 $^{^{61}}$ D. Steward, T. Ramsden, and J. Zuboy. H2A Production Model, Version 2 User Guide. Appendix 3: Default Values and Assumptions. NREL/TP-560-43983. Golden, CO. September 2008. p. 60. 62 Purity levels are driven by H_2 vehicle consumption requirements.

6.2 Pathway Common Parameters

In addition to the financial parameters defined by H2A in the previous section there are other project inputs which must be quantified in order to carry out the DCF analysis. All inputs can be found on the following worksheets in the H2A model;

- Input_Sheet_Template
- ReplacementCosts
- CapitalCosts

Many of these parameters are specific to the location, operation, and type of plant. In the case of our biohydrogen pathways there are some parameters that are the same for all pathways and some that vary by pathway. The parameters in Figure 6-2 are common to all pathways.

Figure 6-2. Parameters Common to all Pathways

Parameter	Assumed Value	Worksheet
Operating Capacity Factor	90%	Input_Sheet_Template
Reference Year Dollars	2005	Input_Sheet_Template
Site Preparation	1% of direct costs minus raceway excavation costs	Input_Sheet_Template
Engineering & design	7% of direct costs	Input_Sheet_Template
Process Contingency	20% of direct costs	Input_Sheet_Template
Project Contingency	\$0	Input_Sheet_Template
Up-Front Permitting Costs	0.5% of direct costs	Input_Sheet_Template
Production Maintenance & Repairs	0.5% of direct costs	Input_Sheet_Template

6.2.1 Operating Capacity Factor

The operating capacity factor can be found on the Input_Sheet_Template worksheet of the model. This analysis assumes that the plant and dispensing station have a 90% operating capacity. This capacity factor takes into considering things such as planned maintenance outages, forced outages, etc. Thus, if the plant is capable of producing $1,111kgH_2/day$, only $1,000kgH_2$ will be dispensed and all economic benefit analysis is based on the amount dispensed or sold.

6.2.2 Reference Year Dollars

The reference year dollars parameter is the year dollars in which the cost of hydrogen is reported. The H2A standard is to report out hydrogen costs in 2005 dollars. The model expects capital costs to be entered in 2005 dollars. In this analysis Reference Year 2005 was selected

6.2.3 Site Preparation

The site preparation parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 1% of direct costs. This analysis uses the same default value; however, the cost basis is slightly altered. Our direct costs include excavation for raceways. We excluded that from the cost basis in this calculation since it is

not a piece of equipment, but rather a separately computed type of site preparation. Excavation is not all inclusive as site preparation is still required for things such as driveways, control building and algae feed subassembly.

6.2.4 Engineering & design

The engineering & design parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 13% of direct costs. This analysis uses 7% of direct costs due to the modularity of the design.

6.2.5 Process Contingency

The process contingency parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 15% of direct costs. This analysis uses 20% of direct costs due to uncertainties in the system configuration.

6.2.6 Project Contingency

The process contingency parameter can be found on the Input_Sheet_Template worksheet of the model. In our analysis we have chosen to include all contingency factors in the process contingency parameter, thus the project contingency is set to \$0.

6.2.7 Up-Front Permitting Costs

The up-front permitting cost parameter can be found on the Input_Sheet_Template worksheet of the model. The H2A default for this parameter is 9% of direct costs. This analysis uses 0.5% of direct costs due to the modularity of the design and its environmental benefits.

6.3 Pathway Specific Parameters

The last types of parameters we identify are those which are specific to each pathway analyzed. Figure 6-3 lists these parameters and rules of thumb applied in computing their values. These are pathway specific because they are associated with feedstock, process design and plant design.

Figure 6-3. Pathway Specific Parameters

Parameter	Rule Applied	Worksheet
Land Required	30% greater than reactor	Input_Sheet_Template
	bed area	
Production facility plant staff	1 worker per shift per	Input_Sheet_Template
	100 raceways + 0.5	
	workers for winders	
Utility Usage	Electricity and water	Input_Sheet_Template
	costs use H2A pricing	
Feedstock Usage	As required by organism	Input_Sheet_Template
Specified Yearly Replacement	LDPE every 5 yrs	ReplacementCosts
Costs		

6.3.1 Land Required

The land required parameter can be found on the Input_Sheet_Template worksheet of the model. In developing the plant design, a land area for the reactor bed was computed. The analysis assumes that the total land required for this design is 30% greater than the reactor bed. The 30% factor is meant to encompass area requirements for pump skids, compressors, gas and algae separators and a small control room. The total land requirement for each pathway is shown in Figure 6-4.

Figure 6-4. Land Required for each Pathway

	Algal O ₂ - tolerant Hydrogenase (1)	Cyanobacterium O ₂ -tolerant Hydrogenase (2)	Algal Sulfate Permease	Immobilize d Algal, Sulfur deprived	PNS bacteria
Bed Area (m²)	B-1 80,968	B-2 80,968	B-3 151,035	B-4 352,070	B-5 216,228
% increase for auxiliaries	30%	30%	30%	30%	30%
Total Land Required (m ²)	105,259	105,259	196,345	457,691	281,096

6.3.2 Production facility plant staff

The production facility plant staff parameter can be found on the Input Sheet Template worksheet of the model. This represents the number of full-time employees required to operate the plant. There is no H2A default value for this. Our analysis for each of the pathways is shown in Figure 6-5. From our analysis we suggest 3 employees are needed for each 1,000kgH₂ module of the B-1, B-2, B-3, and B-5 system design. This is based on the assumptions that each worker can operate 5 of these modules simultaneously but the plant operates 24 hrs/day so three shifts are needed. In the case of the B-4 pathway, an additional employee is required for the manual transfer of algae films between ponds. However, the films only need replacement once every six months, limiting the overall labor needed.. We have assumed a wind and unwind speed of 0.5 ft/second for the polypropylene films. Two old films per raceway will need to be wound and unwound along with new films that will be wound and unwound for replacement. Additionally, we have assumed it will take 15 minutes to reposition and prepare the winder for each wind/unwind cycle. We calculated that it will take about eight hours, or one full FTE for a worker to complete the task of exchanging the mats in one raceway. Thus, the total labor need is the total number of raceways (90) divided by the number of work days in 6 months (120), giving us ~0.75 FTE in addition to the daily raceway operators.

Figure 6-5. Plant Staff Requirements for 1 tonne H₂/day plant

	Algal O2- tolerant Hydrogenase (1)	tolerant Cyanobacterium Algai Hydrogenase O2-tolerant Sulfate Hydrogenase (2) Permeas		Immobilized Algal, Sulfur deprived	PNS bacteria
	B-1	B-2	B-3	B-4	B-5
Modules	1	1	1	1	1
Raceways/ Module	20	20	38	68	54
Raceways/ Worker	100	100	100	100	100
Shifts/Day	3	3	3	3	3
Workers FTE ⁶³	3	3	3	3	3
Winder Workers	N/A	N/A	N/A	0.5 FTE	N/A
Total FTE	3	3	3	3.75	3

6.3.3 Energy Usage

The usage of utilities, feedstocks and creation of byproducts can be found on the Input_Sheet_Template worksheet of the model. There are no H2A default values for these. We are not aware of any Byproducts associated with the bio-hydrogen pathways. In the case of utilities, the utility (electricity, natural gas, steam) of interest is selected from a drop-down box. The amount consumed is based on the plant design and thus varies. For our $1,000 \text{kgH}_2/\text{day}$ system those quantities are shown in Figure 6-6. The model has a cost rate for each utility and thus computes the total costs of utilities.

Figure 6-6. Utilities Usage

	Algal O2- tolerant Hydrogenase (1)	Cyanobacterium O2-tolerant Hydrogenase (2)	Algal Sulfate Permease	Immobilized Algal, Sulfur deprived	PNS bacteria
	B-1	B-2	B-3	B-4	B-5
Electricity (kWh/kgH ₂)	4.36	4.36	6.22	2.26	4.81
Water (gal/kgH ₂)	2.900	2.900	2.852	2.864	1.479

In our bio-hydrogen pathways the feedstocks are nutrients and CO₂ which are not H2A options that can be selected from the drop-down box. Therefore the usage, price and heating value of each feedstock must be entered manually. Those pathway specific required inputs are shown in Figure 6-7.

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⁶³ Full Time Equivalent

Figure 6-7. Feedstock Usage

Carbon Dioxide							
Value	Unit	B1	B2	В3	B4		
Lower Heating Value	mmBTU/ Short Ton	9.37	9.37	9.37	9.37		
Price Startup Year	\$/Dry Short Ton	\$ 1,400	\$ 1,400	\$ 1,400	\$ 1,400		
Startup CO2	lb	5,241	5,241	41,629	206,180		
Usage	lb/day	566	566	-	-		
Usage	DryTon/kg H2	2.83E-04	2.83E-04	0.00E+00	0.00E+00		

Nutrients							
Value Unit B1 B2 B3 B4 B5							
Lower Heating Value	mmBTU/ Short Ton	28.44	28.44	28.44	28.44	28.44	
Price Startup Year	\$/Dry Short Ton	400	400	400	400	400	
Usage	DryTon/kg H2	1.16E-07	1.16E-07	2.16E-07	5.03E-07	3.09E-07	

6.3.4 Specified Yearly Replacement Costs

The specified yearly replacement costs can be found on the Replacement Costs worksheet of the model. There is no H2A default value for this. This analysis recognizes that the transparent film which serves to capture product gas, permit sunlight, and keep culture free of contamination will need periodic replacement. The film is made of LDPE and over time will degrade such that less sunlight will enter the system thereby lowering plant efficiency. This analysis assumes that a 5-yr replacement cycle for the LDPE film is sufficient to keep system performing at acceptable levels. All other components are anticipated to operate for 20 years. There are no other specified replacement costs over the twenty year analysis period for any of the pathways. Figure 6-8 lists the pathway specific costs associated with replacement components.

Figure 6-8. LDPE Film Replacement Costs

rigure 0-0. EDI E riiii Replacement Costs						
	Algal O2- tolerant Hydrogenase (1)	Cyanobacterium O2-tolerant Hydrogenase (2)	Algal Sulfate Permease	Immobilized Algal, Sulfur deprived	PNS bacteria	
	B-1	B-2	B-3	B-4	B-5	
Quantity of Film ⁶⁴ (m ²)	87,080	87,080	165,452	381,075	235,116	
Costs (yrs. 5, 10, 15)	\$60,932	\$60,932	\$115,770	\$205,113	\$164,516	

6.3.5 Baseline Uninstalled Costs

The baseline uninstalled costs can be found on the Capital Costs worksheet of the model. There is no H2A default value for this. These are the capital costs of the equipment that were computed in an earlier part of this project. Those separately calculated values will be imported into this area of the H2A Production Model to access the economic benefit of the capital expenditure. These costs are provided in the bill of materials for each pathway.

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⁶⁴ Quantity includes pathway area and overages explained in Section 5.1.2.

6.3.6 Installation Cost Factor

The installation cost factor parameter can be found on the Capital Costs worksheet of the model. The default value for this is 1.3, however there is an exception. The installation of the reactor beds doesn't rely on a cost factor but rather performs a separate excavation cost calculation which was described above.

6.4 Results for Levelized Hydrogen Costs

The results from the H2A model are provided in tabular form. The total cost of produced hydrogen in a 10 tonne per day (TPD) plant⁶⁵ is provided as well as the cost breakdown of that value over several cost components. Our analysis indicates that for a 10 TPD plant the B-1 and B-2 pathways produce the lowest cost hydrogen as shown in Figure 6-9. B-1 and B-2 provide identical cost of hydrogen because the key assumptions effecting cost are the same for these two pathways. The primary components of the levelized cost of hydrogen are capital costs, fixed O&M and other variable costs as shown in Figure 6-10. The discussion section of this report will delve further into the costs included in these components.

Figure 6-9. Levelized costs for B-1 through B-5 Pathways

Total Cost of Produced H 2						
Cost Component	Hydro	Hydrogen Production Cost Contribution (\$/kg)				
System	B1	B2	B3	B4	B5	
Capital Costs	\$1.74	\$1.74	\$2.82	\$3.87	\$3.37	
Decommissioning Costs	\$0.02	\$0.02	\$0.03	\$0.04	\$0.03	
Fixed O&M	\$0.60	\$0.60	\$0.99	\$1.99	\$1.27	
Feedstock Costs	\$0.40	\$0.40	\$0.00	\$0.00	\$5.43	
Other Raw Material Costs	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	
Byproduct Credits	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00	
Other Variable Costs (including utilities)	\$0.23	\$0.23	\$0.33	\$0.12	\$0.25	
Total	\$2.99	\$2.99	\$4.17	\$6.02	\$10.36	

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⁶⁵ Cost results are based on a 10 metric ton per day hydrogen plant composed of ten 1 metric ton per day modules.

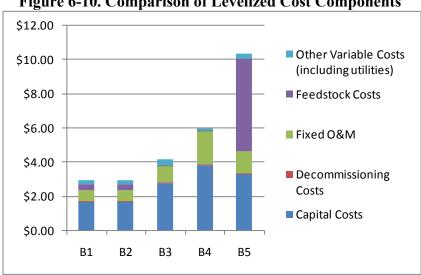


Figure 6-10. Comparison of Levelized Cost Components

6.5 Near Term Performance Results

In addition to calculating the results for the upper bound solar-to-hydrogen (STH) conversion efficiencies, which has been explicated thus far in the report, we also calculated levelized hydrogen costs for "near term" STH efficiencies.

The upper bound performance projections for the B-1, B-2, B-3, and B-5 assume that there is full utilization of the solar photons for hydrogen production due to development of mutants that have reduced antennas and do not have saturation and other electron transfer limits. For near term organisms, utilization will be significantly less than 100%, but is expected to be better than the current status. Based on these anticipated developments, we have made estimates of the organisms' near term properties and estimated the consequent near term production capabilities.

Assumed near term solar-to-hydrogen (STH) conversion efficiencies are shown in Figure 6-11 along with the previously discussed upper bound efficiencies for convenient comparison. . For B-4, the upper bound solar utilization comes from the NREL extrapolation of experimental results to generate a model of the best possible future performance level of B-4. For the B-4 near term projection, we have assumed a reduction in utilization from that best future performance upper bound.

Levelized H₂ costs corresponding to the near term efficiencies are shown in Figure 6-12. The primary components of the levelized cost of hydrogen are capital costs, fixed O&M, and "Other Variable Costs".

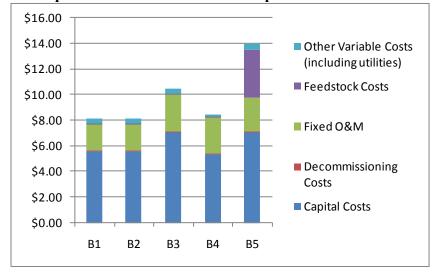
Figure 6-11. Near Term STH Efficiency Assumptions

STH Efficiency	B1	B2	В3	B4	B5
Upper Bound	9.2%	9.2%	5.2 %	2.25%	3.5%
Near Term	2%	2%	1.3%	1.5%	1.5%

Figure 6-12. Levelized H₂ Costs based on Near Term STH Efficiency

Total Cost of Produced H 2								
Cost Component	Hydro	Hydrogen Production Cost Contribution (\$/kg)						
System	B1	B1 B2 B3 B4 B5						
Capital Costs	\$5.61	\$5.61	\$7.04	\$5.36	\$7.10			
Decommissioning Costs	\$0.06	\$0.06	\$0.07	\$0.05	\$0.07			
Fixed O&M	\$2.08	\$2.08	\$2.96	\$2.92	\$2.62			
Feedstock Costs	\$0.00	\$0.00	\$0.00	\$0.00	\$3.73			
Other Raw Material Costs	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00			
Byproduct Credits	\$0.00	\$0.00	\$0.00	\$0.00	\$0.00			
Other Variable Costs (including utilities)	\$() 4 1	\$0.41	\$0.41	\$0.11	\$0.44			
Total	\$8.15	\$8.15	\$10.48	\$8.44	\$13.95			

Figure 6-13. Comparison of Levelized Cost Components for Near Term Efficiencies



7. Discussion of Results

The results discussion will look at how plant sizing impacts the key costs components of levelized costs, namely, capital costs, fixed O&M, and variable costs. An explanation for the low feedstock costs is also provided.

This report's baseline cost analysis assumes a 10 TPD plant consisting of ten 1 TPD modules. One would expect that the levelized costs results from H2A would be different if the plant size chosen was different. Plant sizes of 1TPD, 50TPD and 100TPD were reviewed and our analysis shown below indicates that the 10TPD facility was appropriate for this analysis.

7.1 Capital Costs

Because this analysis is developing a large plant size from several smaller modules, one would expect equipment cost advantages based on modularity. However, recall that each 1

TPD module already has multiple raceways resulting in large quantities of similar components within a single module. Additional capital cost reductions as a result of increased purchase quantity are likely to be minimal since the quantity of most materials is already substantial for one module. The smallest module considered amongst our five pathways has twenty raceways, and the costing already employs a significant economy of scale. Further scaling of lower quantity, larger items, such as drum filters could result in further cost reduction, but has not been considered in this report primarily because low yearly sales of these items makes scaling data unavailable.

Additionally, most components selected are available commercially off the shelf (COTS) and costs were obtained using vendor quotations. Because of this, the capital costs for each module already take into account commodity; high volume pricing and thus capital costs due to large plant size are expected to increase linearly. Figure 7-1 demonstrates the relationship between capital costs and plant size.

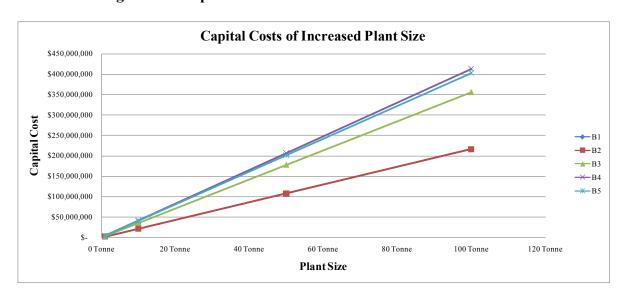


Figure 7-1. Capital Cost Increases from Increased Plant Size⁶⁶

Exceptions to this COTS and high volume logic are the compressors and PSAs that are sized for 1TPD modules. Given the extremely large areas of a single module, we chose not to combine several modules into a common compressor and PSA due to the difficulty of transporting low pressure gas over long distances. Furthermore, unlike the other equipment whose costs were obtained from vendor quotes, the cost of compressors and PSAs are derived from H2A unit costing models. However those models already have built in assumptions to provide an nth unit cost so again no economy of scale can be assumed for these components.

Because the capital costs do not achieve economy of scales we explored fixed O&M for an indication of optimal plant size.

 $^{^{66}\}mathrm{B1}$ and B2 are the exact same and overlap on the graph, which is why B1 does not show up on the graph

7.2 Fixed O&M (Plant Labor)

After capital cost component, fixed O&M is the next largest cost component of the levelized hydrogen cost. Within H2A the fixed O&M consists of primary of labor, G&A (which is a percentage of labor), Property Taxes (which is a percentage of capital costs), and Production Maintenance and Repair (which is a percentage of capital costs). Since we have already established that capital costs scale linearly, we focus on plant labor costs.

One of the most significant differences in plant sizes is the amount of labor needed. Labor rates for a 1, 10, 50, and 100 TPD plant were examined. A summary of the assumed labor requirements and rates is shown in Figure 7-2. The analysis assumes that the plant will need constant supervision (3shifts/day) from workers who can fix any equipment malfunction and monitor plant operation. We assume one worker can effectively watch over 100 raceways working a standard 8-hour shift. Additionally, for the multiple module plants, an overall supervisor will be needed. For the 100 TPD plant, an assistant supervisor is added due to the extremely large area of such the plant. The B-4 system requires an extra worker in order to change one roll of immobilized algae film per day.

Figure 7-2. Labor Assumptions for Different Plant Sizes

	B1/B2				В3			
	1 ton	10 ton	50 ton	100 ton	1 ton	10 ton	50 ton	100 ton
Modules	1	10	50	100	1	10	50	100
Total Raceways	20	200	1000	2000	38	380	1900	3800
Raceways/Worker	100	100	100	100	100	100	100	100
Shifts/Day	3	3	3	3	3	3	3	3
Workers FTE	3	6	30	60	3	12	57	114
Roll/Unroll Workers	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Supervisor FTE	0	3	3	3	0	3	3	3
Asst. Super. FTE	0	0	0	1	0	0	0	1
Total FTE	3	9	33	64	3	15	60	118
FTE/1TPD Module	3	0.9	0.66	0.64	3	1.5	1.2	1.18
	B4				В5			
	1 ton	10 ton	50 ton	100 ton	1 ton	10 ton	50 ton	100 ton
Modules	1	10	50	100	1	10	50	100
Modules Total Raceways	1 90	10 900	50 4500	100 9000	1 54	10 540	50 2700	100 5400
	_				_			
Total Raceways	90	900	4500	9000	54	540	2700	5400
Total Raceways Raceways/Worker	90 100	900 100	4500 100	9000 100	54 100	540 100	2700 100	5400 100
Total Raceways Raceways/Worker Shifts/Day	90 100 3	900 100 3	4500 100 3	9000 100 3	54 100 3	540 100 3	2700 100 3	5400 100 3
Total Raceways Raceways/Worker Shifts/Day Workers FTE	90 100 3	900 100 3 27	4500 100 3 135	9000 100 3 270	54 100 3	540 100 3 18	2700 100 3 81	5400 100 3 162
Total Raceways Raceways/Worker Shifts/Day Workers FTE Roll/Unroll Workers	90 100 3 3 0.8	900 100 3 27 8	4500 100 3 135 38	9000 100 3 270 75	54 100 3 3 N/A	540 100 3 18 N/A	2700 100 3 81 N/A	5400 100 3 162 N/A
Total Raceways Raceways/Worker Shifts/Day Workers FTE Roll/Unroll Workers Supervisor FTE	90 100 3 3 0.8	900 100 3 27 8 3	4500 100 3 135 38 3	9000 100 3 270 75 3	54 100 3 3 N/A 0	540 100 3 18 N/A 3	2700 100 3 81 N/A 3	5400 100 3 162 N/A 3

When these plant sizes are analyzed in H2A, hydrogen costs decrease with plant size as shown in Figure 7-3. This study indicates labor cost reductions are achieved through increasing plant size. In all cases most of the cost benefit is gained in the initial increase in plant size, with the curve flattening towards a 100TPD system. Therefore, it is appropriate to choose the 10TPD plant for analysis. This is also intuitive from the labor assumptions in Figure 7-2 where a comparison in Total Raceways and Raceways/Worker shows that in the 1 ton module workers are underutilized.

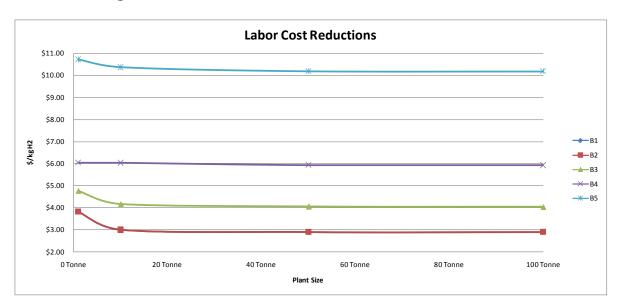


Figure 7-3. Labor Cost Reductions from Increased Plant Size

7.3 Variable Costs

The third largest cost component of the levelized hydrogen cost is variable cost. Within H2A the variable costs consists of utilities, byproduct credits, waste costs, and tax incentives. In our analysis only utilities (specifically electricity) are considered. Since electricity consumption is based on the equipment and we have chosen to duplicate modules and therefore equipment in the larger plants, variable costs are expected to be constant per kgH₂ produced regardless of plant size.

7.4 Feedstock Costs

Feedstock Costs are essentially the cost of nutrients. As we can see they are minimal in all pathways except B-5, where the cost of acetate is substantial. Since nutrient quantity is based on algae and area then we expect the relationship with plant size to be linear. Nutrient costs are currently derived from price quotes for high-quantity agriculture fertilizer purchases and data on international market prices for acetate. Considering the low level of nutrients consumed compared to conventional agriculture, change in pricing due to increased plant size is negligible and ignored.

7.5 Reactor Footprint

Thus all systems produce the same amount of hydrogen. However, due to varying efficiencies, the five systems result in vastly different land area requirements. If we were to normalize based on the land area, or reactor footprint, for the 1 TPD module we can analyze the production data in a different way. Choosing the area of the B-4 systems which has the largest reactor footprint, in Figure 7-4 we show the hydrogen outputs of each system if scaled to match the land area of B-4. This is an important consideration in areas where land may be in short supply.

Figure 7-4. Normalized Hydrogen Production

System	B-1	B-2	B-3	B-4	B-5
Reactor Size (m ²)	352,070	352,070	352,070	352,070	352,070
Algae Removed (kg/day)	175	175	NA	NA	468
Hydrogen Production (kgH ₂ /day)	4,348	4,348	2,331	1,000	1,628

8. Photobiological System Conclusions and Recommendations

Under the premise that low cost hydrogen is the most important factor, then the H2A analysis points us to B-1 and B-2 pathways as the best photobiological pathways. However, one engineering concern for B-1 and B-2, which produce stoichiometric mixtures of hydrogen and oxygen, is to assure that the gases are isolated from any potential ignition sources. Before moving forward with any given system further, additional sensitivities should be done on key assumptions in this analysis. In the previous section we explored the assumptions of plant size and modular design. One parameter that could be further tested is the impact of plant efficiency on levelized costs. The characterization section of this report identified 3 efficiencies for each system: maximum theoretical, assumed reactor operation, and current experimental data. This baseline analysis is based on the assumed reactor operation. However if that value cannot be reached, the impact on cost can be great. Another parameter to consider is component lifetime, which impact replacement costs. Sensitivities on labor rates for plant personnel could also be performed. Furthermore, the probability of success and commercialization timeline of all systems should be considered prior to eliminating any pathway from further analysis.

As mentioned in Section 6.4, a large portion of the levelized cost is from the capital costs of the plant. Figure 8-1 shows the contribution of each subassembly to the overall plant costs. The most costly subsystems are the Photobioreactor and Control System.

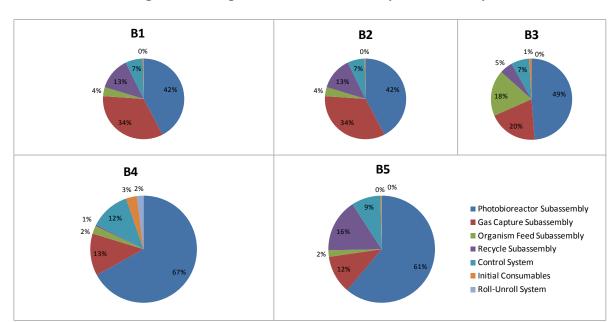


Figure 8-1. Capital Cost Allocations by Subassembly

Within the photobioreactor subassembly the largest cost contributors are the pond installation and paddlewheel mixers. The pond installation is directly proportional to the number of raceways. The costs of the installation were well vetted as described in Section 5.2.5. The plant location could affect labor costs associated with installation and could "provide some relief to capital cost. The second largest cost contributors to this subassembly are the paddlewheel mixers. These costs are well known. The quantities required are conservative estimates based on the land area and water depth. Further research could be done in this area to see if more cost effective mixing solutions are available for our area and bed depth. Any other solutions should have a similar lifetime to be cost effective or significantly cheaper to offset replacement costs.

The control system subassembly has two items which are of large costs. These are the gas analyzers and level indicators. Rather than placing a gas analyzer in each raceway H2 outlet pipe, we group the outlet of two raceways into one analyzer to reduce cost. If the sensor indicates a problem with the gas steam, a worker would need to identify which of the two raceways is affected using a handheld gas analyzer: this approach is considerably less expensive. An important consideration with this equipment is that each raceway contains one of these items thus a cost savings in a single unit is magnified by the number of raceways. Currently the lifetime on all this instrumentation is equal to the plant life so any substitute equipment should have similar lifetimes or take into account replacement costs. Rather than assume that each raceway is instrumented, a separate analysis could consider these instruments as portable. In that way there would be 1 of each sensor per worker rather than per raceway. This method would rely more heavily on the plant personnel which may diminish the number of raceways that can be monitored per worker. This tradeoff could be considered as a separate sensitivity study.

9. Part 1 Appendix A: Key Terms and Definitions

Solar-to-Hydrogen (STH) Efficiency (in %): This is the ratio of the Lower Heating Value (LHV) of the net hydrogen produced from the system divided by the total solar energy input striking the biological beds. Hydrogen LHV is defined to be 33.33kWh/kg⁶⁷. Solar input is defined as total photon energy striking the bed measured in W/m². We typically use daily averages and thus base efficiency calculations on the average Southwest US insolation (average over the year) of 5.5kW/m²/day.

Maximum Theoretical Solar-to-Hydrogen (STH) Efficiency (in %): Converting all of this $5.5 \text{kW/m}^2/\text{day}$ insolation into electrons used for H_2 production yields a 12.2% STH efficiency. Thus our nominal 9.2% STH is close to the theoretical maximum. The 12.2% max efficiency is based on:

1000W/m² full sunlight intensity with 44% PAR (photosynthetically active radiation) and an average wavelength of 550 nm (average of 400-700nm)

=> Photon density of 2.024×10^{-3} ein/m²/s hitting the surface of the water.

Since it takes 4 photons to make an H₂, the maximum energy of H₂ produced from conversion of all of the photons is:

 $(2.024 \times 10^{-3} \text{ ein/m}^2/\text{s}) \times (\text{mol H}_2/\text{4 mol photons}) \times (2.016\text{g H}_2/\text{mol H}_2) \times (\text{kg H}_2/1000\text{g H}_2) \times (33.33 \text{ kWh H}_2/\text{kg H}_2) \times (3600\text{s/hr}) = 0.122 \text{ kWH}_2/\text{m}^2$

Taking the ratio of hydrogen energy to the photon energy yields the maximum Solar-to-Hydrogen efficiency:

 $(0.122 \text{kWH}_2/\text{m}^2) / (1.0 \text{kWphoton/m}^2) = 12.2\%$

Solar Peak Intensity and Daily Variation (W/m²): Based on actual daily intensity data with amplitude varied to achieve the target total solar daily insolation (5.5kWh/m²/day).

Doubling Time (in hours): The time, for an algal colony to double in concentration. Typically based on constant 1000W/m^2 sunlight irradiance.

Hourly Algae Renewal Fraction (in %): This term is the reactor bed volume fraction that is removed every hour. Removal of algae is necessary to maintain a constant colony of living algae both to remove dead/unproductive algae and/or to remove new growth. It is assumed that all algae (dead, young, and old) are evenly mixed together and preferential removal is not possible. Thus all performance numbers are based on average algae performance.

Growth Reactor: A bioreactor with the main function of promoting algae growth.

Production Reactor: A bioreactor with the main function of promoting hydrogen production.

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⁶⁷ The HHV is defined to be 39.4 kWh/kgH2.

Four types of Systems are analyzed:

Single Bed: In this cyclic bioreactor, a single bed first functions as a growth reactor (typically 1-4 days) and then switches to a production reactor (for 1+ day). The end of the production phase is determined by the H₂ production rate dropping below a threshold limit due to death or other impairment of the algae. At the end of the production phase, the bed either returns to the growth phase to rejuvenate the algae or becomes partially or completely removed from the reactor and replaced with fresh, healthy algae.

Dual Bed: In the cyclic bioreactor system, a first bed serves as a growth reactor to supply algae to the production reactor second bed. After the algae in the production reactor reaches the end of its useful life, the algae is removed from the reactor.

Chemostat: Derived from Chemical environment is static, a chemostat system is one in which fresh medium is continuously added to the reactor and "old" reactor medium is continuously removed, so that the reactor volume remains constant. In this embodiment, two reactors are used, a growth reactor and a production reactor, but their operation is constant rather than cyclic. The growth reactor continuously produces new algae at a rate that is fed into the production reactor. The production reactor has the same mass rate removed to maintain the mass balance. A centrifuge separates the water from the "dead" algae with the water being recycled back to the growth reactor and the algae going to a landfill or fermentation unit.

Chemostat II: The Chemostat II is a single bed chemostat system in which growth and production occur simultaneously in the same reactor. In this yet unproven, idealized system, a portion of the incident photon energy (ideally 22%) is used for cell maintenance (i.e. to keep the algae cells unstressed and healthy) and the remaining photon energy (78%) is used for H_2 production for a net Solar-to-Hydrogen efficiency of 9.2%.

Algae Capture Fraction (in %): The mass capture fraction of algae that is separated by the filter (centrifuge or drum filters). This is nominally 99%. Once separated, the algae enter a fermentation unit or are sent to a landfill.

Algae Water Content (in %): This refers to the water fraction of the algae after it is separated from the renewal fraction by the filters. This is nominally 90%.

10. Part 1 Appendix B: Mass Balance

Mass Balance H₂ Production Phase									
	B1 (daily)	B2 (daily)	B3 (3 days)	B4 (2 days)	B5 (daily)				
Start Conditions - H ₂ Produdction									
Algae	1,622	1,622	74,187	98,821	4,330				
Inputs - H ₂ Production									
Process Water	10,985	10,985	38,807	22,367	5,614				
Nutrients	0	0	-	-	9,113				
CO ₂	257	257	-	-	-				
Total	12,863	12,863	112,994	121,188	19,058				
Outputs - H ₂ Production									
H ₂	1,111	1,111	8,235	4,706	1,111				
O_2	9,005	9,005	-	-	-				
H ₂ 0	-	-	-	-	168				
H₂0 Vapor (Evaporation)	951	951	2,010	1,340	650				
CO ₂	-	-	68,696	1,999	606				
Dissolved CO ₂	-	-	21,173	49,355	11,725				
Waste Algae	175	175	-	-	468				
Algae	1,622	1,622	12,879	63,789	4,330				
Total	12,863	12,863	112,994	121,188	19,058				
Balance	0.0	0.0	0.0	0.0	0.0				

Mass Balance Growth Phase									
	B1	B2	B3 (4 days)	B4 (2 day)	B5				
Start Conditions - Growth									
CO ₂ (Dissolved in water)			21,173	1,999					
Algae			12,879	63,789					
Inputs - Growth									
CO ₂ (from PSA)			68,695	49,354					
Process Water			39,477	22,367					
Nutrients			1	1					
Total			142,225	137,509					
Outputs Growth									
Algae			74,187	98,821					
H₂O Vapor (Evaporation)			2,680	1,340					
O ₂			65,359	37,347					
Total			142,225	137,509					
Balance			0.0	0.3					

Ma	Mass Balance Initial Growth Phase									
	B1 (2 days)	B2 (2 Days)	B3 (2 days)	B4 (2 days)	B5 (2 days)					
Inputs - Initial Colony Growth										
Algae	-	-	-	-	-					
Process Water	973	973	7,730	38,286	-					
Nutrients	0	0	0	1	7,793					
CO ₂	2,377	2,377	18,879	93,505	0					
Total	3,350	3,350	26,610	131,793	7,793					
Outputs - Initial Colony Growth										
Algae	1,622	1,622	12,879	63,789	4,330					
H ₂ O	-	-	-	-	1,559					
O ₂	1,728	1,728	13,730	68,004	1,904					
Total	3,350	3,350	26,610	131,793	7,793					
Balance	0.0	0.0	0.0	0.0	0.0					

Days of B3 Growth Mode	4
Days of B4 Growth Mode	1
Overall Growth of B3 in Full Growth Mode	5.76
Overall Growth of B4 in Full Growth Mode	1.55
Starting Concentration of Algae in B3	0.85 g/l
Starting Concentration of Algae in B4	1.81 g/l
End Concentration of Algae in B3	4.91 g/l
End Concentration of Algae in B4	2.80 g/l

Part II: Algae Fermentative H₂ Production Systems

11. Introduction

As mentioned previously in this report, a constant slip stream will be removed from the raceways in the B-2, B-2, and B-5 systems to ensure that the organism concentration remains static. There is no way to ensure that the organisms removed in the slip stream are all exhausted organisms, thus the slip stream volume will be a mix of old exhausted and new replete organisms. The organisms removed from this slip stream will from here on be referred to as waste organisms. These organisms, while spent of their photo-hydrogen capabilities can still produce hydrogen through a fermentation process. In order to obtain maximal H₂ production, Part II of this report addresses use of the waste organisms as feedstock to a fermentation process using hydrogen-generating bacteria to produce additional H₂. The process yields and economics will build on the analysis already completed for the Part I photobiological systems.

In Part I of this report, five photobiological hydrogen production systems were defined: three of the five pathways generate a stream of waste organisms suitable for subsequent fermentation. For the B-3 system, an increase in organism mass in the growth stage is needed to provide enough mass for consumption in the oxidative respiration needed to consume the oxygen produced by water splitting to keep the system anaerobic. This mass consumption through respiration will return the system back to its original concentration by the end of the production stage. Thus, no additional mass need be removed.

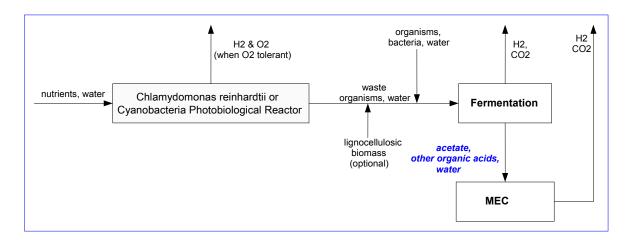
For the B-4 system, the algae were immobilized on a non-fermentable polypropylene substrate to reduce cost. For this embodiment, feeding the waste organisms to a fermentor would be too costly and cumbersome, and thus the waste organisms from this system are not used for fermentation. In contrast, NREL research for immobilized algae utilizes an alginate film for immobilization. Use of the fermentable alginate film in B-4 would increase B-4 cost but also increase the potential C-4 fermentation H₂ production, and that is an option that could be considered in the future.

Subsequent to this fermentation process, liquid fermentation products, such as acetate, can be recycled into a PNS photobiological reactor bed, or they can be transferred to a Microbial Electrolysis Cell (MEC) for additional hydrogen-production. Figure 11-1 below shows process alternatives considered.

H2 & O2 (when O2 tolerant) organisms, bacteria, water H2, nutrients, water Chlamydomonas reinhardtii or CO₂ Cyanobacteria Photobiological Reactor waste organisms, water Fermentation H2, CO2 lignocellulosic biomass Purple non-sulfur (PNS) bacteria water (optional) Photobiological Reactor acetate. other organic acids,

Figure 11-1. Fermentation Process within a Biological System





12. Theoretical and Practical Fermentation Reactions

Fermentation is the process of deriving energy from the oxidation of organic compounds, such as carbohydrates. Dark fermentation reactions, as the name suggests, do not require light energy, so they are capable of constantly producing hydrogen from organic compounds throughout the day and night. In theory, any carbohydrate source could be used as a feedstock for fermentation. Algae and other biomass listed in Figure 12-1 are representative fermentation feedstocks.

Figure 12-1. Potential Fermentative Feedstock Materials

Algae and other biomass

Corn stover hydrolyzate

Sugar cane juices

Wood fiber hydrolyzates from pulp mills

Biomass hydrolyzates from agricultural resides

Energy crops

The feedstock is composed of a starch/glucose component as well as proteins and lipids and other components. If it were possible to convert all of the waste organism starch entering the fermentation processes to hydrogen, the stoichiometric result, using glucose as a representative of starch feedstock, would be:

$$C_6H_{12}O_6 + 6H_2O => 12H_2 + 6CO_2$$
.

However, this theoretical limit does not naturally occur⁶⁸. Instead, the observed glucose reactions are a conversion to H₂, CO₂, and acetate which is represented as:

$$C_6H_{12}O_6 + 2H_2O => 4H_2 + 2CO_2 + 2C_2H_4O_2$$
.

This is known as the Thauer limit and results in 4.5% H₂ output by mass relative to the glucose component⁶⁸. An alternative, less complete, reaction that also takes place forms H₂, CO₂, and butyl acid:

$$C_6H_{12}O_6 => 2H_2 + 2CO_2 + C_4H_8O_2$$

In actual practice, a combination of these reactions takes place, yielding between 2 and 4 moles of hydrogen per mole of glucose.

13. Algae Fermentation Tests

The organisms under consideration consist primarily of starches, lipids, and proteins. Multiple tests have been run by researchers with NREL support on fermentation of *Chlamydomonas reinhardtii*. The consortium ferments the starch and lipid and protein components, at least partially. However, that research is not yet complete ⁶⁹.

The most directly applicable data for starch fermentation is from Project 3.3, Photobiological Systems for Hydrogen Photoproduction, Task 3 – Integrated Systems. Test results from this project for FY2007 and FY2008 were provided as references for the design of the fermentation system. The First Quarter FY08 results are summarized in Figure 13-1. These results have a comprehensive compilation of algae components and hydrogen outputs and were used as guidelines for the fermentation analysis along with the more recent data from the emails referenced.

⁶⁸ Benemann, John R. and Paola M. Pedroni. 4.3 Biological production of H₂: mechanisms and processes.

⁶⁹ Maria Ghirardi. Project 3.3:Photobiological systems for Hydrogen Photoproduction. 1st Quarter 2008 Report.

Figure 13-1. NREL Fermentation Experimental Data 70

	Input ma	ss - Alga	e		H₂ Output			
Algae Characteristics	Total mass [mg]	Starch mass [mg]	Starch [% of algae]	lipid + protein %	Dwell time [hr]	H ₂ [μmol]	weight % per algae [g/g]	Mole % H2 to glucose
			Januar	y 2008				
sulfur deprived, 21 hr	5.77	1.87	32.4%	NA	120	17.68	0.618%	1.70
sulfur deprived,142 hr	29.8	1.79	6.0%	NA	hr	22.97	0.155%	2.31
sulfur and phosphate deprived, 142 hrs	86.2	1.76	2.0%	NA	max	38.44	0.090%	3.93

Results⁶⁹ show that the extent of algal sulfur deprivation has a direct effect on the algae's total glucan content (glucose, starch, and glycogen), with the percentage mass of starch in the tested algae varying from 32% at 21 hours of sulfur deprivation, to 6% at 142 hours of sulfur deprivation, to 2% at 142 hours of sulfur and phosphate deprivation. The bacteria used in fermentation tests with these algae samples carried out fermentation mainly on the starch component, so the H₂ outputs were dependent on the starch percentages. For these 3 samples, test results yielded H₂ masses that were respectively 0.618%, 0.155%, and 0.090% of the algae cdw. The results from the tests referenced are described in Figure 13-1. Note that in the last case, the molar yield of H₂ to glucose is 3.93, very close to the Thauer limit of 4.0, indicating that some H₂ was generated from lipid and protein components.

Previous work on the sulfur deprivation of *C. reinhadtii*⁷¹ indicated that the starch content of cells grown under sulfur replete conditions and resuspended in a sulfur-deprived medium (t=0) is similar to that of cells deprived of sulfur for 142 hours. For the purposes of this analysis, thus, we used the data from the second row of Figure 89 to represent the starch amount of cultures in the three photobiological systems. The data shown in the third row reflects the starch amount of cultures that are immobilized in alginate films (not addressed in this analysis).

Current NREL research with different bacteria consortia have shown that H_2 can also be generated from the lipid and protein content of the algae. Therefore, it is expected that future research will raise H_2 output from this algae, and it was assumed that an H_2 output between the 0.62% level and the 0.16% level would be representative of future capabilities, and a level of 0.4% H_2 /algae cdw was used in this analysis.

Though First Quarter FY08 results were for a test time of 120 hours, other tests (Fourth Quarter FY07 and Fourth Quarter FY08) indicate that cumulative H₂ production plateaus after 72 hours into a fermentative cycle. Thus, it was assumed that the fermentation process took 72 hours.

Kosourov, S.; Seibert, M.; Ghirardi, M. L. (2003). Effects of Extracellular pH on the Metabolic Pathways in Sulfur-Deprived H2-Producing Chlamydomonas Reinhardtii Cultures. Plant and Cell Physiology. Vol. 44(2), 2003; pp. 146-155; NREL Report No. JA-590-34437.

⁷⁰ Maria Ghirardi. *Project 3.3: Photobiological Systems for Hydrogen Photoproduction. 1st Quarter Report.* 22 January 2008.

13.1 Fermentor Feedstock

As discussed above, feedstock of interest is waste organisms from photobiological processes. To facilitate the integration system task that comes after this fermentation analysis, the feedstock quantities and composition evaluated here are those identified in the Photobiological Characterization Report. Based on the previous photobiological systems examined, three possible fermentor feedstocks are shown in Figure 89. These are the waste algae or bacteria from photobiological systems B-1, B-2, and B-5. For the sake of consistency, the fermentor systems will be tagged C-1, C-2, and C-5 to correspond with the photobiological system from which it obtains its feedstock. Because the efficiencies and composition of each of photobiological systems vary, the slurry feedstock to the fermentor will differ. Note that there is no C-3 or C-4 fermentation pathway for reasons discussed earlier.

Figure 13-2. Analysis Feedstocks Defined (from 10TPD Photobiological System)

		C-1	C-2	C-5
Photobiological Reactor Bed Type		Chemostat II	Chemostat II	Chemostat II
Organism		Chlamydomonas reinhardtii	Cyanobacteri a	purple non-sulfur proteobacterium (PNS)
Slurry extracted from 10 TPD photobio reactor bed	%/day	10%	10%	10%
(0.2 g/L organism density)	gal/hr	96,391	96,391	257,414
	L/hr	364,840	364,840	974,312
Organism mass extracted (organism dry mass)	kg/hr	73	73	195
	kg/day	1,751	1,751	4,677
Fermentor Input				
% organism/water by weight ^{73,74}	%	20%	20%	20%
Mass organism / liter	g/L	200	200	200
Daily Quantity	L/day	8,756	8,756	23,383
Fermentation time	hrs	72	72	72
	days	3	3	3

13.1.1 C-1 Feedstock

The organism in the C-1 system is an oxygen-tolerant hydrogenase, *Chlamydomonas* reinhardtii cc124 as defined in the B-1 Photobiological Pathway. These algae have been cultivated in a Chemostat II reactor bed⁷⁵ which is continuously extracting a slipstream of organism/water slurry to maintain a constant cell concentration. As mentioned previously, since there is no way to sort the organisms so that only exhausted ones are expunged from

⁷²James, Brian D. *Task B: Photobiological H*₂ *Production Subsystems Characterization Report.* NREL Contract# AFH-8-88601-01. 24 December 2008.

Aden, A. et al.. Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL Contract# DE-AC36-99-GO10337. June 2002, NREL/TP-510-32438.

⁷⁴ Remainder is water.

While a generic chemostat system in defined as a reactor in which a constant volume of medium is maintained, the Characterization Report defines a Chemostat II as a chemostat system in which organism growth and hydrogen production simultaneously occur.

the reactor bed, we must assume a normally distributed cell age within the slurry. The quantities listed in the table above are computed based on the slipstream amount from a standard reactor bed size.

13.1.2 C-2 Feedstock

The organism in the C-2 system is cyanobacteria, an oxygen-tolerant hydrogenase, based on the Synechocystis PCC6803 mutant from the B-2 Photobiological Pathway. These organisms have also been cultivated in a Chemostat II reactor bed which is continuously extracting a slipstream of organism/water slurry to maintain a constant cell concentration.

Certain filamentous cyanobacteria acquire both longer filament lengths with age and develop gas vacuoles with age leading to compulsory flotation, while younger less buoyant cells remain dispersed. Separation of organisms by age may thus be more readily carried out for these bacteria, allowing removal of only the old organisms. This attribute could be exploited in a future design

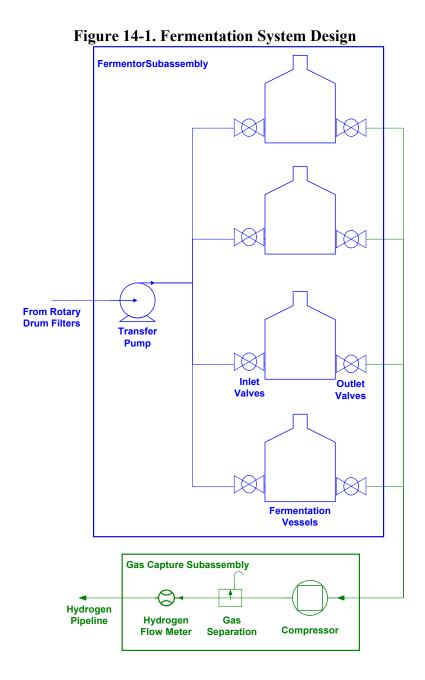
The quantities listed in Figure 13-2 above are computed based on the slipstream amount from a standard reactor bed size. However there is no data on the fermentation of these organisms, thus we assume the organism fermentation is similar to *Chlamydomonas* reinhardtii.

13.1.3 C-5 Feedstock

The organism in the C-5 system is a purple non-sulfur proteobacterium from the B-5 Photobiological Pathway. These bacteria have been cultivated in a Chemostat II reactor bed which is continuously extracting a slipstream of organism/water slurry to maintain a constant cell concentration. Since there is no way to sort these organisms, we assume a normally distributed cell age. The quantities listed in the table above are computed based on the slipstream amount from a standard reactor bed size.

14. Basic Fermentation System Diagram

In Figure 11-1 the fermentation system within a biological process is shown. This section of the report will delve into that portion of the system and describe in detail the components and the operation. Figure 14-1 shows the fermentation system is made of two subassemblies, fermentation and gas capture. Each of these subassemblies is described further below.



14.1 Fermentation Operation Scheme

In a prior section, it was mentioned that H_2 cumulative production at lab scale tests plateaus in a 72 hour cycle. Thus we have taken 72 hours to be the duration of the fermentation process. Data indicates that the production rate over the 72 hours is not constant, but varies from minimal output for the first 24 hours, to max rate over the next 44 hours, and drops down to zero over the next 4 hours.

In the fermentation process at larger scales, mixing will be a major concern to remove oxygen and to control variables such as pH and residual oxidants (oxygen and nitrate). For this purpose, the fermentation tanks each include a tank agitator. In addition, it will be needed to continuously monitor and control variables such as pH.

Because of the 3 day fermentation period, there are 3 fermentors running in parallel, with a fourth in recharging status or in reserve. At the end of the 72 hour process the vessel will contain solids residue which will need to be cleaned out prior to beginning the next batch. The fourth vessel will be cleaned while the other three are used.

There are two options available to handle the variability. First, downstream equipment can be sized for peak rates and operate at reduced capacity during non-peak production. Second, the downstream equipment can be sized for average rates, and the plant design and operation adjusted to accommodate the variable gas production. The decision of which route to take is an economic one. In our case the downstream components are a compressor, gas separation system, and a flow meter. The flow meter operation is not impacted by the variability in hydrogen production, however the compressor and gas separator are. We choose to operate the downstream equipment at steady-state conditions and accommodate the variable gas production.

There are several ways the plant design could be modified to ensure the gas capture subassembly encounters a constant and continuous flow of output gas. The most direct would be to install a buffer storage tank between the two subassemblies. While simple in practice, storage of hydrogen at low pressures is voluminous. Thus in our design we have opted to build several fermentation vessels and stage the start of the fermentation process in each so that the cumulative hydrogen production from all vessels is leveled.

14.2 Fermentor Subassembly

The fermentor subassembly conveys algae into the fermentors and processes it at the necessary conditions to produce hydrogen. In order to accomplish this, the subassembly is comprised of a pump, inlet valves, fermentation vessels, outlet valves, and piping. The pump transfers wet organisms and bacteria into the subassembly. In an integrated system one could assume that the organisms are collected from the rotary drum filters described in the photobiological systems report. The inlet and outlet valves are considered manual and necessary to isolate each vessel. The need to isolate each vessel will be evident when the operation scheme is described. Piping is needed to move material into the vessels. Because the quantities are low, pipe cross-sectional area is also low. Only short piping runs are needed due to the relatively low diameter of the fermentation tanks and the resulting close spacing of the tanks.

The last piece of equipment in this system is the fermentation vessel itself. These vessels are designed for atmospheric pressure and temperature.

15. <u>Capital Cost of the Fermentation System</u>

Based on the system configurations described above, bills of material (BOM's) were prepared for each of the fermentative systems. These BOM's appear in Figure 15-1 through Figure 15-2.

Figure 15-1: BOM for Fermentor Systems C-1 and C-2 (sized for the organism wastestream of a 10TPD B-1 or B-2 Photobiological Hydrogen production system)

Description	Size Req'd	Units	Unit Size	Units	-	Unit cost	Qty Req'd	Т	Total Cost	Material / Part Description
Fermentation Subassembly										
Tank	2312	gal	1	gal	\$	2.00	9,247	\$	18,493	This is a scaled cost based on the capital costs from NREL Report TP-510-32438
Slurry Piping - 0.5"	500	ft	1	ft	\$	0.52	500	\$	260	Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
Slurry Piping - 1"	3734	ft	1	ft	\$	1.00	3,734	\$	3,734	Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
Pump	2312	gal/day	4	gal/min	\$	198.50	1	\$	199	http://www.grainger.com/Grainger/items/1P795
Inlet Valves	1	in	1	each	\$	67.23	4	\$	269	http://www.valvestore.com/products.asp?dept=1485
Outlet Valves	0.5	in	1	each	\$	46.85	4	\$	187	http://www.valvestore.com/products.asp?dept=1485
Water	18,493	gal	1	gal	\$	0.001665	18,493	\$	30.79	H2A Costing
as Capture Subassembly										
Compressor	0.29	kgmol/h	0.29	kgmol/hr	\$	9,233.00	1	\$	2,679	H2A Costing
PSA					\$	5,738	1	\$	5,738	H2A Costing
Gas Piping - 0.5"	100	ft	1	ft	\$	0.52	100	\$	52	Sized using the Continuity Equation. Assumes 1 mol of H2, 0.5 Mol of CO@, and water vapor
Hydrogen Flow Meter			1		\$	5,500.00	1	\$	5,500.00	Information from Emerson Process Management

System Initial Cost \$ 37,142

Figure 15-2: BOM for 10 TPD Fermentor System C-5 (sized for the PNS waste-stream of a 10TPD B-5 Photobiological Hydrogen production system)

Description	Size Req'd	Units	Unit Size	Units	-	Unit cost	Qty Req'd		Total Cost	Material / Part Description
Fermentation Subassembly										
Tank	6173	gal	1	gal	\$	2.00	24,693	,		This is a scaled cost based on the capital costs from NREL Report TP-510-32438
Slurry Piping - 0.5"	500 1	ft	1	ft	\$	0.52	500	Ş	260	Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
Slurry Piping - 1"	5077	ft	1	ft	\$	1.00	5,077	5	5,077	Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
Pump	6173	gal/day	4	gal/min	\$	198.50	1	ç	199	http://www.grainger.com/Grainger/items/1P795
Inlet Valves	1	in	1	each	\$	67.23	4	,	269	http://www.valvestore.com/products.asp?dept=1485
Outlet Valves	0.5	in	1	each	\$	46.85	4	,	187	http://www.valvestore.com/products.asp?dept=1485
Water	49,386	gal	1	gal	\$	0.001665	49,386	,	82.23	H2A Costing
Gas Capture Subassembly										
Compressor	0.77	kgmol/h	0.77	kgmol/hr	\$	9,233.00	:	LŞ	7,154	H2A Costing
PSA				-	\$	8,115	1	,	8,115	H2A Costing
Gas Piping - 0.5"	100	ft	1	ft	\$	0.52	100	,	5 52	Sized using the Continuity Equation. Assumes 1 mol of H2, 0.5 Mol of CO@, and water vapor
Hydrogen Flow Meter			1		\$	5,500.00	1	LŞ	5,500.00	Information from Emerson Process Management

System Initial Cost \$ 76,28

As shall be noted when examining the cost results, tank capital cost and labor assumptions play an important role in the cost examination. For this reason, they are discussed in more detail below.

15.1 Tank Cost

Capital cost of the stainless steel fermentation vessels is based on data from an NREL report⁷⁶ by Aden et al that gives us a \$2.00/gallon cost for fermentor tanks in this size range operating at atmospheric pressure. As shown in the system bills of material, typical fermentor tank size for systems C-1, C-2, and C-5 is around 2,000-7,000 gallons.

16. Fermentation Outputs for C-1 through C-5

Based on the above assumptions, the daily hydrogen output resulting from fermentation of algae from the photobiological pathways (B-1, B-2 and B-5) was calculated.

⁷⁶ Aden, A. et al.. Lignocellulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover. NREL Contract# DE-AC36-99-

Figure 16-1. Fermentative Hydrogen Ouput (from 10TPD Photobiological System)

		C-1	C-2	C-5
Photobiological Reactor Bed Type		Chemostat II	Chemostat II	Chemostat II
Organism		Chlamydomonas reinhardtii	Cyanobacteria	purple non-sulfur proteobacterium (PNS)
Hydrogen Produced weight % relative to organism =0.4%	kg/day	7.0	7.0	18.7

For the C-1/C-2 process this amounts to only 7.0 kg H₂/day for the system producing 10,000 kg/day from the photobiological process.

17. Levelized Costs Assumptions & Calculations (H2A)

Thus far, this report has discussed the capital cost and expenditures associated with building a fermentative hydrogen plant. While this is critical and valuable information, the build decision is ultimately based on the financial and economic benefits of these capital expenditures. The investment is quite large and cannot be properly evaluated without some knowledge of the expected return on that investment. In order to evaluate the return, DTI has performed a discounted cash flow (DCF) analysis using the H2A Forecourt Production Model, Version 2.0.

Discounted cash flow is a method of evaluating an investment by estimating the present value of future cash flows and taking into consideration the time value of money. The method uses future free cash flow projections and discounts them using the weighted average cost of capital (WACC) to arrive at a present value (PV). Two basic DCF methods are the net present value (NPV) method and the internal rate of return (IRR) method, both of which take into account the time-value of money, and are similar to the methods used in computing interest-income on bank deposits. This analysis uses the IRR method. Recall that IRR is the discount rate where the PV of total cash inflows equals the PV of the total cash outflows.

The H2A model uses the DCF methodology described above. However future cash inflows from sale of the hydrogen are highly speculative. Thus, the DCF results in this analysis are presented in a slightly different manner. Rather than predict cash inflows from sales and compute the IRR, our analysis pre-selects an IRR value which would be agreeable to investors. It then assumes sales are equal to the amount of product that can be produced over the analysis period. With those two values in places, this analysis computes the price of hydrogen necessary for the IRR at the given sales volume. This price is expressed in \$/kgH₂. This is often referred to as the levelized cost of hydrogen. Levelized cost is the PV of the all costs associated with building and operating a generating plant over its economic life, converted to equal payments.

17.1 Standard H2A parameters

In order to develop levelized costs, several parameters must be defined. Because this analysis focuses on a plant which is still in its conceptual stage, many of the values for these parameters must be assumed. The assumptions are documented in this section. These are meant to represent a baseline system and analysis. Later in the discussion portion of this report, the assumed values can be altered for sensitivity analyses.

Standard H2A values and assumptions shown in Figure 17-1 apply to all biohydrogen pathways. This list does not encompass all parameters which must be defined in order to run the analysis; just those were there is an H2A Default value which has been accepted for this analysis. The remaining parameters are defined later in this section. Some of those parameters are common to all fermentative pathways and others are pathways specific. No dispensing parameters are listed here because they are not factored into the analysis.

Figure 17-1. H2A Default Values and Assumptions used for all Fermentative Pathways⁷⁷

ssumptions
model
cases (default value = 0)
cases (default value = 0)
forecourt
for forecourt model
or central model
t model
r costs
< 10 ppm, sulfur < 10 ppm
e; 38.9% effective
ant price of hydrogen in
int dollars
1.6 1 . 1 . 1
ed for central model;
model
cases
cost for central model
nitial capital cost
0/ IDD, in also dea leveline d
% IRR; includes levelized
For 0%–25% IRR; model
s that facilities and related
sale and through a general
and uniough a general
for central model
lange in total operating costs

_

⁷⁷ Appendix 3: Default Values and Assumptions. H2A Production Model, Version 2.0 User Guide, Rev. DRAFT, June 2008, p. 63.

17.2 Pathway Common Parameters

In addition to the financial parameters defined by H2A in the previous section there are other inputs which must be quantified in order to carry out the DCF analysis. All inputs can be found on the following worksheets in the H2A model;

- Input_Sheet_Template
- ReplacementCosts
- CapitalCosts

Many of these parameters are specific to the location, operation, and type of plant. In the case of our biohydrogen pathways there are some parameters that are the same for all pathways and some that vary by pathway. The parameters in Figure 17-2 are common to all pathways.

Figure 17-2. Parameters Common to all Pathways

Parameter	Assumed Value	Worksheet Name
Operating Capacity Factor	90%	Input_Sheet_Template
Reference Year Dollars	2005	Input_Sheet_Template
Site Preparation	1% of direct costs minus raceway excavation costs	Input_Sheet_Template
Engineering & design	1% of direct costs	Input_Sheet_Template
Process Contingency	20% of direct costs	Input_Sheet_Template
Project Contingency	\$0	Input_Sheet_Template
Up-Front Permitting Costs	0.5% of direct costs	Input_Sheet_Template
Licensing, Permits, and Fees	\$1000	Input_Sheet_Template
Production Maintenance & Repairs	0.5% of direct costs	Input_Sheet_Template

17.2.1 Operating Capacity Factor

The operating capacity factor can be found on the Input_Sheet_Template worksheet of the model. This analysis assumes that the plant and dispensing station have a 90% operating capacity. This capacity factor takes into considering things such as planned maintenance outages, forced outages, etc.

17.2.2 Reference Year Dollars

The reference year dollars parameter is the year dollars in which the cost of hydrogen is reported. The H2A standard is to report out hydrogen costs in 2005 dollars. The model expects capital costs to be entered in 2005 dollars. In this analysis Reference Year 2005 was selected

17.2.3 Site Preparation

The site preparation parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 1% of direct costs. This analysis uses the same default value.

17.2.4 Engineering & design

The engineering & design parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 13% of direct costs. This analysis uses the same default value.

17.2.5 Process Contingency

The process contingency parameter can be found on the Input_Sheet_Template worksheet of the model. In central plants, H2A defaults this value to 15% of direct costs. This analysis uses 20% of direct costs due to uncertainties in the system configuration.

17.2.6 Project Contingency

The process contingency parameter can be found on the Input_Sheet_Template worksheet of the model. In our analysis we have chosen to include all contingency factors in the process contingency parameter, thus the project contingency is set to \$0.

17.2.7 Up-Front Permitting Costs

The up-front permitting cost parameter can be found on the Input_Sheet_Template worksheet of the model. The H2A default for this parameter is 9% of direct costs. This analysis uses the same default value.

17.3 Pathway Specific Parameters

The last type of parameters we identify are those which are specific to each pathway analyzed. Figure 17-3 lists these parameters and rules of thumb applied in computing their values. These are pathway specific because they are associated with feedstock, process design and plant design.

Figure 17-3. Pathway Specific Parameters

Parameter	Rule Applied	Worksheet Name
Land Required	Teure 11pp11eu	Input_Sheet_Template
Production facility plant staff		Input_Sheet_Template
Utility Usage	Electricity and water costs use H2A pricing	Input_Sheet_Template
Feedstock Usage	None	Input_Sheet_Template
Specified Yearly Replacement Costs	None	ReplacementCosts

17.3.1 Land Required

The land required parameter can be found on the Input_Sheet_Template worksheet of the model. In developing the plant design, a land area for the fermentor system was computed and then increased by 30% for conservatism. The 30% factor is meant to encompass area requirements for pump skids, compressors, gas and other process flow components and a small control room. The total land requirement for each pathway is shown in Figure 17-4.

Figure 17-4. Land Required for each Pathway

Pathway	Area (m ²)
C-1	1,012
C-2	1,012
C-5	1,012

17.3.2 Production facility plant staff

The production facility plant staff parameter can be found on the Input_Sheet_Template worksheet of the model. This represents the number of full-time employees required to operate the plant. There is no H2A default value for this. Our analysis for each of the pathways is shown in Figure 17-5.

Figure 17-5. Plant Staff Requirements for Fermentor plant

Pathway	Total Workers Needed
C-1	1 man/3 shifts/day
C-2	1 man/3 shifts/day
C-5	1 man/3 shifts/day

17.3.3 Energy Usage

The usage of utilities, feedstocks and creation of byproducts can be found on the Input_Sheet_Template worksheet of the model. There are no H2A default values for these.

Figure 17-6. Electricity Usage

Pathway	Electricity (kWh/kg H ₂)
C-1	6.15
C-2	6.15
C-5	3.90

17.3.4 Specified Yearly Replacement Costs

The specified yearly replacement costs can be found on the Replacement Costs worksheet of the model. There is no H2A default value for this and no fermentative system component replacements are assumed.

17.3.5 Baseline Uninstalled Costs

The baseline uninstalled costs can be found on the Capital Costs worksheet of the model. There is no H2A default value for this. These are the capital costs of the equipment that were computed in an earlier part of this project. Those separately calculated values will be imported into this area of the H2A Production Model to access the economic benefit of the capital expenditure. These costs are provided in the bill of materials for each pathway.

17.3.6 Installation Cost Factor

The installation cost factor parameter can be found on the Capital Costs worksheet of the model. The default value for this is 1.3.

17.4 Levelized Costs

Once all the cost parameters are specified, the H2A Production Model can perform levelized cost calculations. Parameters can be changed in a sensitivity analysis to access the impact on the cost per kilogram of hydrogen.

18. Cost Results for the Fermentative Systems

Based on the system diagrams, performance, and capital cost presented above, the projected hydrogen cost was next calculated using the H2A analysis model⁷⁸. The total levelized cost of hydrogen for each fermentative pathway is shown in Figure 18-1.

Figure 18-1: H2A Model Projected Hydrogen Cost per kg from Fermentor Systems C-1, C-2, and C-5

Total Cost of Produced H 2			
Cost Component	Hydrogen Production Cost Contribution (\$/kg)		
System	C1/C2	C5	
Capital Costs	\$6.69	\$2.91	
Decommissioning Costs	\$0.03	\$0.01	
Fixed O&M	\$165.70	\$62.10	
Feedstock Costs	\$0.00	\$0.00	
Other Raw Material Costs	\$0.00	\$0.00	
Byproduct Credits	\$0.00	\$0.00	
Other Variable Costs (including utilities)	\$0.32	\$1.14	
Total	\$172.73	\$66.17	

Note that the project cost of hydrogen is quite high (~\$70-\$170/kg) due to two primary factors. The first is the low kg/day of hydrogen production being produced from the system: 7-19 kg H₂/day. This has an amplifying affect since all costs must be amortized over a small amount of hydrogen. The second factor is labor cost, which is reflected under fixed O&M (operating and maintenance) cost. Labor cost is set at 1 laborer per shift, for each of the three shifts per day. Sensitivity to production scale and labor costs is examined in the next section.

⁷⁸ H2A Forecourt Production Model, Version 2.0.

19. <u>Processing of Fermentor Liquid Outputs</u>

For the 3 photobiological systems feeding the fermentor, each system producing 10 tonnes/day, the major useful outputs from the fermentor are shown in Figure 19-1.

Figure 19-1: Fermentor Outputs

Fermentor	Fermentor Feedstock	Output from Fermentor (kg/day)			
System	Source	H_2	CO_2	Acetate Lipid,Prot & Other	
C-1, C-2	B-1, B-2	7.01	76.5	104.3	1563.6
C-5	B-5	18.7	204.1	278.6	4175.2

For the C-5 system, the acetate is used as feedstock to the ponds for PNS organism growth. It is not determined whether the acetate would be separated from the other fermentation byproducts or whether the entire byproduct stream could be used. At any rate, at the quantities produced in the fermentor, the acetate is only 3% of the B-5 system requirements.

One alternative for obtaining additional gaseous products from the unused fermentation byproduct is a separate fermentation step. The remaining unreacted lipids and proteins could potentially be converted to gases (H₂, CO₂, CH₄, and NH₃) in additional fermentation reactions with different bacteria. Research work is ongoing to examine capabilities in those areas.

Another post-processing alternative for the acetate and other simple organic liquids from C-1 and C-2 is the use of a Microbial Electrolysis Cell (MEC) system. The MEC is an electrolysis unit that uses bacteria on the anode along with a moderate electrode voltage to carry out an electrolysis reaction of acetate (and other organic acids and alcohols) with water, producing H_2 at the cathode and CO_2 at the anode. The details of the MEC are discussed in a following section on lignocellulose fermentation and processing.

The MEC sizing is determined by the volume of the diluted liquid organic input stream and the required residence time of the reaction. We assumed an acetate concentration of 2.0 gram acetate per liter. Residence time in the MEC depends on the voltage applied, with MEC size and cost decreasing with increased voltage up to a maximum of around 0.9-1.0 volt. For these algae reactions a voltage of 0.9 Volts was assumed, which requires a 1 day residence time. For systems C-1 and C-2, (corresponding to biological pathways B-1 and B-2), the processing of the liquid streams and the H₂ output is shown in Figure 19-2.

Figure 19-2: MEC Flows

Parameters	Units	System C-1 and C-2
Acetate Flow Rate	kg/day	104.3
Reactant water	kg/day	56.3
MEC - H ₂ output	kg/day	12.6
MEC Flow Rate	gal/day	13,782
MEC Residence Time	days	1
Total MEC Volume	gal	13,782
Number of MECs	tanks	1

Mass Balances summarizing the flows for C-1/C-2 and C-5 are shown in Figure 19-3 and Figure 19-4:

Figure 19-3. C-1/C-2 Fermentation + MEC

C-1/C-2 Fermentation + MEC

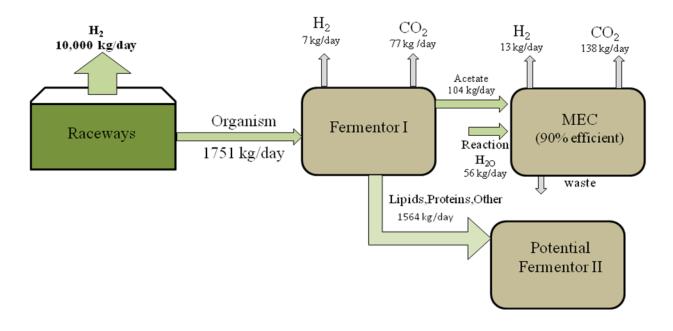
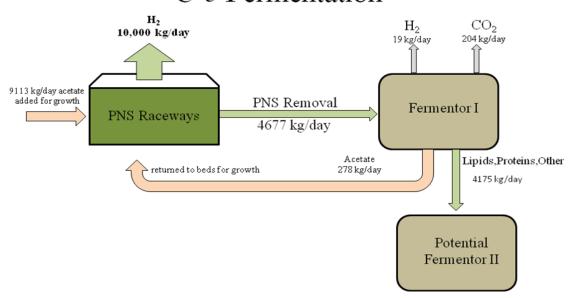


Figure 19-4. C-5 Fermentation

C-5 Fermentation



The heat balance will involve heating/cooling to maintain fermentation temperature. At the current stage of the algae fermentation research, this requirement has not been quantified.

20. Algae Fermentation System Conclusions and Recommendations It is apparent that the initial fermentation step doesn't produce much H_2 (~7-19 kg H_2 /day) when compared to the 10,000 kg H_2 /day photobiological system production rate from which it draws its organism feedstock.

If the full stoichiometric level of H_2 fermentation of algal glucose were achievable through use of additional processing systems, one could potentially obtain three times more hydrogen. However, this is still only a small fraction of the targeted production rate of $10,000 \text{ kg } H_2/\text{day}$. It is also possible that a substantial amount of hydrogen can be obtained from the protein and lipid components, which constitute about 67% of the waste algae mass. Research is being carried out to optimize the fermentative process and to assess how much additional hydrogen might be available in these components.

For the C-5 system, the fermentor byproduct acetate can be used as nutrient to the photobiological beds, providing 3% of the requirement. Future research might bring about a more complete fermentation reaction that would produce more acetate, more in line with the B-5 bed needs.

The algal fermentor may also be useful to produce acetate for an MEC. Addition of the MEC provides an additional 180% H₂, raising total C-1/C-2 output from 7kg/day to 20 kg/day, but that is still a small amount compared with the photobiological production of 10,000 kg/day. MEC operation is discussed in detail in the section on Lignolcellulosic fermentation and postprocessing. Integrated operation of a Fermentor and an MEC is discussed in the section on integrated system.

Part III: Lignocellulosic Fermentative H₂ Production Systems

& Microbial Electrolysis Systems

21. Lignocellulosic Hydrogen Production

An important pathway available for production of renewable hydrogen is fermentation of carbohydrate-rich feedstock. Fermentation is the process of oxidation of organic compounds, such as carbohydrates. Dark fermentation reactions with select bacteria are capable of producing hydrogen from organic compounds throughout the day and night. In theory, any carbohydrate source could be used as a feedstock. Examples of potential lignocelluloses fermentative feedstocks are shown in Figure 21-1. The rate of H₂ production via fermentation is relatively fast, and the reaction takes place continuously⁷⁹. These features simplify reactor design and operation compared to photobiological pathways.

Figure 21-1. Potential Fermentative Feedstock Materials

Algae and other biomass
Corn Stover
Switchgrass
Wood fiber

The lignocellulosic biomass feedstocks of concern in this section of the report consist of cellulose, hemicellulose, and lignin components as shown in Figure 21-2.

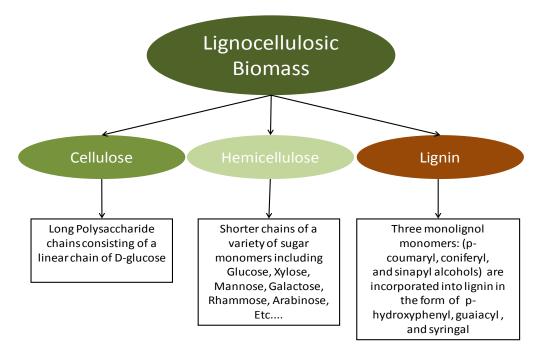


Figure 21-2. Lignocellulosic Biomass

⁷⁹ Hawkes, F.R, Dinsdale, R., Hawkes, D.L., and Hussy, I. 2002. Sustainable fermentative hydrogen production: challenges for process utilization. Intl. J. Hydrogen Energy 27, 1339-1347.

Several technical issues are concerns relative to the economic feasibility of the fermentation process. Those identified by the HFC&IT Program⁸⁰ are:

- Glucose feedstock cost (barrier AT);
- H₂ molar yield (mol H₂/mol hexose) (AR); and
- Waste acid accumulation (AS)

The cost of feedstock and H₂ molar yield thus play important roles in determining the viability of this process. This was confirmed by a preliminary boundary analysis for H₂ production by fermentation, conducted by Tim Eggeman⁸¹ for a DOE Workshop on "Hydrogen Production via Direct Fermentation."

21.1 Fermentation Reactions

As cellulose and hemicellulose feedstock consist of long chains of glucose, xylose, and other sugar compounds, they can generally be represented in a reaction equation as glucose. If it were possible to convert all of the glucose in the fermentation processes to hydrogen, the stoichiometric result would be:

$$C_6H_{12}O_6 + 6H_2O => 12H_2 + 6CO_2$$
.

However, this theoretical limit does not occur in vivo because the overall energetics is not favorable. The complete set of enzymes needed for this multi-step conversion does not function in vivo toward hydrogen production. Instead microbes opt to produce a mixture of organic acids including acetic acid and butyric acid thus lowering the yield of hydrogen⁸². In an "ideal" fermentation reaction, the glucose reacts with water to produce H2 and CO2 gas plus acetic acid as the only non-gaseous by-product:

$$C_6H_{12}O_6 + 2H_2O => 4H_2 + 2CO_2 + 2CH_3COOH$$

This is known as the Thauer limit and results in a maximal 4.5% H₂ output by mass relative to the glucose component⁶⁸. No known single microbe is able to achieve this yield. An alternative, less favorable, reaction could also take place and form H₂ with butyrate as the organic acid product:

$$C_6H_{12}O_6 => 2H_2 + 2CO_2 + CH_3CH_2CH_2COOH$$

www.eere.energy.gov/hydrogenandfuelcells/mypp/

⁸⁰ "Hydrogen, Fuel Cells & Infrastructure Technologies Program, Multi-Year Research, Development and Demonstration Plan," Section 3.1 Hydrogen Production, U.S. Department of Energy: Energy Efficiency and Renewable Energy; Hydrogen, Fuel Cells, and Infrastructure Technology Program. April 2007.

Eggeman, T. "Boundary Analysis for H2 Production by Fermentation, Neoterics International, Prepared for the National Renewable Energy Laboratory, March 12, 2004. Accessible from Proceedings of Workshop on "Hydrogen Production via Direct Fermentation."

http://www1/eere.energy.gov/hydrogenandfuelcells/wkshp proceedings.html#hydrogen

⁸² Benemann, John R. and Paola M. Pedroni. 4.3 Biological production of H₂: mechanisms and processes.

To breakdown the cellulose and hemicelluloses, the fermentation process includes a hydrolysis step, a saccharification step, and, finally, a fermentation step for reacting the various sugars produced in the initial steps. In actual practice, the saccharification and fermentation reactions take place in the fermentor. In our analysis we assumed 90% efficiency of the hydrolysis step and 90% efficiency in the saccharification /fermentation step. This leads to 3.2 moles of hydrogen, 1.6 moles of carbon dioxide and byproducts consisting of organic acids and alcohols plus unreacted glucose and other solids (lignin, xylane, etc.). This has been demonstrated in experiments.

Production of 3.2 moles of hydrogen per mole of glucose leads to a mass conversion efficiency in the fermentation process of 3.6% (gram H₂/gram cellulose and hemicellulose). The feedstock chosen for this analysis is corn stover which is only 64% cellulose and hemicellulose, leading to an estimated corn stover hydrogen conversion efficiency of 2.32% (gram H₂/gram corn stover).

21.2 Assumptions

While much of the process design for our hydrogen fermentation plant is derived from a Lignocellulosic ethanol report⁸³, there are some important assumptions in the bacteria performance and process parameters that differentiate the two.

21.2.1 Bacteria Assumptions

While testing for bacteria optimization is ongoing, we are hypothesizing performance based on hypothetical genetically engineered organisms capable of a fermentation H_2 molar yield approaching 4. We assume in our analysis that rates of H_2 production are stable for long duration. There will be two types of organisms used concurrently that will carry out saccharification and fermentation of the cellulose and the hemicellulose, avoiding the need for separation and independent reactors. The organism that ferments the cellulose will create its own cellulase enzyme which obviates the need for an outside cellulase source. Finally, we are assuming that the non-gas products of the fermentation reaction are primarily acetic acid with lignins not reacting.

21.2.2 Process Assumptions

Several of the processes involved in the ethanol fermentation report have been combined or eliminated in our version, simplifying the overall process. First, we assume that hydrolysis pretreatment breaks down the hemicellulose and cellulose inputs into reactable products. This pretreatment relies on high temperature acid hydrolysis alone, rather than the steam explosion process used in the ethanol report. We are using a feedstock cost that is minimal compared to a pure glucose feedstock. We have also assumed that saccharification and fermentation can occur in the same reactor. In our process, liming is done in the hydrolysis tank without any detrimental effect to the rest of the process. Lastly, we have assumed 20% solids content in the processed feedstock.

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

21.3 Lignocellulosic Fermentative Parameters

The baseline conditions that have been used for a fermentative pathway for hydrogen production using a lignocellulosic feedstock are summarized in Figure 21-3.

Figure 21_3 Parameters for Fermentation System

Figure 21-3. Parameters for Fermentation System				
Syste	em Parameters			
Corn Stover Usage (MT/day)	2352 ⁸⁴			
H ₂ Production Rate (kgH ₂ /day)				
At Fermentor outlet	46,477			
At PSA outlet	37,181 ⁸⁵			
Plant Area (Acres)	11			
Land Utilization (kg H ₂ /acre/year)	1,112,422			
Water Usage	, ,			
(gal/day)	10,539			
(gal/kgH ₂)	0.28			
Electricity Required				
kWhr/day	152,389			
kWh/kgH ₂	4.10			
kWh/kWh H ₂	0.12			
Ferme	entor Parameters			
Bacteria Cell lines	Clostridium Consortium and Clostridium			
	thermocellum			
Duration of Cycle (hrs)	36			
Target Temperature (°C)	55			
Assumed Reaction Efficiency				
Hydrolysis	90%			
Saccharification and	90%			
Fermentation				
Feedstock - to - H ₂ Conversion				
Efficiency	3.6%			
gram H ₂ /gram glucose	2.3%			
gram H ₂ /gram corn stover				
Reactor Volume ⁸⁶				
Gallons	4,813,255			
Liters	18,220,095			
Theoretical Product Ratio	4 mol H ₂			
	2 mol CO ₂			
	2 mol Acetate			
Assumed Goal Product Ratio	3.2 mol H ₂			
	1.6 mol CO ₂			
	1.6 mol Acetate			

Note that in current tests the molar yield of H₂ is closer to 2.0 mole H₂ per mole of glucose.

 $^{^{84}}$ Assumes 15% water weight, for dry Corn Stover mass of 2,000 Metric Tonnes (MT)/day 85 Assumes 80% $\rm H_2$ recovery in the PSA.

⁸⁶ Volume is main fermentation tanks only- does not include pre-treatment tank volume.

21.4 Engineering Parameters

The lignocellulosic hydrogen production plant has been divided into 7 interconnected subassemblies, namely,

- Corn Stover Prep Subassembly,
- Pretreatment/Hydrolysis Subassembly,
- Fermentation Subassembly,
- Seed Production Subassembly,
- Storage Subassembly,
- Wastewater Treatment Subassembly, and
- Gas Compression and Separation Subassembly

A general diagram showing the basic flow of this system is shown in Figure 21-4. This diagram does not include all of the subassemblies. For a more detailed look at the interaction between the subassemblies please refer to the individual assembly diagrams shown in the subsequent sections. The subassemblies have several components that will also be identified in later sections of this document.

Plant design was based upon a prior NREL report analyzing the design and costs of a lignocellulosic ethanol producing plant⁸⁷. Using information from this report we extrapolated the costs and material requirements into a simplified, future hydrogen production plant using the same feedstock and similar processes. Hydrogen production involves different fermentative bacteria than ethanol production, and there are some additional assumptions made concerning potential advances in fermentation that will allow us to combine processes into one tank. These assumptions have been outlined previously in this report. Given the complexity of scaling such a complex system, we chose to emulate the ethanol plant's scale. Therefore, all components in the following subassemblies are sized and priced analogous to the corresponding ethanol plant components. The volume of hydrogen produced is based upon the fermentation of 2,000 Metric Tons (MT) of corn stover (dry weight), which was determined by the ethanol report to be the most cost-effective volume of feedstock.

Altering certain materials from the NREL report was considered for capital cost savings. Specifically, we analyzed use of concrete tanks instead of stainless steel. The Philadelphia Suburban Water Company conducted a life cycle analysis of concrete tanks and stainless steel tanks used in their water treatment system⁸⁸. The conclusion drawn was that, the long-term durability of stainless steel made it the more cost effective tank solution. Coupled with the NREL reports decision to use stainless steel, we felt that there was no compelling reason to switch tank materials.

⁸⁷ Aden A. et al. <u>Lignocelulosic Biomass to Ethanol Process Design and Economics Utilizing Co-Current Dilute</u> <u>Acid Prehydrolysis and Enzymatic Hydrolysis for Corn Stover</u>. NREL/TP-510-32438, June 2002

Philadelphia Suburban Water Co. <u>Steel vs. Concrete – A Life Cycle Analysis</u>. http://www.steeltank.com/LinkClick.aspx?fileticket=L1jYUfta9aw%3D&tabid=219&mid=701

System for Lignocellulosic Fermentation Feedstock **Assumptions** Combine Saccharification and Feed Wash Tank Fermentation Bacteria in single reactor Water Shredder Use Bacteria that create their own Cellulase Enzyme H₂O Vapor Air Water Fermentor 1. Add Heat Condenser Fermentation Exchanger **PSA** Compresso 80% H₂ to Pipeline Bacteria /HX CO₂, H₂, Fermentation o H₂O Vapor Hemicellulose 3. Cellulose Saccharifaction H₂O Liquid **Hydrolysis** Cellulose Air Fermentation Tank Acetic Acid, Ethanol, and other Acids + Waste Lignin Acid hydrolysis o Hemicellulose 2. Ca(OH), to precipitate small soluble lignin Neutralize Acid (Liming) Heater 20% H₂

Figure 21-4. Simplified Lignocellulosic Hydrogen Production Plant

21.5 Corn Stover Prep Subassembly

The corn stover prep subassembly processes bales of corn stover in preparation for hydrolysis. The components of this subassembly in general terms are listed in Figure 21-5 and shown in Figure 21-6.

Figure 21-5. Corn Stover Prep Components

Organism Feed Subassembly Components
Bale Transport Conveyor
Bale Unwrapping Conveyor
Belt Press Discharge Conveyor
Shredder Feed Conveyor
Truck Scales
Truck Unloading Forklift
Bale Moving Forklift
Corn Stover Wash Table
Shredder
Concrete Feedstock-Storage Slab
Polymer Feed System
Wash Table Pump
Wash Water Pump

Clarifier Underflow Pump
Clarified Water Pump
Belt Press Sump Pump
Clarifier Thickener
Belt Press
Magnetic Separator
Wash Water Tank
Clarifier Thickener Tank

Bales of corn stover are received by the plant on trucks. The trucks are weighed and unloaded by forklifts. Some bales are sent to storage while the rest are taken directly to conveyors. From there, the bales travel to an automatic unwrapping system that cuts away the plastic wrapping. Unwrapped bales are conveyed to a wash table, which starts breaking up bales and washes dirt from the corn stover. The washed stover is then conveyed past a magnetic separator which removes metal. Then, the stover is passed through primary and secondary shredders which shred the stover into a smaller, more easily processed size. Finally, the processed stover is conveyed to the pretreatment/hydrolysis subassembly.

Dirty wash water is recycled and cleaned utilizing a clarifier-thickener system. The wash water is pumped to the clarifier where clean water is drawn off and recycled back to the wash tables. The underflow from the clarifier is then dewatered in a belt press. Because most of the wash water is recycled through this system, the fresh water requirement is low.

Bale Transport Bale Unwrapping Conveyor Coneyor **Truck Scales Hay Bale Storage Belt Press Sump Pump** Wash Water Wash Pump **Belt Press** Water Tank Clarified Water **Polymer Feed** Pump System Clarifier Thickener **Wash Table** Tank **Pump** Clarifier **Underflow Pump Magnetic Separator Corn Stover Wash Table** Shredder Feed Conveyor Shredder To Hydrolysis **Impurities Waste Conveyor** To Off-site

Figure 21-6. Corn Stover Prep Subassembly Design

The equipment in Figure 21-6 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$4,038,990 as shown in Figure 21-7.

Figure 21-7. Capital Cost of Corn Stover Prep Subassembly

Corn Stover Prep	Material Chosen	Total Pri	cing
Components			
Bale Transport	400 ft long, 8' wide, 50 HP motor	\$	800,000
Conveyor	<i>5.</i>		
Bale Unwrapping	90 bale / hr		
Conveyor		\$	300,000
Belt Press Discharge	3' wide X 50' long.		
Conveyor		\$	50,000
Shredder Feed	8' wide X 30' long. 6001 lbs 31 fpm	Ф	240.000
Conveyor	C	\$	240,000
T1- C1	Concrete. 8' wide X 30' long. 6001 lbs 31	¢.	69,000
Truck Scales Truck Unloading	fpm Propose Cas Forklift	\$	68,000
Forklift	Propane Gas Forklift	\$	72,000
Bale Moving Forklift	Propane Gas Forklift	\$	
Corn Stover Wash	A238. 55 ton/hr	Ф.	72,000
Table	A238. 33 toll/lll	\$	208,000
Shredder	Alloy Steel. 55 ton/hr	\$	1,208,000
Concrete Feedstock-	Concrete Slab. 350' X538'	Ψ	1,200,000
Storage Slab	Concrete Stab. 330 A330	\$	450,655
Polymer Feed System		\$	30,000
Wash Table Pump	Rubber. 2500 gpm, 50 ft head	\$	40,000
Wash Water Pump	SS316. 5000 gpm, 50 ft head	\$	30,000
Clarifier Underflow	Rubber. MOD SRL 2X3-10 100 GPM	Ф	
Pump	50 TDH	\$	6,000
Clarified Water Pump	SS316. 5000 gpm, 50 ft head	\$	15,000
Belt Press Sump Pump	VJC 1.5X2.11 100 GPM 40 TDH	\$	19,000
Clarifier Thickener	5000 GPM mechanism	\$	135,000
Belt Press	304 SS. 1.5 meter	\$	100,000
Magnetic Separator	Tramp iron magnet separator	\$	10,355
Wash Water Tank	(20' Diameter X 22' Tall, 50,000 gal)	\$	50,000
Clarifier Thickener	Cement. (80' diameter)	\$	135,000
Tank			
TOTAL		•	\$4,038,990

21.6 Pretreatment/Hydrolysis Subassembly

The feedstock corn stover consists primarily of three components: cellulose, hemicelluloses, and lignin. Based on the Aden et al. report we have assumed a composition by weight of 36.7% cellulose, 27.4% hemicellulose, 30.8% lignin, and 5.1% other non-reacting matter. The feedstock is mixed with water to the ratio of 20% dry weight and 80% liquid. The purpose of the pretreatment/hydrolysis subassembly is to break down the components of the corn stover into complex sugars on which bacteria are capable of carrying out saccharification and

fermentation. The components of this subassembly in general terms are listed in Figure 21-8 and shown in Figure 21-9.

Figure 21-8. Pretreatment/Hydrolysis Components

Pretreatment/Hydrolysis Subassembly Components
Hydrozylate Mix Tank Agitator
Hydrozylate Mixing Tank
In-line Sulfuric Acid Mixer
Sulfuric Acid Pump
Sulfuric Acid Tank
Lime Solids Feeder
Lime Unloading Blower
Lime Dust Vent Baghouse
Lime Storage Bin
Hydrolysis Tank Pump
Hydrolysis Feed Boiler

The pretreatment/hydrolysis subassembly utilizes dilute acid hydrolysis reactions at 150 °C and 4.7 atmospheres to convert the washed and cleaned corn stover feedstock into hemicellulose-derived soluble sugars and crystalline cellulose that allow for subsequent bacterial sacchrification and fermentation. Cleaned corn stover from the corn stover prep subassembly mixed with water is heated by two heat exchangers, HX-1 and HX-2, and then heated in a boiler to 150 °C. In the boiler, heat is added to the mixture by burning the byproductH₂/CO₂ mixture coming from the waste side of the PSA separator. The heated slurry is then pumped into the hydrolysis reactor. The hydrolysis reaction hydrolyzes and breaks down the hemicelluloses portion of the feedstock by adding dilute (1.1%) sulfuric acid at 150 °C. The slurry is treated in this way for two minutes before the overliming process begins. This process raises the pH and re-solidifies the soluble lignin components for later separation. The subassembly components are shown in Figure 21-9.

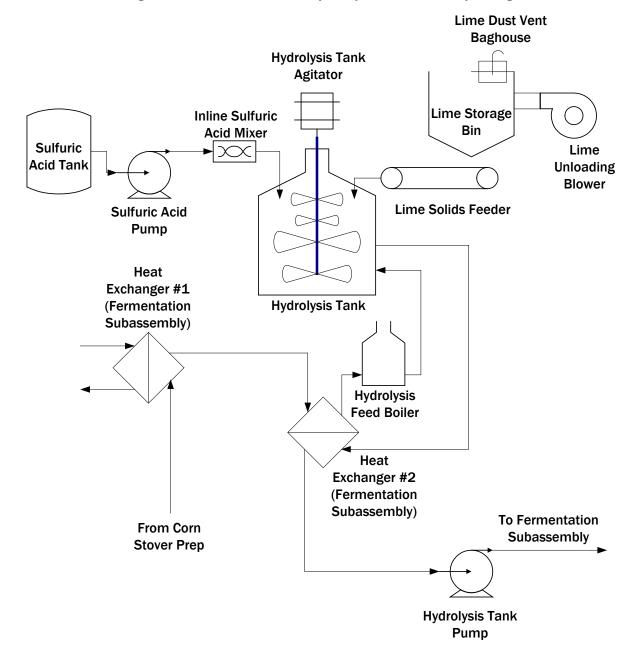


Figure 21-9. Pretreatment/Hydrolysis Subassembly Design

The equipment in Figure 21-9 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$847,017 as shown in Figure 21-10.

Figure 21-10. Capital Costs of Pretreatment/Hydrolysis Subassembly

Pretreatment/Hydrolysis Components	Material Chosen	Total Pricing
Hydrozylate Mix Tank	SS. Top-Mounted, 1800 rpm, 50 hp	
Agitator		\$ 28,421
Hydrozylate Mixing Tank	SS304. 24770 gal., 13' dia. X 25' high, 15	
Trydrozyrate Wilxing Tank	min. res. time, 90% wv, atmospheric	\$ 32,237
In-line Sulfuric Acid Mixer	SS304. Static Mixer, 248 gpm total flow.	\$ 2,542
Sulfuric Acid Pump	SS304. 4 gpm, 245 ft. head	\$ 8,289
Sulfuric Acid Tank	Plastic. 6444 gal., 24 hr. residence time,	
Sulfulle Acid Talik	90% wv	\$ 9,441
Lime Solids Feeder	A285C. 8" dia., 140 cfh, 7000 lb/hr max	
Line Sonds i cedei	flow conveyor	\$ 3,900
Lime Unloading Blower	C.S. 7425 cfm, 6 psi, 22275 lb/hr	\$ 99,594
Lime Dust Vent Baghouse	A285C, Polyester. 8333 cfm, 1389 sf, 6	
Line Dust Vent Dagnouse	cfm/sf	\$ 140,707
Lime Storage Bin	4455 cf, 14' dia x 25' high, 1.5x rail car vol.,	
Line Storage Bin	atmospheric	\$ 136,370
Hydrolysis Tank Pump	SS304. 737 gpm, 200 ft head	\$ 69,516
Hydrolysis Feed Boiler	6000 kW Boiler, 200 PSI. SS304	\$316,000
TOTAL		\$847,017

21.7 Fermentation Subassembly

The fermentation subassembly carries out two processes: Saccharification and fermentation. The sacharification converts the hydrolyzer complex sugars into simple sugars using enzymes. Fermentation describes the subsequent conversion of these simple sugars into hydrogen gas by carefully designed fermentative organisms. As mentioned earlier, these organisms will produce a cellulase enzyme for the saccharification of the cellulose component of the feedstock. The components of this subassembly in general terms are listed in Figure 21-11 and shown in Figure 21-12.

Figure 21-11. Fermentation Components

Fermentation Subassembly Components
Fermentation Tank
Fermentation Agitator
Fermentation Recirculation Pump
Lignin Wet Cake Screw
Acetate Product Storage Tank
Acetate Transfer Pump
Pneumapress Filter
Heat Exchanger #1
Heat Exchanger #2
Fermentor Temperature Control

In this subassembly the pretreated slurry is pumped into the saccharification/fermentation tank and inoculated with bacteria produced in the seed production subassembly, which will be

discussed later in this report. A fraction of the pretreated slurry will also be routed to the seed production subassembly for use in the cultivation of fermentative organisms. To maintain the temperature most conducive to fermentation, a portion of the slurry will be removed from the reactor, cycled through the fermentor temperature control heat exchanger for cooling, and returned to the tank. Residence time for one saccharification and fermentation cycle is a total of 40 hours.

In addition to hydrogen and carbon dioxide gases, the fermentation reaction will also produce acetic acid, which may be further processed into hydrogen by separate bacteria in a subsequent MEC system. This acetate is then pumped from the fermentation tank into temporary storage before being sent on for further hydrogen production or discarded. The subassembly components are all shown in Figure 21–12.

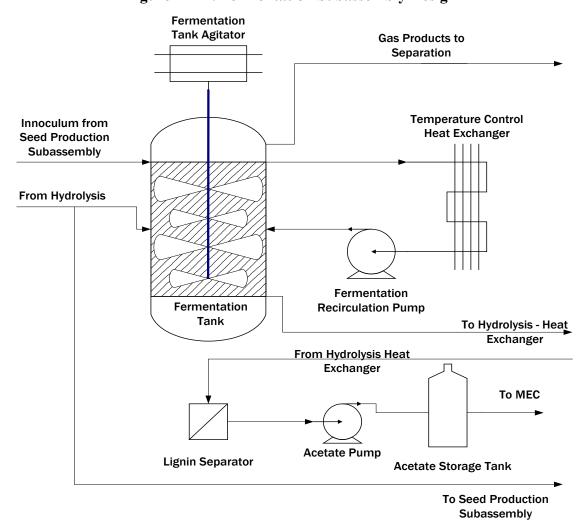


Figure 21-12. Fermentation Subassembly Design

The equipment in Figure 21–12 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$8,458,507 as shown in Figure 21–13.

Figure 21-13. Capital Costs of Fermentation Subassembly

Fermentation Components	Material Chosen	Total Pricing
Fermentation Tank	SS304. 962,651 gal. each, 90% wv, API, atmospheric	\$ 2,466,955
Fermentation Agitator	SS304. Side Mounted, 2 per vessel, 75 hp each, 0.15 hp/1000 gal	\$ 196,760
Fermentation Recirculation Pump	SS304. 1060 gpm, 150 ft head	\$ 68,330
Lignin Wet Cake Screw	14" Dia X 100' Long	\$ 84,185
Acetate Product Storage Tank	SS304. 456617 gal., 45' dia x 40' high, 4 hr res. Time, 90% wv, atmospheric	\$ 160,829
Acetate Transfer Pump	SS304. 1231 gpm total, 615 gpm each, 100 ft head	\$ 53,737
Fermentor Temperature Control	Plate-Frame, SS304, atmospheric	\$ 33,905
Heat Exchanger #1	Plate-Frame, SS304, atmospheric	\$ 22,346
Heat Exchanger #2	Plate Frame, SS304, 4.68 atmospheres	\$ 194,905
TOTAL		\$ 8,424,607

21.8 Seed Production Subassembly

The purpose of the seed production subassembly is to breed hydrogen producing fermentative bacteria for use in the fermentation reactor. The components of this subassembly in general terms are listed in Figure 21-14 and shown in Figure 21-15.

Figure 21-14. Seed Production Components

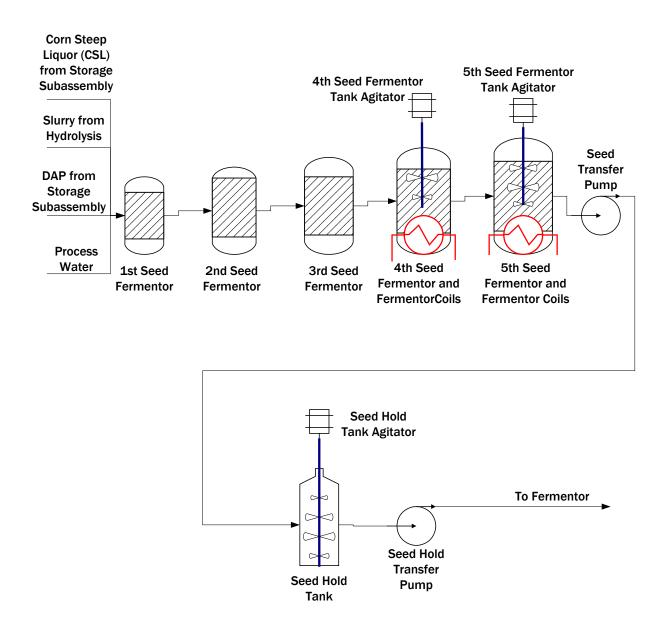
1 Iguit 21-14. Seed I roduction Components
Seed Production Subassembly Components
Seed Hold Tank
Seed Hold Tank Agitator
Seed Hold Transfer Pump
1st Seed Fermentor
2nd Seed Fermentor
3rd Seed Fermentor
4th Seed Fermentor
5th Seed Fermentor
4th Seed Agitator
5th Seed Agitator
4th Seed Fermentor Coil
5th Seed Fermentor Coil
Seed Transfer Pump

The bacteria is grown in a series of seed fermentation vessels. Hydrolyzed slurry and nutrients, such as corn steep liquor (CSL) and Diammonium Phosphate (DAP) are combined with an initial seed inoculum grown in a very small vessel in a laboratory. The result of each seed batch is used as the inoculum for the next size seed increment. This series of scale-ups is continued until the last step is large enough to support fermentation. Finally, the seed inoculum, nutrients, and saccharified slurry are combined in each fermentation tank. The number of fermentors will

be five 1-million gallon vessels in a line with a 40 hour reaction residence time in each. The subassembly components are shown in Figure 21-15.

Figure 21-15. Seed Production Subassembly Design

Seed Production Subassembly



The equipment in Figure 21-15 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$1,007,829 as shown in Figure 21-16.

Figure 21-16. Capital Costs of Seed Production Subassembly

Seed Production Components	Material Chosen	Total Pricing
Seed Hold Tank	SS304. 233,333 gal., API atmospheric	\$ 160,829
Seed Hold Tank Agitator	SS304. Top Mounted, 1800 rpm, 23 hp, 0.1 hp/1000 gal	\$ 12,492
Seed Hold Transfer Pump	SS304. 172 gpm, 150 ft head	\$ 22,050
1st Seed Fermentor	SS304. 20 gal, jacketed, agitated, 1.3' dia., 2' high, 15 psig	\$ 29,400
2nd Seed Fermentor	SS304. 194 gal., jacketed, agitated, 3' dia., 4' high, 2.5 psig	\$ 65,200
3rd Seed Fermentor	SS304. 1950 gal., jacketed, agitated, 6.5' dia, 8' high, 2.5 psig	\$ 162,200
4th Seed Fermentor	SS304. 19444 gal., 12' dia x 23' high, atmospheric	\$ 78,320
5th Seed Fermentor	SS304. 194500 gal., API, atmospheric	\$ 293,097
4th Seed Agitator	SS. Top Mounted, 1800 rpm, 6 hp, 0.3 hp/1000 gal	\$ 23,289
5th Seed Agitator	SS. Top Mounted, 1800 rpm, 19 hp, 0.1 hp/1000 gal	\$ 20,582
4th Seed Fermentor Coil	SS. 27 sf, 1" sch 40 pipe, 105 BTU/hr sf F	\$ 4,658
5th Seed Fermentor Coil	SS. 307 sf, 3" sch 40 pipe, 92 BTU/hr sf F	\$ 28,238
Seed Transfer Pump	SS304. 1231 gpm total, 615 gpm each, 100 ft head	\$ 107,474
TOTAL		\$1,007,829

21.9 Storage Subassembly

The purpose of the storage subassembly is to provide bulk storage of chemicals used in the hydrogen production process. It also serves as the location for the main process water tank, which provides water needed in the various subassemblies of the system. The components of this subassembly in general terms are listed in Figure 21-17 and shown in Figure 21-18.

Figure 21-17. Storage Components

Storage Subassembly Components
CSL Storage tank Agitator
CSL Pump
CSL Storage Tank
CSL/DAP Day Tank
CSL/DAP Pump
CSL/DAP Day Tank Agitator
DAP Solids Feeder
DAP Unloading Blower
DAP Vent Baghouse
DAP Storage Bin
Sulfuric Acid Pump
Sulfuric Acid Storage Tank

Storage Subassembly Components
Propane Storage Tank
Cooling Water Pump
Make-up Water Pump
Process Water Circulating Pump
Process Water Tank

In addition to the main process water tank, stored chemicals include sulfuric acid, of which a five day supply is held, Corn Steep Liquor (CSL), a by-product of the corn wet-milling industry, and Diammonium Phosphate (DAP), both nutrient sources for fermentation seed growth. Propane gas for use in the bale handling forklifts. The subassembly components are all shown in Figure 21-18.

Propane Storage Tank To Forklifts **CSLTank Sulfuric Acid** Agitator To Hydrolysis Storage Tank Sulfuric Acid Pump **CSL Tank CSL Storage Tank** Pump Hopper **DAP Vent** Baghouse CSL/DAP Day **Tank Agitator To Seed Production DAP Unloading DAP Storage** & Fermentation **Blower** Bin Subassemblies **DAP Solids Feeder** CSL/DAP Day CSL/DAP Tank

Figure 21-18. Storage Subassembly Design

The equipment in Figure 21-18 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$924,749 as shown in Figure 21-19.

Figure 21-19. Capital Costs of Storage Subassembly

Storage Components	Material Chosen	Total
zoruge components	1/1 /1/1/1/1/1 21/0301	Pricing
CSL Storage tank Agitator	SS304. Top Mounted, 1800 rpm, 23 hp, 0.1 hp/1000 gal	\$ 2,143
CSL Pump	SS304. Top Mounted, 1800 rpm, 23 hp, 0.1 hp/1000 gal	\$ 6,188
CSL Storage Tank	Cs. 431 gpm, 150 ft head	\$ 61,949
CSL/DAP Day Tank	SS304. 10,000 gal, 24 hr res time, 90% wv, 9.5' dia x 18.9' high, atmospheric	\$ 28,470
CSL/DAP Pump	CS. 431 gpm, 150 ft head	\$ 6,188
CSL/DAP Day Tank Agitator	SS304. Top Mounted, 1800 rpm, 5 hp, 0.5 hp/1000 gal	\$ 12,348
DAP Solids Feeder	A285C. 8" dia., 140 cfh, 7000 lb/hr max flow	\$ 3,900
DAP Unloading Blower	CS. 7425 cfm, 6 psi, 22275 lb/hr	\$ 49,014
DAP Vent Baghouse	A285C, Polyester. 8333 cfm, 1389 sf, 6 cfm/sf	\$ 9,595
DAP Storage Bin	CS. 1425 cf, 9' dia x 19.5' high, 1.5x vessel vol. Req. for 7-day res time, atmospheric	\$ 34,255
Sulfuric Acid Pump	SS316. 215 gpm, 150 ft head	\$ 13,814
Sulfuric Acid Storage Tank	SS316. 18697 gal, 120 hr res time, 90% wv, 12' dia x 22' high, atmospheric	\$ 60,470
Propane Storage Tank	A515. 2000 gal, 10 day res time, 90% wv, 4' dia x 23.6' length, 250 psig	\$ 30,825
Cooling Water Pump	CS. 41000 gpm, 70 ft head.	\$ 242,216
Make-up Water Pump	CS. 1083 gpm, 75 ft. head	\$ 8,735
Process Water Circulating Pump	CS. 1199 gpm ea, 75 ft. head	\$ 17,635
Process Water Tank TOTAL	CS. 756000 gal. 8 hr res time	\$ 337,004 \$924,749

21.10 Wastewater Treatment Subassembly

The function of the wastewater treatment subassembly is to treat process water for reuse to reduce the plant makeup water. The waste water is first screened, removing large particles to be subsequently sent to a landfill. Following screening, the organic matter in the water is then removed with anaerobic and aerobic digestion. This digestion produces a waste sludge and methane gas that could be used as a fuel for heating, however, we will not consider this further in this report. The components in this subassembly in general terms are listed in Figure 21-20.

Figure 21-20. Wastewater Treatment Subassembly Components

Wastewater Treatment Subassembly Components
Equalization Basin Agitator
Anaerobic Agitator
Anaerobic Digester Feed Cooler
Nutrient Feed System
Biogas Emergency Flare
Anaerobic Reactor Feed Pump
Aerobic Digester Feed Pump
Bar Screen
Equalization Basin
Anaerobic Digester
Aerobic Lagoon Agitator
Filter Precoat System
Aerobic Sludge recycle Pump
Aerobic Sludge Pump
Aerobic Digestion Outlet Pump
Sludge Filtrate Recycle Pump
Treated Water Pump
Belt Filter Press
Aerobic Digester
Clarifier

The design for the wastewater treatment section mirrors that of the ethanol report, which relied upon the analysis of Merrick Engineering. Their design was carefully scaled and optimized for their flow rates, which differ slightly from ours. We have scaled linearly the components of the system to match our increased flow rate. The subassembly components are show in Figure 21-21.

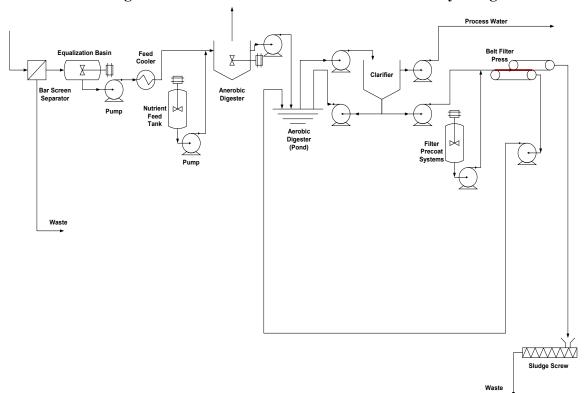


Figure 21-21. Wastewater Treatment Subassembly Design

The equipment in Figure 21-21 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$12,039,997 as shown in Figure 21-22.

Figure 21-22. Capital Cost of Wastewater Treatment Subassembly

Material Chosen	Total
	Pricing
SS. 38 HP each, Fixed Prop, 0.1 HP/1000 gal	\$ 94,624
SS. Fixed Prop, 41 HP, 0.05 hp/1000 gal	\$ 100,955
SS316. TEMA BES type, floating head	\$ 428,475
CS. 5 tanks and pumps	\$ 71,301
SS. Flare and Pilot	\$ 69,099
CS. Centrifugal Pump, 876 GPM, 150 ft. head	\$ 37,983
CS. Centrifugal Pump, 830 GPM, 150 ft. head	\$ 35,651
CS. 0.5" Mehc. Cleaned Screen	\$ 392,551
Concrete. 377516 Gal. Residence time 7.2 hr	\$ 1,168,809
Expoxy Lined. 810250 gal each, space velocity 12g/COD/day	\$ 2,935,620
CS. Twister Surface Aerators, 50 HP each	\$ 1,665,920
Cs. Tank, Agitator, Pump	\$ 9,996
SS316. Slurry Pump 2.5 GPM, 150 ft. head	\$ 36,983
SS316. Slurry Pump 25.3 GPM, 150 ft. head	\$ 36,983
CS. Centrifugal Pump, 828 GPM, 150 ft. head	\$ 35,651
CS. Centrifugal Pump, 22 GPM, 150 ft. head	\$ 20,324
CS. Centrifugal Pump, 803 GPM, 100 ft. head	\$ 35,317
304SS. Filter Press Separator	\$ 2,166,438
Polymer Lined Pit. 19500000 gal, 16.3 day residence time.	\$ 2,116,294
Concrete. 195,289 gal, residence time 3.9 hr	\$ 581,023 \$12,039,997
	SS. 38 HP each, Fixed Prop, 0.1 HP/1000 gal SS. Fixed Prop, 41 HP, 0.05 hp/1000 gal SS316. TEMA BES type, floating head CS. 5 tanks and pumps SS. Flare and Pilot CS. Centrifugal Pump, 876 GPM, 150 ft. head CS. Centrifugal Pump, 830 GPM, 150 ft. head CS. 0.5" Mehc. Cleaned Screen Concrete. 377516 Gal. Residence time 7.2 hr Expoxy Lined. 810250 gal each, space velocity 12g/COD/day CS. Twister Surface Aerators, 50 HP each Cs. Tank, Agitator, Pump SS316. Slurry Pump 2.5 GPM, 150 ft. head SS316. Slurry Pump 25.3 GPM, 150 ft. head CS. Centrifugal Pump, 828 GPM, 150 ft. head CS. Centrifugal Pump, 828 GPM, 150 ft. head CS. Centrifugal Pump, 803 GPM, 100 ft. head CS. Centrifugal Pump, 803 GPM, 100 ft. head

21.11 Gas Compression and Separation Subassembly

The function of the gas compression and separation subassembly is to compress the gaseous outputs from the fermentor to 300 psi, separate the product hydrogen from water vapor and CO_2 , and deliver the hydrogen to the production facility limits. The outlet pressure of hydrogen

at the plant gate is 300psi. This pressure was selected to provide with a system comparable to other DOE H2A Production Plants. The components of this subassembly in general terms are listed in Figure 21-23.

Figure 21-23. Gas Compression and Separation Components

Gas Capture Subassembly Components
Fermentor Compressor
Fermentor PSA Separator
Fermentor Condenser 1
Fermentor Intercooler 1
Fermentor Intercooler 2
Hydrogen Flow Meter

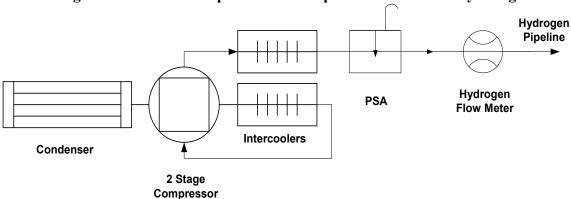
The hydrogen/CO₂/water vapor mixture is at atmospheric pressure and 55°C at the outlet from the fermentor:

- H_2 46,477 kg/day
- CO₂ 507,340 kg/day
- H₂O 113,542 kg/day

The gas mixture is initially sent to a condenser to cool the gas to 45°C condense about 40% of the water. This counter-flow gas/water heat exchanger has been scaled from a comparable condenser used in the Ethanol Report.

After the condenser, the gas enters a 2-stage compressor, which compresses the gas to 302 psi. to accommodate pressure losses in the PSA gas separation unit and the pipeline runs, which are estimated as 2 psi. A gas/water intercooler (FIC-1) is used between first and second stage compression to reduce the compressed gas temperature to 45°C and to condense additional water. A second intercooler (FIC-2) is used between second stage compression and the PSA to reduce the gas temperature to 45°C and to condense additional water. In the condenser and intercoolers, a total of 97% of the water vapor from the fermentor output is condensed out before the fermentor PSA, with the remaining water vapor mole fraction reduced to 0.00460. The gas/water intercoolers were scaled from a comparable heat exchanger used in the Ethanol Report. The subassembly components are shown in Figure 21-24.

Figure 21-24. Gas Compression and Separation Subassembly Design



The equipment in Figure 21-24 has been priced previously in several reports. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly components are shown in Figure 21-25.

Figure 21-25. Capital Cost of Gas Compression and Separation Subassembly

Gas Compression and	Material Chosen Pricing	
Separation Components		
Compressor	Source: Using H2A Cost guidelines and scaling factors	\$15,729,564
PSA Separator	Source: Using H2A Cost guidelines and scaling factors	\$1,527,494
Fermentor Condensor 1	Shell –Tube, SS304, atmospheric	\$ 29,623
Fermentor Intercooler 1	Shell-Tube, SS304, 4 atmospheres	\$ 57,651
Fermentor Intercooler 2	Shell-Tube, SS304, 20 atmospheres	\$ 311,057
Hydrogen Flow Meter	Information from Emerson Process Management	\$5,000
Total		\$17,660,889

21.12 Bill of Materials

The flow chart outlining mass flows and subsystem parameters is shown in Figure 21-26. The detailed mass and energy balance data is included in Part III, Appendix A. The full bill of materials for the lignocellulosic hydrogen production plant is shown in Figure 21-27. The system described in this section of the report has a capital cost of \$44,944,078.

Figure 21-26. Lignocellulosic Fermentation Flow Chart

Fermentation System - Batch Process Efficiencies- Hydrolysis: 90%, Fermentation: 90%

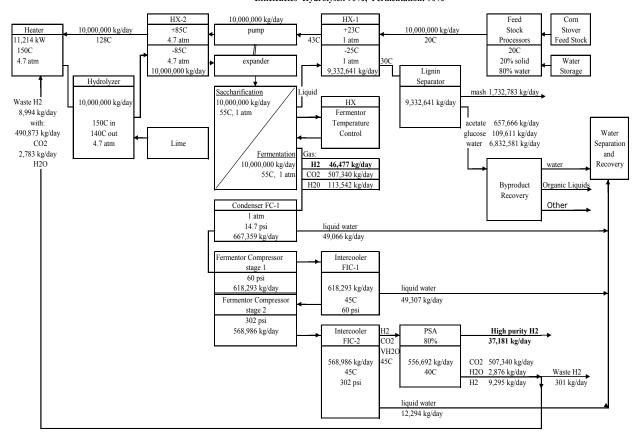


Figure 21-27. Bill of Materials Lignocellulosic Fermentation

Description Install Packer Size Regrid Units Unit code Other Oth
Balle Transport Conveyor
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Shwedder Feed Conveyor
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Fermentation Recirculation Pump
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Acetate Transfer Pump
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Belt Filter Press 1.8 650,223 3 \$ 2,166,
Aerobic Digestor 1 635,173 3 \$ 2,116,
Clarifier 1.96 174,385 3 \$ 581,
Gas Capture Subassembly 1.3 1704 kgmol/hr \$ 9,233 1,704 \$ 15,729
FC-1 13 \$ 29.623 1 \$ 29
FIC-1 1.3 \$ 57/651 1 \$ 57 FIC-2 1.3 \$ 311/057 1 \$ 311
FIC -2 1.3 \$ 311,057 1 \$ 311 PSA Fermentor 1.3 \$ 1,527
PSA Fermentor 1.3 1 1 1,527 Hydrogen Flow Meter 1.3 5 5,500 1 5 5,50

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22. Microbial Electrolyis Cell (MEC) Hydrogen Production

A Microbial Electrolysis Cell (MEC), also referred to as a Bio-Electrochemically Assisted Microbial Reactor (BEAMR) can be used to generate H_2 from simple organic liquids, such as acetic acid and ethanol, using electrolysis enhanced by a microbial reaction at the anode. The H_2 gas is evolved at the cathode and CO_2 gas is evolved at the anode.

In this section we will consider the MEC as a stand-alone hydrogen production unit, with a purchased acetic acid feedstock. Integration of the MEC system with the fermentation system to utilize the fermentator byproducts will be discussed in a later section.

22.1 Theoretical Reaction and Assumptions

Assuming an acetic acid input and MEC electrode voltages above 0.4 Volts, a complete reaction in the MEC would be:

$$C_2H_4O_2 + 2H_2O => 4H_2 + 2CO_2$$

The MEC process has been extensively researched and demonstrated at Penn State University. Output from a MEC using an acetic acid feedstock has been demonstrated in lab-scale tests to be as high as $96\% \pm 1\%^{89}$. With 95% reacted into H₂ and CO₂, 3.8 moles H₂ is generated per mole acetic acid. For this reaction, the input acetic acid was diluted with water to 1 gram per liter. For our calculations we assumed an average of 90% efficiency due to scale-up losses and anode/cathode degredation. This leads to an estimated acetic acid to hydrogen conversion ratio of 12.08% (gram H₂/gram acetic acid).

The following major MEC assumptions are used in the analysis:

- Both the anode and cathode materials are low cost and sufficiently durable for long-term operation (20 years)
- External electrical power will be provided to sustain the reactions.
- The volume of acetic acid feedstock chosen for use was chosen based on the amount of acetic acid and glucose that would be used in an integrated system utilizing the fermentation effluent
- The cost of the acetic acid feedstock is \$0.595/kg based on the international market price as reported by the Korean Chemical Journal ⁹⁰

22.2 MEC Operating Parameters

For this study the baseline MEC system was sized so that it could be integrated with the fermentation system described in the previous section. The baseline conditions that have been used for MEC hydrogen production using an acetic acid feedstock are summarized in Figure 22-1.

⁸⁹ Call, Douglas and Logan, Bruce, "Hydrogen Production in a single Chamber Microbial Electrolysis Cell Lacking a Membrane." Environmental Scientific Technology 42 (2008): 3401-3406.

Lee, Sang Yup. "Plastic Bacteria? Progress and Prospects for Polyhydroxyalkanoate Production in Bacteria." Trends in Biotechnology 14 (1996): 431-438.

Figure 22-1. Parameters for MEC System

MEC (0.9V) Acetic Acid Usage (kg/day) 767,277 H ₂ Production Rate (kgH ₂ /day) 88,085 ⁹¹ Plant Area (Acres) 10 Land Utilization (kg H ₂ /acre/ 2,788,553 year)
H_2 Production Rate (kg H_2 /day) 88,085 ⁹¹ Plant Area (Acres) 10 Land Utilization (kg H_2 /acre/ 2,788,553
Plant Area (Acres) 10 Land Utilization (kg H ₂ /acre/ 2,788,553
Land Utilization (kg H ₂ /acre/ 2,788,553
, e
y car y
Water Usage
(gal/day) 9,242,555
(gal/kg_{H2}) 105
Electricity Required
kWhr/day 3,288,962
kWh/kgH ₂ 37.34
$\frac{kWh/kWh}{kWh/kWh} H_2 \qquad \qquad 1.12$
MEC Parameters
Bacteria Cell lines (anode) Pseudomonas spp. And Shewanella
spp. 92
Duration of Cycle (hrs) 24
Target Temperature (°C) 30
Assumed Reaction Efficiency 90%
Feedstock - to - H ₂ Conversion
Ratio
gram H ₂ /gram acetic acid 12.08% Reactant Volume
Gallons 91,524,080
Liters 346,682,121
Reactor Volume ⁹³
Gallons 96,100,285
Liters 364,016,227
Theoretical Product Ratio 4 mol H ₂
2 mol CO ₂
Assumed Actual Product Ratio 3.6 mol H ₂ 1.8 mol CO ₂

⁹¹ Assumes 95% H₂ recovery in the PSA.
92 Logan, Bruce et al. "Microbial Enectorlysis Cells for High Yield Hydrogen Gas Production from Organic Matter." Environmental Scientific Technology 42 (2008): 8630-8640.
93 Including electrode volume and spare capacity of 5%

22.3 MEC System Description

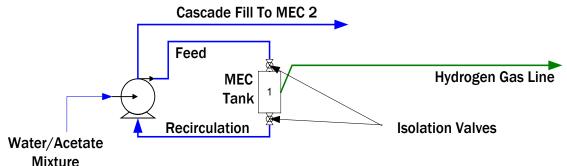
The MEC hydrogen production plant has been divided into 3 interconnected subassemblies, namely,

- MEC Subassembly,
- Storage Subassembly, and
- Gas Compression and Separation Subassembly

22.3.1 MEC Plant Layout

The interfaces between the subassemblies are shown in Figure 22-2. The subassemblies have several components that will be identified in later sections of this document.

Figure 22-2. Simplified MEC Hydrogen Production Unit



For the hydrogen production rate shown in the previous section, a large number of units, each comprised of a million gallon reactant tank and electrodes, are necessary. Residence time in the reactor at 0.9V potential is 24 hours per electrolysis cycle. Each reactant tank can be operated in a semi-continuous process, with daily replenishment of acetate and water. With the MEC system designed to consume 690,549 kg acetate and 414,314 kg water per day, these amounts will be replenished daily. Periodically, after an appropriate number of cycles, a tank would be emptied, cleaned and replenished with new electrolyte, and also anode organisms if necessary. A representative tank field layout is shown in Figure 22-3.

Water From Storage Acetate From Storage Mixing Valve Hydrogen to Gas Capture 5 6 7 8 9 10 Transfer Waste Pump Water **MEC Bank** ~ 10 MEC and 1 Transfer Pump **BANK BANK** BANK **BANK** BANK BANK **BANK BANK** BANK **BANK** BANK **BANK** 2 10 12 1 3 5 6 8 9 11

Figure 22-3. MEC Unit Field Layout

MEC Module = ~ 12 MEC Banks

22.3.2 MEC Reactor Subassembly

As mentioned, to generate H_2 from acetic acid or from the acetic acid, succinic acid, lactic acid, formic acid, glucose, and alcohol liquid byproducts of a fermentation reaction, a Microbial Electrolysis Cell (MEC) also referred to as a Bio-Electrochemically Assisted Microbial Reactor (BEAMR), can be used to electrolyze the mix of organic materials and water to produce hydrogen.

Ordinarily, a water electrolysis unit requires about 1.8 V to electrolyze water. The MEC uses microbe reactions at the anode with the organic materials, and water to generate a significant voltage. This is supplemented with an externally applied anode-to-cathode voltage to initiate and sustain an electrolysis process to generate H₂ and CO₂ from the organics and water. The current generated provides the electrons to produce H₂ at the cathode, with CO₂ produced at the anode. The microbes on the anode develop sufficient voltage such that the additional potential needed for the electrolysis of organic byproduct is only 0.2-0.9 V.

With acetic acid input, a complete redox reaction in the MEC would be:

$$C_2H_4O_2 + 2H_2O => 4H_2 + 2CO_2$$

The components of the subassembly in general terms are listed in Figure 22-4.

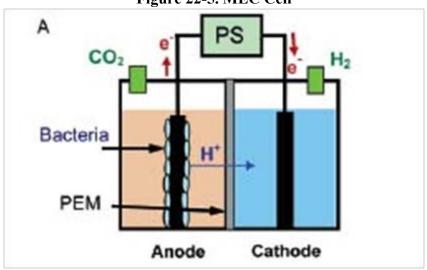
Figure 22-4. MEC Components

MEC Subassembly Components
MEC Tank
Cathode
Anode
Power Supply
Process Water Circulating Pump
MEC Transfer Pumps
MEC Intercooler 1
MEC Intercooler 2

22.3.2.1 *MEC Cell Description*

A representative MEC reactor cell is shown in Figure 22-5. Though the cell is shown with a PEM membrane, it can be operated without one, resulting in a small amount of gas dilution.

Figure 22-5. MEC Cell



Tests have been run by PSU with a high surface area brush anode (brush fiber surface area/brush envelope volume = $18,200 \text{ m}^2/\text{m}^3$) and a cathode made from carbon cloth loaded at $0.5 \text{ mg/cm}^2\text{Pt}^{94}$. Data from these tests in Figure 22-5 shows the linear relationship between H_2 output Q (m^3 -hydrogen per day/ m^3 MEC) as a factor of applied voltage with Q=0 at V=0.2. The figure also shows energy efficiency increasing with decreasing voltage. However, at lower voltage, the reaction is slower and system size increases substantially. These tests run without a membrane provided good separation of the H_2 and CO_2 .

^{0.4}

⁹⁴ Call Douglas and Bruce E. Logan. "Hydrogen Production in a single Chamber Microbial Electrolysis Cell Lacking a Membrane." <u>Environmental Scientific Technology 42</u> (2008): 3401-3406.

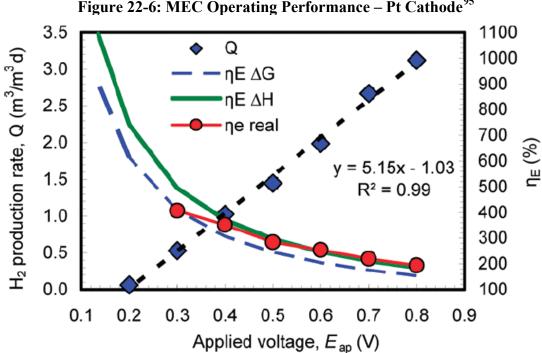


Figure 22-6: MEC Operating Performance – Pt Cathode 95

Because of the high cost of Pt cathodes, additional research has been carried out by PSU, substituting a stainless steel brush for the carbon/Pt cathode⁹⁶. With a very high surface area brush cathode, the H₂ production rate was only slightly less than with the Pt loaded cathode. These tests demonstrated a Q of 1.7 at a voltage of 0.6V. Assuming that the Q vs. V relationship for the brush cathode is also linear with a zero output at 0.2V, a line for the cell output through Q of 1.7 and V of 0.6 can be superimposed on Figure 22-6. The resulting performance line is the solid blue line labeled "brush cathode" in Figure 22-7. The equation for the Pt Cathode Q is:

$$O = 5.15V - 1.03$$

And the similar equation for the Brush Cathode (the solid blue line in Figure 22-7) is:

$$Q = 4.25V - 0.85$$

Logan, Bruce et al. "Microbial Electrolysis Cells for High Yield Hydrogen Gas Production from Organic Matter." Environmental Scientific Technology 42 (2008): 8630-8640.

⁹⁶ Call, Douglas et al. "High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells." Environmental Scientific Technology (2008)

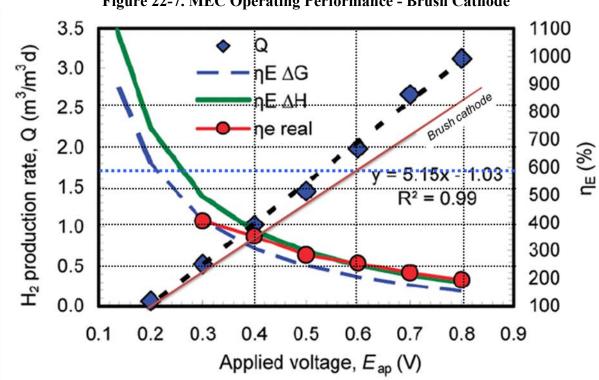


Figure 22-7. MEC Operating Performance - Brush Cathode

The conclusion drawn from these performance graphs is that while a low voltage is more efficient from a power consumption standpoint, a high voltage results in a markedly smaller MEC volume for a given volume of H₂ product, thus reducing capital costs significantly.

MEC Hydrogen Production Cost Optimization 22.3.2.2

MEC capital costs decrease with increased voltage, due to higher production rate. However, electrical costs increase with voltage. Thus, higher electrical costs go along with lower tank and electrode costs. These costs were modeled as a function of voltage to examine the minimum H₂ cost design for the MEC. The five primary H₂ production cost components are:

- MEC Tank
- Brush Cathode
- Brush Anode⁹⁷,
- Power Supply, and
- Electric Power

Figure 22-8 plots the cumulative H₂ production cost buildup from these five components. We used component sizing methodology used by PSU. The most dominant factor was the cost of stainless steel brush wires (based on SS wire costs from various suppliers). Though we looked at wire diameters down at 0.02 mm, the best cost-to-surface-area ratio was with 0.08 mm wire. To reduce brush costs, we reduced the surface area required by a factor of 2 relative to the

Logan, Bruce et al. "Graphite Fiber Brush Anodes for Increased Power Production in Air Cathode Microbial Fuel Cells." Environmental Scientific Technology (2007)

brushes used in the PSU tests, per the suggestion of Bruce Logan who pointed out that the brush size is not yet optimized.

The results shown in Figure 22-8 indicate that 0.9V achieves the lowest cost. We therefore used this point in our cost analyses.

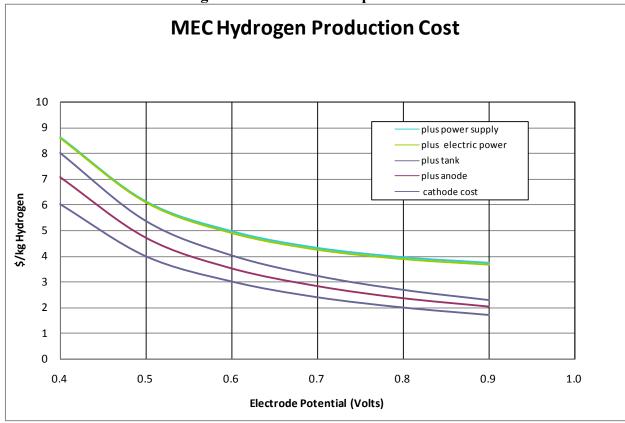
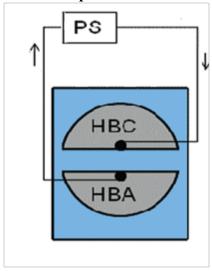


Figure 22-8. MEC Cost Optimization

22.3.2.3 MEC Brush Cathode

For the brush cathode, the ratio of its surface area to the brush envelope volume, S/Ve, was approximately 2500 m²/m³. For the PSU test cells, the ratio of brush cathode surface area to the reactor volume, S/Vr, was between 650 and 810 m²/m³. A top view of the MEC cell with a half-brush anode and half-brush cathode which gave the best performance is shown in Figure 22-9. The brushes are semicircular to improve the packing density and reduce the ion transport distance relative to circular brushes.

Figure 22-9: MEC Test Unit Top view with Half-Brush Cathode and Anode



For the MEC design and costing analysis, carbon fiber brush anodes and 304 stainless steel brush cathodes as discussed in the references were assumed. Cell performance was based on the test results but reduced from 95% to 90% to account for scale-up losses and brush degradation. The specific brush sizes used in the PSU tests were laboratory scale (1 inch length by 0.5 inch radius) and are obviously not appropriate for large-scale production cells. For this analysis, the surface area ratio used was reduced to half of that used in the small scale tests. Using this ratio for a large system the materials requirements are quite substantial, and effort will have to be dedicated in the future to designing lower cost high effective area cathodes and anodes amenable to a large scale system.

In addition, to reduce costs, the cells were operated without an ion exchange membrane. Potential future developments future for a scaled-up MEC system would include:

- reduced reactor volume per hydrogen generation, increased reactant concentration
- lower cost cathodes
- additional bacteria-generated voltage
- minimized CH4 output
- optimized solution electrolyte & conductivity
- addressal of long term corrosion issues
- cathode and anode scale-up for large cells

22.3.2.4 Total Hydrogen Production Cost

The system size was chosen to be compatible with the fermentation system output reactable organic liquids. For the stand-alone MEC, a similar mass flow of acetate was substituted for the output organic liquid mass flow of the fermentor. Thus, the feedstock reacted for the stand-alone MEC was:

• Acetic Acid: 767,277 kg/day (12,788 moles/day)

For the overall system layout, the output H_2 gas from the multiple MEC units feed a manifold that feeds a single gas compression and separation subassembly, discussed in the following section.

For this effluent, the capital cost of the subassembly is \$541,705,673 as shown in Figure 22-10.

Figure 22-10. Capital Costs of MEC Subassembly

_ Tiguite 22-10. Capital Costs of MILC Subassembly							
Seed Production	Material Chosen	Total Pricing					
Components							
MEC Tanks	SS304. 962,651 gal. each, 7 day residence total, 90% wv, API, atmospheric	\$ 57,488,911					
Brush Cathode	0.08 mm SS316 Wire	\$ 400,686,098					
Brush Anode	0.0072 mm Carbon Threads	\$ 62,316,288					
Power Supply	Based on Electrolyzer Power Supply, Scaled for 122,184 kW	\$ 18,550,000					
MEC Transfer Pumps	CS. 41000 gpm, 70 ft head.	\$ 2,906,592					
TOTAL		\$541,705,673					

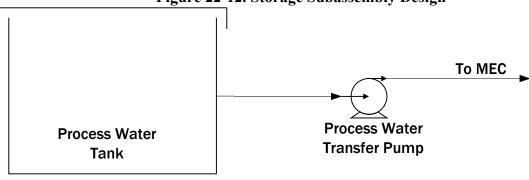
22.3.3 Storage Subassembly

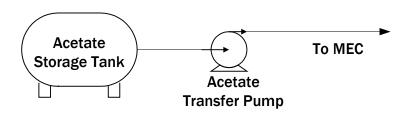
The storage subassembly for the MEC system is substantially smaller than for the fermentation system. The only storage needed is for the acetate feedstock and process water. The components of this subassembly in general terms are listed in Figure 22-11 and shown in Figure 22-12.

Figure 22-11. Storage Components

Storage Subassembly Components
Acetate Storage Tank
Acetate Transfer Pump
Process Water Circulating Pump
Process Water Tank
Process Water Transfer Pump

Figure 22-12. Storage Subassembly Design





The equipment in Figure 22-12 is all very commonly available within the agricultural industry. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly is \$884,167 as shown in Figure 22-13.

Figure 22-13. Capital Costs of Storage Subassembly

Storage Components	Material Chosen	Total Pricing
Acetate Storage Tank	SS316. 18697 gal, 90% wv, 12' dia x 22' high, atmospheric	\$ 35,270
Acetate Transfer Pump	SS316. 215 gpm, 150 ft head	\$ 391,000
Process Water Circulating Pump	CS. 1199 gpm ea, 75 ft. head	\$ 161,593
Process Water Tank	CS. 756000 gal. 8 hr res time	\$ 54,088
Process Water Transfer Pump TOTAL	CS. 41000 gpm, 70 ft head.	\$ 242,216 \$884,167

22.3.4 Gas Compression and Separation Subassembly

The function of gas compression and separation subassembly of the MEC is to compress the gaseous outputs from the MEC, to separate the product hydrogen, and to deliver it to the production facility limits at 300 psi. The components of this subassembly in general terms are listed in Figure 22-14.

Figure 22-14. Gas Compression and Separation Components

Gas Capture Subassembly Components
MEC Compressor (2 stage)
MEC PSA
MEC Compressor Intercooler 1
MEC Compressor Intercooler 2
Hydrogen Flow Meter

The outlet pressure of hydrogen at the plant gate of 300 psi was selected to provide with a system comparable to other DOE H2A Production Plants.

At the MEC hydrogen outlet, the gas is at atmospheric pressure and 30°C. Since the temperature is only 30°C, there is a substantially lower mole fraction of water than is in the outlet gas from the fermentor, so no condenser is needed. In addition, the MEC electrolysis process separates most of the hydrogen from the CO₂. It is estimated that only 5% of the MECproduced CO₂ is mixed in the output hydrogen stream. The MEC-exit stream into the compressor is:

- 92,721 kg/day • H₂
- CO₂ 50,607 kg/day
- H₂O 36,752 kg/day

The gas mixture is sent to the 2-stage compressor. After the compressor and two intercoolers, the remaining gas mixture at 302 psi enters the PSA. Pressure loss in the PSA and the pipeline is estimated as 2 psi. A gas/water intercooler (MIC-1) is used between first and second stage compression to reduce the gas temperature to 45°C and to condense out water. A second intercooler (MIC-2) is used between second stage compression and the PSA to reduce the gas temperature to 45°C and to condense additional water, so that a total of 89% of the water vapor from the MEC output is removed before the MEC PSA., with the remaining water vapor mole fraction reduced to 0.00460. The gas/water intercoolers were scaled from a comparable heat exchanger used in the Ethanol Report.

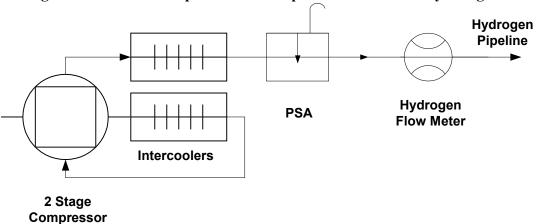
Since the PSA input is 1,914 moles/hr H₂, 48 moles/hr CO₂, and 9 moles/hr H₂O, we have assumed that the PSA can recover 95% of the inlet H₂. Thus the PSA output is:

- H₂ (high purity) 88,085 kg/day
- Waste:
 - $\begin{array}{ccc} \circ & CO_2 & & 50,607 \text{ kg/day} \\ \circ & H_2O & & 3,921 \text{ kg/day} \end{array}$

 - \circ H₂ (loss) 4,636 kg/day

Subassembly components are shown in Figure 22-15.

Figure 22-15. Gas Compression and Separation Subassembly Design



Gas compression and separation is has been priced previously in several reports. Thus pricing for the equipment was easily located in reference documents and through discussions with suppliers. The capital cost of the subassembly components is \$16,099,326 as shown in Figure 22-16.

Figure 22-16. Capital Cost of Gas Compression and Separation Subassembly

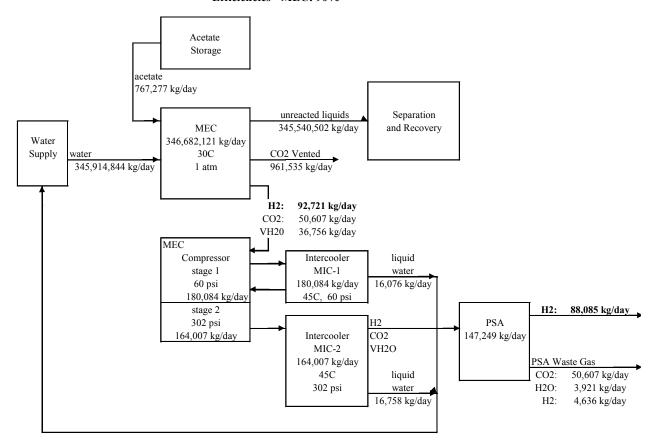
Gas Compression and Separation Components	Material Chosen	Pricing
Compressor	Source: Using H2A Cost guidelines and scaling factors	\$15,267,690
PSA	Pressure Swing Adsorption	\$182,960
	Source: Using H2A Cost guidelines and sc	aling factors
MEC Intercooler 1	Shell-Tube, SS304, 4 atmospheres	\$ 88,542
MEC Intercooler 2	Shell-Tube, SS304, 20 atmospheres	\$ 554,634
Hydrogen Flow Meter	Information from Emerson Process Management	\$5,500
Total		\$16,099,326

22.4 Bill of Materials

The flow chart outlining mass flows and subsystem parameters is shown in Figure 22-17. The detailed mass and energy balance is included in Part III, Appendix B.

Figure 22-17. MEC System Flow Chart

MEC System - Batch Process Efficiencies- MEC: 90%



The full bill of materials for the MEC stand-alone hydrogen production plant is shown in Figure 22-18. The MEC system described in this section of the report has a capital cost of \$558,689,165.

Figure 22-18. MEC Stand-Alone Bill of Materials

Description	Install Factor	Size Req'd	Units	Unit Size	Units	Unit cost	Qty Req'd	Total Cost
MEC Subassembly								
MEC Tanks	1.3					\$ 0.51	1.13E+08 \$	57,488,911
Brush Cathode	1.2					\$ 14.60		400,686,098
Brush Anode	1.2					\$ 7.92		62,316,288
Power Supply	1.3					\$ 350,000.00		18,550,000
MEC Pumps	2.8					242,216	11 \$	2,664,376
Storage Subassembly								
Process Water Circulating Pump	2.8					17,635	2 \$	35,270
Process Water Tank	1.4					195,500	2 \$	391,000
Acetate Product Storage Tank	1.4					\$ 161,593	1 \$	161,593
Acetate Transfer Pump	1.3					\$ 54,088	1 \$	54,088
Process Water Transfer Pump	2.8					242,216	1 \$	242,216
Gas Capture Subassembly								
Compressor MEC	1.3	1654	kgmol/hr	1654	kgmol/hr	\$ 9,233	1 \$	15,267,690
MIC-1	1.3		•			\$ 88,542	1 \$	88,542
MIC - 2	1.3					\$ 554,634	1 \$	554,634
PSA MEC	1.3						1 \$	182,960
Hydrogen Flow Meter	1.3			1		\$ 5,500	1 \$	5,500.00
						System	Initial Cost \$	558,689,165

23. Cost Assumptions and Calculations

In addition to the capital costs which have been described in the previous sections, there are some additional costs associated with this system, mostly electricity, labor, and various feedstock costs. These costs for both the MEC system and the Fermentation system are explained in detail in this section.

23.1 Variable Costs

Aside from the fixed capital costs, there are numerous variable costs including electricity, labor, water usage, and additional consumables. The usage and associated costs of these will each be defined in the following sections.

23.1.1 Electric Power Requirements

There are numerous elements of the Lignocellulosic Fermentation System requiring power, but they mostly center around pumps, conveyors and agitators. However, the largest power needs comes from the compressor, which is compressing an enormous amount of gas. PSA power is minimal as it is only needed to actuate valves. The gas compressor is a 2-stage piston compressor (N=2) with interstage cooling. Its power was calculated by assuming compression from 45°C inlet temperature with efficiency of 75%. Overall pressure ratio was 20.5 for an outlet pressure of 302psi.

$$P = \frac{dm}{dt} Cp T N \frac{1}{\eta} \left(\frac{P2^{\frac{\gamma-1}{\gamma N}}}{P1} - 1 \right)$$

Figure 23-1 lists the electricity usage anticipated for each of the Fermentor components previously described and provides a total consumption value for the Fermentor to be used in further analysis. The previously mentioned duty cycles and operational cycle have been taken into account in these computations. We have assumed a pump efficiency of 80% and a density of all liquids as 1 g/cc. H2A accounts for electricity usage and costs in the "Other Variable Costs" section.

Figure 23-1. Power Requirements for Fermentor without MEC

Figure 23-1. Power Requirements for Fermentor without MEC Power Requirements							
Conveyors	Power	Unit					kW
Bale Transport Conveyor	50	HP					37
Bale Unwrapping Conveyor	50	HP					37
–							
Belt Press Discharge Conveyor	50	HP					37
Shredder Feed Conveyor	50	HP					37
Lignin Wet Cake Screw DAP Solids Feeder	50	HP					37
	50	HP					37
Agitators	Power	Unit					
Fermentation Agitator	75	HP					56
Hydrozylate Mix Tank Agitator	50	HP					37
Seed Hold Tank Agitator	23	HP					17
4th Seed Agitator	6	HP					4
5th Seed Agitator	19	HP					14
CSL Storage tank Agitator	23	HP					17
CSL/DAP Day Tank Agitator	5	HP					4
Pumps	Throughput	Unit	Head		M3/hr	Meter	
Wash Table Pump	2500	GPM	50	ft	568	15	29
Wash Water Pump	5000	GPM	50	ft	1136	15	59
Clarifier Underflow Pump	100	GPM	50	ft	23	15	1
Clarified Water Pump	5000	GPM	50	ft	1136	15	59
Belt Press Sump Pump	100	GPM	40	ft	23	12	1
Sulfuric Acid Pump	4	GPM	245	ft	1	75	0.2
Process Tank Pump	737	GPM	200	ft	168	61	35
Fermentation Recirculation Pump	1060	GPM	150	ft	241	46	38
CSL Pump	431	GPM	150	ft	98	46	15
Sulfuric Acid Pump	215	GPM	150	ft	49	46	8
Cooling Water Pump	41000	GPM	70	ft	9318	21	677
Make-up Water Pump	1083	GPM	75	ft	246	23	19
Process Water Circulating Pump	1199	GPM	75	ft	273	23	21
CSL/DAP Pump	431	GPM	150	ft	98	46	15
Seed Hold Transfer Pump	172	GPM	150	ft	39	46	6
Seed Transfer Pump	1231	GPM	100	ft	280	30	29
Miscellaneous	Throughput	Unit					
DAP Unloading Blower	253	НР					189
Compressor							4535
PSA PSA							50
Lime Unloading Blower	253	НР					189
Total Power Usage (kW)							6,350
kWhr/day							152,389
kWhr/year							55,621,907
\$/year						\$	2,781,095
\$/kg H ₂						\$	0.23
kWhr/kg H ₂							4.10
kwhr/kwhr H ₂							0.12

The power requirement of the MEC system comes primarily from the MEC cell itself. The power draw of the MEC electrolysis process is estimated from the electron current required to reduce the H+ and the applied voltage and the system electric efficiencies experimentally

determined in Penn State tests⁹⁸. Figure 23-2 lists the electricity usage anticipated for the MEC system.

Figure 23-2. Power Requirements MEC System

	ı	Power R	equirem	ents			
							kW
MEC							122184
Compressor MEC							6619
PSA							50
Pumps	Throughput	Unit	Head		M3/hr	Meter	kW
Cooling Water Pump	41000	GPM	70	ft	9318	21	8125
Acetate Transfer Pump	1083	GPM	75	ft	246	23	19
Process Water Circulating Pump	1199	GPM	75	ft	273	23	42
kW							137,040
kWhr/day							3,288,962
kWhr/year							1,200,471,198
\$/year						\$	60,023,560
\$/kg H2						\$	2.07
kWh/kg H2							37.34
kWh/kWh H2							1.12

23.1.2 Labor

Labor rates for the fermentation system are similar to those in the ethanol report. We eliminated lab technicians and managers, since we will not require use of a lab. We also removed clerks and secretaries, who are accounted for separately in the H2A spreadsheet. Due to the vastly smaller and less complex plant as compared to an ethanol plant, the resulting labor numbers are probably somewhat high. However, given the relatively small impact that labor has on the cost of produced hydrogen, we felt that this was an acceptable overestimation. Figure 23-3 shows labor categories and number of personnel. The same number of personnel is assumed for the fermentation-only alone plant as is assumed for the fermentor with MEC plant. H2A accounts for labor costs in the fixed O&M.

Figure 23-3. Labor Breakdown - Fermentor

Position	Number of Personnel
Plant Manager	1
Plant Engineer	1
Maintenance Supervisor	1
Shift Supervisor	5
Maintenance Technician	8
Shift Operators	20
Yard Employees	32
General Manager	1
Total FTEs	68

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⁹⁸Call, Douglas et al. "High Surface Area Stainless Steel Brushes as Cathodes in Microbial Electrolysis Cells." Environmental Scientific Technology (2008) table 1.

For MEC labor, due to the similar size but reduced complexity, we have assumed 1/4 of the labor is required.

23.1.3 Additional Chemical Consumables

There are many consumables that are needed for full operation of the lignocellulosic fermentation plant. The rates and costs of these consumables for the fermentation system are listed in Figure 23-4. Rates and costs for these consumables are derived from the ethanol production report.

Figure 23-4. Additional Consumables Costs – Fermentation system

Additional Consumables Cost								
Raw Material	Unit	Rate		Cost (\$/kg)		\$/year		\$/kg H2
CSL	kg/day	31,344	\$	0.18	\$	2,023,606	\$	0.165678
Sulfuric Acid	kg/day	78,912	\$	0.03	\$	785,743	\$	0.064331
Lime	kg/day	57,480	\$	0.08	\$	1,606,244	\$	0.131508
DAP	kg/day	3,912	\$	0.16	\$	221,778	\$	0.018158
Propane	kg/day	480	\$	0.005	\$	848	\$	0.000069
Clarifier Polymer	kg/day	672	\$	2.75	\$	674,520	\$	0.055225
Totals					\$	5,312,739	\$	0.43

Given that these consumables are not options within the H2A Modeling tool, we have calculated the cost per kilogram of hydrogen from these variable operating costs and manually added these to the results obtained from H2A for levelized hydrogen costs.

The MEC consumable for the stand-alone system is acetic acid at \$0.595/kg and costing \$5.70 per kg of produced hydrogen.

23.1.4 Water Consumption

There are several sources of water loss within each system. For the fermentation system, water is primarily lost in the fermentation reaction. Further water is trapped in solids that are removed as waste. Most of the process water vapor is returned by condensation in the condenser and intercoolers. Using the molar ratios of the fermentation equation and the volume of hydrogen gas generated, we are able to calculate the daily use of reactant water in hydrogen production. In addition, substantial water is recovered from liquid byproducts.

For the MEC developed by PSU, the substrate is much more dilute than the fermentor output. Further, additional water is needed because we have assumed that after going through ten cycles of MEC acetate replenishment, the system will be flushed and the process water will need to be replaced. Thus, every day, 10% of the overall process water will need to be replaced in addition to the water used up in the production of hydrogen.

The water losses for the Fermentor and MEC is shown in Figure 23-5.

Figure 23-5. Water Use

Water Loss (gal/day)							
	Fermentor	MEC					
Size	37 TPD	88 TPD					
Water Used in reaction	54,826	109,375					
Water Loss in Lignin Separator	223,397	NA					
MEC Waste Water (10%)	NA	9,132,152					
Water Lost in PSA	759	1,035					
Net Loss	278,983	9,241,551					
Net Loss (gal/kgH ₂)	7.5	105					

23.1.5 Total Variable Feed Costs

The sum of all the variable costs, excluding labor, for the Fermentation system is indicated in the Figure 23-6. The variable costs for the MEC system are shown in Figure 23-7.

Figure 23-6. Total Variable Costs for Fermentor

	Variable Operating Costs											
Raw Material	Unit	Rate	Cost (\$/kg)			\$/year	\$/kg H2					
Corn Stover	kg/day	2,000,000	\$	0.03	\$	24,090,000	\$	1.972317				
Process Water	gal/day	278,983	\$	0.004	\$	373,089	\$	0.030546				
CSL	kg/day	31,344	\$	0.18	\$	2,023,606	\$	0.165678				
Sulfuric Acid	kg/day	78,912	\$	0.03	\$	785,743	\$	0.064331				
Lime	kg/day	57,480	\$	0.08	\$	1,606,244	\$	0.131508				
DAP	kg/day	3,912	\$	0.16	\$	221,778	\$	0.018158				
Propane	kg/day	480	\$	0.005	\$	848	\$	0.000069				
Clarifier Polymer	kg/day	672	\$	2.75	\$	674,520	\$	0.055225				
Totals					\$	29,775,828	\$	2.44				

Figure 23-7. Total Variable Costs for MEC

Variable Operating Costs											
Raw Material Unit Rate Cost (\$/kg) \$/year \$/k											
Acetic Acid	kg/day	767,277	\$	0.595	\$:	166,633,382	\$	5.758714			
Process Water	gal/day	9,242,551	\$	0.002	\$	5,618,279	\$	0.194163			
Totals					\$ 3	172,251,661	\$	5.95			

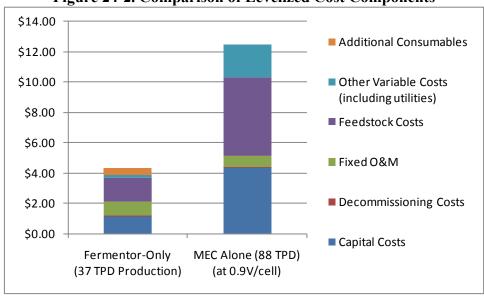
24. <u>Hydrogen Production Costs for Fermentor and MEC</u>

The summation of the various costs per kg of hydrogen produced is listed in Figure 24-1. Note that due to slight differences in H2A costing methodology, the prices shown in these subtotals might be different from those shown in the final results. The primary components of the levelized cost of hydrogen are capital costs, fixed O&M and other variable costs as shown in Figure 24-2.

Figure 24-1: Total Hydrogen Cost

	igure 24-1. Total frydrogen Co									
Total Cost of Produced H ₂										
Cost Component	Hydrogen Production Cost Contribution (\$/kg)									
System	Fermentor-Only (37 TPD Production)	MEC Alone (88 TPD) (at 0.9V/cell)								
Cost Component	Hydrogen Production Cost Contribution (\$/kg)	Hydrogen Production Cost Contribution (\$/kg)								
Capital Costs	\$1.19	\$4.37								
Decommissioning Costs	\$0.01	\$0.05								
Fixed O&M	\$0.87	\$0.71								
Feedstock Costs	\$1.60	\$5.18								
Other Raw Material Costs	\$0.00	\$0.00								
Byproduct Credits	\$0.00	\$0.00								
Other Variable Costs (including utilities)	\$0.23	\$2.12								
Additional Consumables	\$0.43	\$0.00								
Total	\$4.33	\$12.43								

Figure 24-2. Comparison of Levelized Cost Components



For the Stand-alone Fermentor system, there is a substantial liquid organic byproduct which has value, but for which we have not taken a cost credit due to the uncertainty of the constituents

and the market values. From NREL testing, the fermentor byproduct (section 2.3.2) is as shown in Figure 24-3.

Figure 24-3. Fermentor Liquid-Organic Output Value

Fermentor Product	mM	MW	Mass fraction	Market Cost per kg
Acetic Acid	26.0	60.05	51.1%	\$0.57
Ethanol	14.0	46.06	21.1%	\$0.54
Succinic Acid	5.6	118.10	21.6%	NA
Lactic Acid	1.8	90.08	5.3%	\$2.03
Formic Acid	0.6	43.03	0.8%	NA

Thus, after a distillation separation process, the resulting components would have a current average market value of about \$0.55/kg. However, any large addition to the world market would reduce prices, so the actual cost benefit of the organic byproduct is difficult to estimate. With the fermentor organic liquid byproduct of about 700,000 kg/day, if the value of this raw byproduct were \$0.20/kg, the byproduct value would be \$140,000 per day. This would yield a credit of \$3.78/kg H₂, substantially driving down the H₂ cost/kg to \$0.60/kg. Even with a byproduct value as low as \$0.12/kg, the H₂ cost/kg is \$2.09/kg, near the goal of \$2.00/kg H₂.

25. <u>Lignocellulose Fermenation and MEC System Conclusions and</u> Recommendations

25.1 Lignocellulose Fermentation System

The lignocellulose fermentation system used corn stover at 2,000 tonnes/day as a feedstock to generate 37 tonne/day purified H_2 . The process is complex and involves feedstock preprocessing, hydrolysis, saccharification, fermentation, solid/liquid separation, and H_2 gas separation. The unique 150° C acid hydrolysis process used to convert cellulose and hemicellulose into complex sugars has been demonstrated by NREL. The subsequent saccharification process utilizes organisms developed at NREL to rapidly convert the hydrolysis products into simple sugars. The ensuing fermentation process occurs in the same reactor and uses separate NREL-developed bacteria to produce H_2 and CO_2 gases plus simple organic liquids, such as acetic acid and ethanol.

In the initial calculation, with no value recovered from the byproducts, the lignocellulosic processing achieved a moderately low H₂ cost of \$4.33/kg H₂. For this system producing 37 tonnes of pure H₂, these byproducts are essentially: 692 tonnes of organic acid and alcohol liquids, 115 tonnes of unreacted sugars, and 846 tonnes of solids including lignin and a small amount of unreacted xylan. The liquid organic byproducts, equaling 35% of the input organic feedstock by weight, include 51% acetate and 21% ethanol which have intrinsic value, but require a subsequent separation process such as distillation. As an alternative to byproduct recovery, the liquid organics can be processed in an MEC to produce additional hydrogen.

There is high potential for H_2 cost reduction from sales of the liquid organic byproduct. If this byproduct had a market value of 0.12kg (as compared to the acetic acid market price of 0.60kg), the net H_2 cost would be reduced to 0.09kg.

In addition to the liquid byproducts, the remaining solids, lignin and some residual xylan, (42% of the organic feedstock by weight) have additional value, as they can be used as a low grade fuel for industrial processes.

Recommendations:

- Conduct further analysis to verify the values of the lignocellulose fermentation liquid and solid organic byproducts to significantly reduce the cost of the hydrogen.
- Conduct further analysis to address the separation of byproduct components (acids, ethanol, etc.), such as in a distillation process
- Examine in greater detail the current experimental efficiencies and reaction times for the hydrolysis, saccharification, and fermentation processes, and propose potential future testing to verify these quantities.

25.2 Microbial Electrolysis Cell (MEC) System

For the MEC electrolysis process the microbial electrolysis voltage is supplemented by an external voltage. Low external voltage results in highest efficiency, but increases reaction times, thus increasing system size and cost. For lowest H_2 production cost, the system should be operated at a higher than normal voltage (0.9V) to minimize capital plant costs. The very low concentration of the input acetic acid \sim 2 g acetate/liter of water, (as opposed to the fermentor at 200 g organics/liter of water) resulted in a very large system, i.e., 96,000,000 gallons of total reactor volume for 88 tonnes pure H_2 /day. These volumes, based on current PSU research results, resulted in large tankage and the resultant large area anodes and cathodes, which were the major cost drivers. In addition, the effective operation of these electrodes in a very large scale reactor tank has not yet been analyzed or demonstrated.

For the MEC system, the H₂ cost using pure acetic acid feedstock was a moderately high \$12.43/ kg H₂. This was primarily a product of the use of a very dilute acetic acid/water reactant, which necessitated very large reactor volumes and very large, costly anodes and cathodes. Along with the high capital cost was high acetate feedstock cost, which could be reduced by using a low purity simple organic feedstock such as the fermentor byproduct. However, the current large system size dominates the costs. The immaturity of the full scale system concepts and components indicated that there is extensive potential for future cost reductions.

Recommendations:

- Develop optimized production process and components for low capital cost systems, addressing issues such as:
 - o Increased solution density,
 - o Pressurized operation (to minimize separate compressor costs)
 - Lower cost cathodes
 - Lower cost anodes
 - Cathode and anode geometry optimization for large reactors
- Determine the extent of ion transport losses as reactor size grows to production scale
- Examine potential efficiencies of the process carried out at large scale

	<u>t III Appe</u>	<u>enaix</u>	<u> A: Fe</u>		Mass/		Bala						
Process			%	Mass flow kg/day	kg/hr	mole flow kgM/hr	°C	T ave	≅T °C	P psi	Cp kJ/kg °C	h kJ/kg	dq/dt kJ/hr
Feedstock	Corn stover		20.0%	2,000,000	83,333	Kgiviiii	20		<u> </u>	14.7	Norteg C	ito/itg	NO/111
Inputs		cellulose	36.7%	734,000	30,583								
		hemicell	27.4%	548,000	22,833								
		Lignin,etc total	35.9% 100.0%	718,000 2,000,000	29,917 83,333								
	water	1.0.1	80.0%	8,000,000	333,333		20			14.7			
	total slurry		100.0%	10,000,000	416,667		20			14.7			
HX-1	from feedstock			10,000,000	416,667		20.0			14.7	4.180		
	to HX-2 from fermentor			10,000,000 9,332,641	416,667 388,860.06		43.3 55.0	31.7	23.3	14.7	4.182		40,655,31
	to LigSep			9,332,641	388,860		30.0	42.5	-25.0	14.7	4.102		-40,655,31
HX-2	from HX-1 primary			10,000,000	416,667		43.3			68.8	4.206		
	to hydrolyzer heater			10,000,000	416,667		128.5	85.9	85.2				149,281,25
	from hydrolyzer			10,000,000	416,667		140.0	07.5	85.0	68.8	4.215		440.004.05
I badabasa	to sacchrification	117.0		10,000,000	416,667		55.0	97.5					-149,281,25
Hydolyzer Heater	heating of slurry from	Πλ-Z		10,000,000 10,000,000	416,667 416,667		128.5 150.0	139.3	21.5	68.8	4.290		38,387,18
	heating of CO2 from F	PSA		490,873	20,453		45.0	100.0	20	00.0	1.200		00,007,10
	CO2/H2mass			490,873	20,453		150.0	97.5	105.0	14.7	0.913		1,960,729
	heating of H2O from F			2,783 2,783	116 116		45.0 150.0	97.5	105.0	14.7	1.970		22.00
	H2O/H2mass Total heat input re		glecting H2		116		150.0	91.5	105.0	14./	1.970		23,98 40,371,90
	Waste H2 burner		effic =	,									10,011,00
	H2 LHV kJ/kg =	= 119,705	90%	8,994	375					14.7			40,371,902
				10,000,000	416,667								
Total heating from HX-1													230,308,47
Hydrolyzer	In from Heater	aallulaaa	26 70/	10,000,000	416,667		150.0			68.8			
	inputs	cellulose hemicell	36.7% 27.4%	734,000 548,000	30,583 22,833					psi 4.68			
		Lignin,etc	35.9%	718,000	29,917					atm			
		water	80.0%	8,000,000	333,333								
officiones =	output	total	2010	10,000,000 1,153,800	416,667 48,075		140.0			68.8			
efficiency= 90%	output	complex su xylan	gars	128,200	5,342		140.0			00.0			
3070		Lignin,etc		718,000	29,917								
		organics		2,000,000	83,333								
		water total		8,000,000 10,000,000	333,333 416,667								
	Endothermic heat abs			10,000,000	410,007		10.0						
	to HX-2			10,000,000	416,667		140.0			68.8			
Saccharification	from HX-2			10,000,000	416,667		55.0			14.7			
in fermentor tan	k to fermentation proces	SS		10,000,000	416,667		55.0						
Fermentor	in from	total		10,000,000	416,667		55.0			14.7			
efficiency =	sacchrification	simple suga	ars	1,153,800	48,075	267 (glucose)							
90%	process	Lignin,xylar	n,etc	846,200	35,258	(gracose)	1						
		water		8,000,000	333,333								
	HOO resided in	reactants		10,000,000	416,667								
	H2O reacted in fermer gas out	ntation H2		207,676 46,476.6	8,653 1,937	961	55			14.7			
	3	CO2		507,339.5	21,139	480							
		V H2O		113,542	4,731	263	55			1			
	slurry out to HX-1	total gas slurry total		667,359 9,332,641	27,807 388,860	1,704	55			1			
	Sidiny out to FIX-1	Lignin,xylar	n,etc	846,200	35,258		33						
		Acetate		692,280	28,845								
		Glucose	10%	115,380	4,808								
		L-H20 total		7,678,781 9,332,641	319,949 388,860								
	total mass out	iotui -		10,000,000	416,667		1						
Condenser	gases in	H2		46,477	1,937		55			14.7	14.496		
FC-1	from fermentor	CO2		507,340	21,139		55			14.7	0.953		
		V H2O		113,542	4,731		55			14.7	1.912		
	gases out to	total H2		667,359 46,477	27,807 1,937	960.6	45	50	-10	14.7	14.496		-280,719
				507,340	21,139	480.3	45	50	-10	14.7	0.953		-201,350
	Compressor-F-1	CO2											
	Compressor-F-1	V H2O		64,477	2,686.5	149.1	45	50	-10	14.7	1.912		-51,367
	Compressor-F-1				2,686.5 25,762 2,044	149.1	45 45	50	-10 -10	14.7	1.912 4.200		-51,367 -533,436 -62,477

Process			0/	Mass flow	1/-	mole flow	T	T ave	, T	P	Cp	h	dq/dt
Compressor	lin	H2	%	kg/day 46,477	kg/hr 1,937	kgM/hr 961	°C 45	°C	°C	psi 14.7	kJ/kg °C	kJ/kg	kJ/hr
stage 1	""	CO2		507,340	21,139	480	45			14.7			
F-1		V H2O		64,477	2,687	149	45			14.7			
		total		618,293	25,762	1,590	45			14.7			
	out	H2		46,477	1,937	961	190.8			60			
		CO2		507,340	21,139	480	190.8			60			
		V H2O		64,477	2,687	149	190.8			60			
		total		618,293	25,762	1,590							
Intercooler	Gas in	H2		46,477	1,937	961	190.8			60	14.496		
FIC-1		CO2		507,340	21,139	480	190.8			60	0.953		
Primary		V H2O		64,477	2,687	149	190.8			60	1.912		
	0	total		618,293	25,762	000.0	45	447.0	440		44.400		4 000 004
	Gas out	H2 CO2		46,477	1,937	960.6 480.3	45 45	117.9	-146 -146	58 58	14.496 0.953		-4,092,88° -2,935,688
		V H2O		507,340 15,169	21,139 632.1	35.1	45 45	117.9 117.9	-146	58	1.912		-2,935,000
		total gas		568,986	23,708	33.1	40	117.3	-140	30	1.312		-7,204,769
	Liquid out	L H2O		49,307	2,054		45		-146	58	4.200		-915,401
			change heat	,	_,							-2222	-4,565,040
	total out		<u>J</u>	1,187,279	49,470								-12,685,209
Secondary	water in			3,642,123	151,755		20				4.180		
	water out			3,642,123	151,755		40	30	20		4.180		12,685,209
Compressor	in	H2		46,477	1,937		45			58			
stage 2		CO2		507,340	21,139		45			58			
F-2		V H2O		15,169	632		45			58			
		total		568,986	23,708	1,476							
	out	H2		46,477	1,937	960.6	218			302			
		CO2		507,340	21,139.15	480.3	218			302			
		V H2O		15,169	632	35.1	218	ļ		302			
		total		568,986	23,708	1,476.0							
FIC-2	Gas in	H2		46,477	1,937		218			302			
Primary		CO2		507,340	21,139		218			302			
		V H2O total		15,169 568,986	632		218			302			
	Gas out	H2		46,477	23,708 1,937	960.6	45	131.45	-173	300	14.496		-4,853,629
	Gas out	CO2		507,340	21,139.15	480.3	45	131.45	-173	300	0.953		-3,481,348
		V H2O		2,876	120	6.7	45	131.45	-173	300	1.912		-39,619
		total gas		556,692	23,196	1,447.6		.00					-8,374,596
	Liquid out	L H2O		12,293	512	,	45		-173	300	4.200		-270,646
		V-L Phase	change heat									-2222	-1,138,145
	total out			568,986	23,708								-9,783,386
Secondary	water in			2,808,964	117,040		20				4.180		
	water out			2,808,964	117,040		40	30	20		4.180		9,783,386
PSA	in	total		556,692	23,196		45			300			
fermentor		H2		46,477	1,937	960.6	45			300			
		CO2		507,340	21,139	480.4	45			300			
	out	V H2O	80%	2,876 37,181	120 1,549	6.7	45 45			300			
	out	H2 outlet H2 loss	20%	9,295	387	192.1	45			300			
		CO2	20 /0	507,340	21,139	480.4	45			300			
		CO2/H2 ma	ass ratio	54.6	21,100	100.4	,0			"			
		V H2O	.00 1000	2,876	120	6.7	45			300			
		VH2O/H2 n	nass ratio	0.31									
		waste gas o		519,511	21,646	679.2							
	Burner us	e of waste H2=	97%										
LigninSeparator	in from HX-1	total from H	IX-1	9,332,641	388,860								
		Lignin,etc		846,200	35,258		30			14.7			
		Acetate		692,280	28,845								
		Glucose		115,380	4,808								
		L-H20		7,678,781	319,949			-		<u> </u>	-		
	out mech	total	1000/	9,332,641	388,860		30	-		-			
	out - mash	Lignin,etc Acetate	100% 5%	846,200 34,614	35,258 1,442		30						
		Glucose	5% 5%	5,769	240								
		L-H2O	= lignin wt	846,200	35,258								
		IL-ロバリ				l	1	1		ı	I		
		total		1,732,783	72.199					l			
	out - liquid		95%		72,199 27,403		30				-		
	out - liquid to MEC	total		1,732,783 657,666 109,611	72,199 27,403 4,567		30						
		total Acetate	95%	657,666 109,611 6,832,581	27,403 4,567 284,691		30						
		total Acetate Glucose	95%	657,666 109,611	27,403 4,567		30						

27. Part III Appendix B: MEC Mass/Heat Balance

<u> 27. Par</u>	<u>rt III App</u>	<u>endix B:</u>	MF		<u>ieat Ba</u>								
				Mass flow		mole flow	T	Tave	ΔΤ	Р.	Ср	h	dq/dt
	T	T	%	kg/day	kg/hr	kgM/hr	°C	°C	°C	psi	kJ/kg °C	kJ/kg	kJ/hr
MEC	Inputs:	Acetate	-	767,277	31,970	532.4	30			14.7			
0.9V system	Acetate	water input		345,914,844	14,413,119								
	dilution (g/L) =	H2O + substrate =	-	346,682,121 346,682,121	14,445,088					1			
	2.213	total input 91,524,080 gallons		340,002,121	14,445,088								
	reacted acetate	91,524,000 gallons	90%	690,549	28,773	479.1							
	reacted water		30 /0	414,314	17,263	958.3							
90%	output-gas	H2		92,721	3,863	1,916.5	30			14.7			
reaction	output-gas	CO2 total out		1,012,142	42,173	958.3	00			14.7			
completion		CO2 mixed in H2	5%	50,607	2,109	47.9	0.05						
oompiouo		H2O-V	0,0	36,755	1,531.5	85.0	0.00			14.7			
		total cathode gas		1,141,619	47,567	2,049				1			
	output liquid	unreacted acetate	10%	76,728	3,197		30						
		H20-L		345,463,775	14,394,324								
		total liquid		345,540,502	14,397,521								
	total output			346,682,121	14,445,088								
CO2 Vented from ME	EC		95%	961,535	40,064								
		LIO				4.040	20	_		447	_		
Compressor MC-1	in	H2 CO2		92,721	3,863	1,916 48	30 30			14.7			
INIO-1		V H2O		50,607 36,755	2,109	48 85	30			14.7 14.7			
				36,755	1,531.5 7,503		30			14.7	-		
	out	total H2		180,083 92,721	3,863	2,049 1,916	204			14.7	-		
	out	H2 CO2		92,721 50,607	2,109	47.9	204			60			
		V H2O		36,755	1,531	47.9 85	204			60			
		total		180,083	7,503	2,049	204			60			
	-					2,043							
Intercooler	Gas in	H2		92,721	3,863		204			60			
MIC-1		CO2		50,607	2,109		204			60			
Primary		V H2O		36,755	1,531		204			60			
		total		180,083	7,503	1.010	45	1010	450		44.400		0.000.111
	Gas out	H2		92,721	3,863	1,916	45	124.3	-159	58	14.496		-8,882,141
		CO2		50,607	2,109	47.9	45	124.3	-159	58	0.953		-318,543
		V H2O		20,679	861.6	47.8	45	124.3	-159	58	1.912		-261,287 -9,461,971
	l invital and	total L H2O		164,007	6,834 670		45		-159	58	4.000		
	Liquid out	V-L Phase change he	- ot	16,076	670		45	-	-159	00	4.200	-2222	-324,656 -1,488,369
	total out	V-L Phase change no	al	180,083	7,503							-2222	-11,274,996
Secondary	water in			3,237,228	134,885		20				4.180		-11,274,330
Gecondary	water out			3,237,228	134,885		40	30	20		4.180		11,274,996
0		Luc						00	20		1.100		11,211,000
Compressor	in	H2		92,721	3,863		45			58			
MC-2		CO2		50,607	2,109		45			58			
		V H2O		20,679 164,007	862	2,012	45 45			58 58			
	out.	total H2		92,721	6,834	1,916	267	-		302			
	out	CO2		50,607	3,863 2,109	1,916	267			302			
		V H2O		20,679	862	48	267			302			
		total		164,007	6,834	2,012	201			302	<u> </u>		
						2,012	007			000			
Intercooler	Gas in	H2		92,721	3,863		267			302			
MIC-2		CO2		50,607	2,109		267			302			
Primary		V H2O total		20,679 164,007	862 6,834		267			302			
	Gas out	+		92,721		1 016	45	156	-222	300	14 406		-12 //22 757
	Gas out	H2 CO2		50,607	3,863 2,109	1,916 48	45 45	156	-222	300	14.496 0.953		-12,432,757 -445,880
		V H2O		3,921	163.4	9.1	45 45	156	-222	300	1.912		-445,000 -69,347
		total gas		147,249	6,135	3.1	+0	100		500	1.312		-12,947,984
	Liquid out	L H2O		16,758	698		45		-222	300	4.200		-473,726
		V-L Phase change he	eat	10,700	000					230		-2222	-1,551,548
				164,007	6,834								-14,973,258
	total out						20				4.180		, 5,200
Secondary	total out water in	,		4,299,057	179,127								14,973,258
Secondary		, , , , ,			179,127 179,127		40	30	20		4.180		14,973,230
	water in water out	TH2		4,299,057 4,299,057	179,127	1 01/		30	20	300	4.180		14,973,230
PSA	water in	H2		4,299,057 4,299,057 92,721	179,127 3,863	1,914 48	45	30	20	300 300	4.180		14,973,230
•	water in water out	CO2		4,299,057 4,299,057 92,721 50,607	3,863 2,109	48	45 45	30	20	300	4.180		14,973,230
PSA	water in water out	CO2 V H2O		4,299,057 4,299,057 92,721 50,607 3,921	3,863 2,109 163		45 45 45	30	20	300 300	4.180		14,973,230
PSA	water in water out in	CO2 V H2O total	95%	4,299,057 4,299,057 92,721 50,607 3,921 147,249	179,127 3,863 2,109 163 6,135	48	45 45 45 45	30	20	300 300 300	4.180		14,973,250
PSA	water in water out	CO2 V H2O total H2 out	95% 5%	4,299,057 4,299,057 92,721 50,607 3,921 147,249 88,085	3,863 2,109 163 6,135 3,670	48	45 45 45 45 45	30	20	300 300 300 300	4.180		14,973,250
PSA	water in water out in	CO2 V H2O total	95% 5%	4,299,057 4,299,057 92,721 50,607 3,921 147,249 88,085 4,636	179,127 3,863 2,109 163 6,135 3,670	48 9	45 45 45 45	30	20	300 300 300	4.180		14,973,230
PSA	water in water out in	CO2 V H2O total H2 out H2 waste		4,299,057 4,299,057 92,721 50,607 3,921 147,249 88,085	3,863 2,109 163 6,135 3,670	48	45 45 45 45 45 45	30	20	300 300 300 300 300	4.180		14,973,230

Part IV: Integrated Systems

28. Systems Integration

Having characterized and assessed costs for several pathways for biological hydrogen production, it is important to consider how combinations of different pathways could enhance hydrogen production and potentially lower costs. Combining capital costs, making use of waste products and increasing solar capture makes it possible to improve the cost-effectiveness of the overall system. This report is focused on examining different combinations of the biological hydrogen production pathways and evaluating costs associated with these integrations as compared to the individual systems.

There are three types of biological systems that have been evaluated in this effort: photobiological, fermentation, and Microbial Electrolysis. These types can be used in integrated systems. Integrations are shown in Figure 28-1. Combinations can occur within the photobiological subset of systems, within the fermentation subset of systems or a combination of a photobiological and fermentation system. While other combinations may exist, our task required the evaluation of four systems. We have chosen to study the four that are most representative and have sufficient synergies to make integration a possibility. Higher multiples of the systems could be possible but are not considered necessary to evaluate in the boundary analysis. Those could be reviewed in more detail if any of these combinations prove fruitful.

Photobiological Fermentor/MEC Stacked Beds Integration B-3 Algal Sulfate Lignocellulosic B-5 PNS Permease Fermentation Reactor Bed Reactor Bed **B-3 Algal Sulfate** Raw Acetate Waste Waste Permease Mutant acetate (~5% of organism organism [top Reactor Bed] req'mt) byproduct Algal Algal B-5 PNS Bacteria MEC Fermentation Fermentation [lower reactor bed (C-3)(C-5)Acetate

Figure 28-1. Potential Biological Integration Methods

The four potential system combinations analyzed are as follows:

- stacked photobiological systems (B-3/B-5) to capture a greater portion of the solar spectrum
- photobiological H₂ production (B-1) combined with algal fermentation (C-1)
- photobiological PNS H₂ production (B-5) combined with waste PNS fermentation (C-5) and waste acetate consumption in the PNS photosynthesis
- lignocellolosic fermentation combined with microbial electrolysis

For more details on the specifics of each of the systems mentioned please refer to Part I, Part II and Part III of this report.

28.1 Stacked Photobiological Pathway

The best way to evaluate integrated photobiological beds is by considering them vertically stacked. Side-by-side integration would increase the land requirements and only share auxiliary subsystem costs. Organisms and bed designs as defined would not absorb the full spectrum or intensity of solar light available. Thus, it seems probable that a stacked system would take advantage of this and allow for greater hydrogen production per area. In order to stack systems the organisms chosen for the top and bottom reactor must have sufficiently different PAR spectra to produce significant increases in hydrogen production in a stacked configuration. As has been noted before, the PNS bacteria in the B-5 pathway utilize a different PAR spectrum than the Chlamydomonas algae and Cyanobacteria in systems B-1, B-2, B-3, and B-4. Thus stacking one of these beds on top of a B-5 photobio bed could improve H₂ production by increasing the range of the solar spectrum captured by the beds. For the upper bed, B-3 was chosen rather than the B-1 and B-2 systems because of the additional greater precautions necessary in handling the stoichiometric H₂/O2 mix from the latter systems. The B-4 system was not used because the polypropylene mats used for the immobilized algae, combined with the high algae density on these mats, would block the transmission of photons to the lower layer. Therefore, the stacked system we chose to investigate consisted of a sulfate permease mutant B-3 system stacked on top of a B-5 PNS bed, increasing the effective PAR of the integrated system from 44% to 71%, leading to an increase in hydrogen production relative to the B-3 system by itself. Furthermore, many hardware components can be combined for the two systems, including most of the reactor bed subassembly, control system subassembly, and gas capture subassembly costs. The assumptions and changes from the B-3 system to create a stacked bed include:

- A second layer of film to separate the two beds
- The components of the Organism Feed Subassembly and Recycle Subassembly are all doubled in order to provide nutrients and maintain concentration in both beds
- In order to capture the additional photons, roughly 1/5 of the normal concentration of PNS will be needed, and thus the acetate nutrient requirements are 1/5 of the full B-5 system
- Since the B-5 system will be stacked below the B-3 system, it will be impossible to provide paddlewheel mixing. Thus, we have added recirculation pumps and perforated pipe that extends the length of the raceways every 10 feet

A process diagram of the integrated system is shown in

Figure 28-2. The conceptual design of a tiered reactor bed system is illustrated in Figure 28-3. Overall cost for the B-3/B-5 stacked system for a 1 ton per day (TPD) plant is \$4,274,085. The bill of materials for the B-3/B-5 stacked system is shown in Figure 28-4.

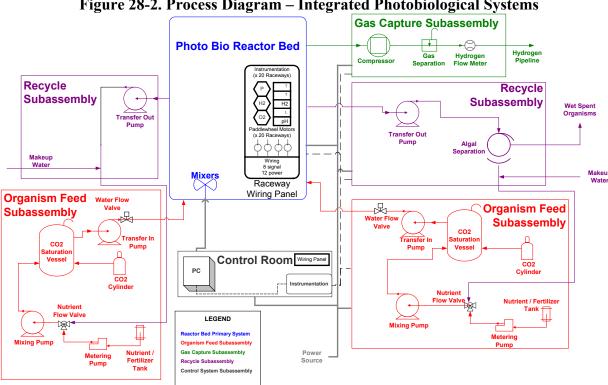


Figure 28-2. Process Diagram – Integrated Photobiological Systems

Figure 28-3. Tiered Reactor Bed Conceptual Design

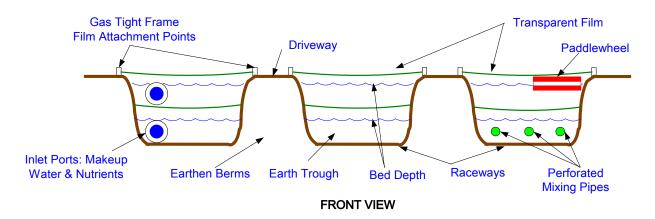


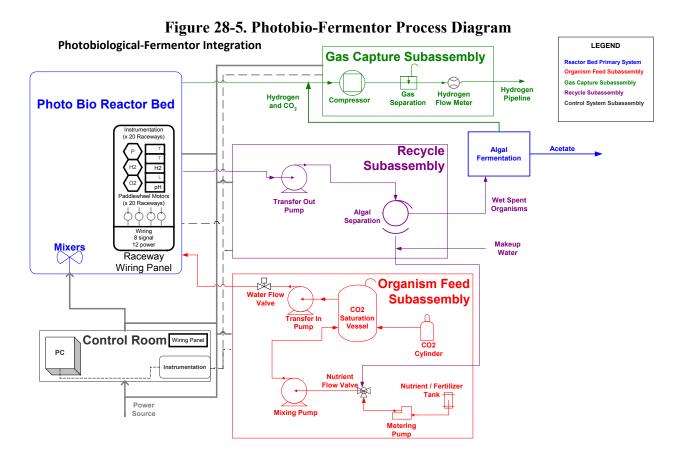
Figure 28-4. Bill of Materials for B-3/B-5 Stacked Beds

Description		UI IVI	Units		Unit cost	Oty Boold	Total Cost	Material / Part Description
Description	Size Req'd Units	Unit Size	Units		Unit cost	Qty Req'd	TOTALCOST	Material / Fart Description
Photo Bio Reactor Bed Subassembly								
Transparent Film	165452 m2	1	m2	\$	0.54	165,452		4 Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Film Layer 2	165452 m2	1	m2	\$	0.54	165,452		4 Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	178597 m2	1	m2	\$	0.47	178,597		2 Butyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for
Pond Edging	26566 m	1	m	\$	7.00	26,566		5 Unit Cost is engineering estimate at \$7/m
Installation of Ponds		1	raceway	\$	26,083.00	38	\$ 991,15	4 Based on California labor rates.
Paddlewheel Mixers		1	each	\$	5,000.00	76	\$ 380,00	Est. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in	1	each	\$	43.46	38	\$ 1,65	1 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032
Outlet Water Valve	0.5 in	1	each	\$	43.46	38	\$ 1,65	1 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032
Outlet Gas Valve	1.0 in	1	each	\$	67.23	38		5 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032
Flanges	0.5 in	1	each	Ś	8.00	114		2 Price from http://www.ancorp.com/line.aspx?id=819
PNS Recicirculaiton Pump	76	-	Cucii	ś	187.99	76		
PNS Perforated Piping	248900			Š	0.24	248,900		
1 No 1 entorated 1 iping	248300			Ţ	0.24	240,500	\$ 33,73	•
Gas Capture Subassembly								
Compressor	67 kgmol/hr	67	kgmol/hr	\$	9.233.00	1	\$ 622.07	8 Using H2A Unit cost
PSA	or agmorn	0,	KBIIIOI/III	\$	78,900	1		
Raceway Collection Pipe	76 ft	1	ft	\$	1.00	76		6 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity,
		_						9 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity,
Main Collection Pipe	2160 ft	1	ft	\$	6.18	2160		
Gas Capture Pipe	350 ft	1	ft	\$	6.18	350	-,	3 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity,
PNS Gas Collection Pipe				\$	1.00	380	\$ 38	0 Diverts PNS gas to Main Gas Piping
Organism Feed Subassembly								
	150	150		ė	10.252	10		C. Est Decedes Decede Chambel Headback Distance Color and Foresting
Transfer In Pump	150 gpm	150	gpm	\$	10,252	18		6 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
Nutrient Metering Pumps		1468	Gal/Hr.	\$	2,594			8 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
Mixing Pump	150 gpm	150	gpm	\$	10,252	18		6 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
CO2 Cylinder	50 lb	50	lb	\$	360	1		0 (http://kegman.net/carbon.htm)
CO2 Saturation Vessel	15000 gal	15000	gal	\$	30,000	10		0 Economics
Nutrient Tank	14 gal	10	gal	\$	30.00	2	\$ 6	0 085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe (B3 and B5)	184 ft	1	ft	\$	2.12	184	\$ 39	O Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and
Main Slurry Collection Pipe (B3 and B5)	5280 ft	1	ft	\$	8.51	5280	\$ 44,93	3 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and
Recycle-Feed Transfer Pipe (B3 and B5)	360 ft	1	ft	\$	8.51	360	\$ 3,06	4 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate an
Recycle Subassembly								
Rotary Drum filter	17980 gph	3750	gph	\$	87,000.00	5	\$ 435,00	O Information from Dana Kent at Advanced Aquaculture Inc. on Hydrotech Drum Filter
Transfer Out Pump	150 gpm	150	gpm	\$	10,252	18	\$ 184,53	1 Timmerhaus
Main Slurry Feed Pipe (B3 and B5)	5280 ft	1	ft	\$	6.18	2040	\$ 12.60	7 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and
Raceway Slurry Feed Pipe (B3 and B5)	184 ft	1	ft	\$	1.00	72		2 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and
, , ,								•
Consumables								
Initial CO2	41629 lb	50	lb	\$	35.00	833	\$ 29,15	5 Cost based on average fertilizer use for Aquaculture and average fertilizer costs from the
Initial Nutrients	2 lb	1	lb	\$	0.20	2	Ś	O NFC Company, Chicago, IL (800) 734 4515
Initial Water	7991266 gal	1	gal	\$	0.00	7583248.679	\$ 12.62	6 H2A Feedstock Costs
Initial Acetate	5442 kg	1	kg	\$	0.60	5442		
			Ü					
Control System								
Control Room	160 ft2	1	ft2	\$	50.00	160	\$ 8,00	http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.html
Control Room Wiring Panel		1		Ś	3,000.00	1	\$ 3,000.0	O Consultation with Innomation Systems Inc.
Raceway wiring Panel		1		Ś	146.00			8 Information from Tessco Technologies Inc.
Computer and Monitor		1		\$	1,500.00	1		O Information from Emerson Process Management
Labview Software		1		Ś	4,299.00	1		O Information from Emerson Process Management
Level Indicators		1		Ś	714.00	38		
		-						O Omega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors		1		\$	345.00			O Omega Engineering Inc. PX209 Pressure Trnasducer + DPi32 Meter
Hydrogen Area Sensors		1		\$	7,600.00			O Honeywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/an
Air Temperature Meter		1		\$	599.00	1		O Omega DP81T Meter
Air Temperature Indicator		1		\$	38.00			O Omega TH-10-44000 Thermistor Probe
Water Temperature Indicator		1		\$	-		\$ -	Comes with the PH sensor
pH level Indicator		1		\$	435.00			O Omega Engineering Inc. PHE - 6510 PH electrode + DP24 - PH Meter
Oxygen Area Sensors		1		\$	-	38	\$ -	Comes with H2 Sensor
Nutrient Flow Valve		1		\$	5,500.00	1	\$ 5,500.0	O Information from Emerson Process Management
Water Flow Valve		1		Ś	5,500.00	1		O Information from Emerson Process Management
Hydrogen Flow Meter		1		\$	5,500.00	1		O Information from Emerson Process Management
Instrument Wiring	213180 ft	1	ft	Ś	0.02	213180		9 Information from Waytek Inc. at waytekwire.com
	213100 10	_						
	264360 ft	1	ft	٠.	חחי	264260	\$ 51700	Q Information from Waytok Inc. at waytokwire com
Power Wiring Conduit	264360 ft 8820 ft	1	ft ft	\$	0.02 0.58	264360 8820		8 Information from Waytek Inc. at waytekwire.com 4 Information from Waytek Inc. at waytekwire.com

System Initial Cost \$ 4,274,085

28.2 Photobiological-Fermentor Integration

In the current photobiological pathway configurations, algae and bacteria filtered out of the photobiological systems by the rotary drum filters are discarded as waste. However, as analyzed in Part II, this waste biomass can be utilized in a fermentation reactor to generate additional hydrogen. This integration combines a photobiological pathway in series with a fermentation pathway, thus little capital cost efficiencies are expected. Due to the small additional hydrogen generated from the fermentation system, it is possible to route the fermentation hydrogen produced into the gas capture subassembly of the photobiological system to improve costs slightly. As mentioned in Part II, the major cost component of the stand-alone algae fermentation systems is the labor cost, which is enormous relative to the minimal hydrogen produced. However, the minimal size of the fermentation unit will require no additional labor from that already needed for the photobiological plant, leading to massive cost savings relative to the stand-alone fermentation system. The process diagram for the photobiological-fermentor integration is shown in Figure 28-5.



Our analysis combines the waste organisms of the B-1, B-2 and B-5 systems with fermentation. Since the capital costs and the reactor specifications for B-1 are the same as B-2, we have assumed the results for both systems to be the same. Neither the B-3 nor the B-4 systems produce any waste algae, since all the algae mass is needed for respiration to keep the systems anaerobic. Additionally, the algae in the B-4 system are mounted on an immobilized mat, and its waste organisms would to require additional processing which would not result in an economically beneficial integration. The B-5 system is similar conceptually to the B-1 and B-2 system with the exception that it is able to use the waste acetate stream from fermentation to feed the photosynthetic organisms. Because of this additional requirement there is an acetate retrieval pump required, making the B-5 Photobio-Fermentor Integration a separate integration pathway. The Bill of Materials for the B-5 with Fermentation is shown as an example in Figure 28-6. The Bill of Materials for B-1 and B-2 with fermentation would be similar.

Figure 28-6. BOM for B-5/C-5 Integrated System

								ntegrateu System
Description	Size Req'd Units	Unit Size	e Units	Un	it cost	Qty Req'd	Total Cost	Material / Part Description
Photo Bio Reactor Bed Subassembly								
Transparent Film	235116 m2	1	m2	\$	0.54	235,116	\$ 126,55	1 Polyethylene price quote at \$0.54/m2 (\$0.05/ft2)
Pond Lining	253795 m2	1	m2	\$	0.47	253,795	\$ 119,91	2 Butyl rubber, PVC, and LDPE (low density polyethylene)based on quote of \$175.56 for 4,000ft2.
Pond Edging	37752 m	1	m	\$	7.00	37,752	\$ 264.26	6 Unit Cost is engineering estimate at \$7/m
Installation of Ponds	37732 111	1			6,083.00	54		2 Based on California labor rates.
Paddlewheel Mixers		1	each		5,000.00	108		0 Est. paddlewheel cost. 4 per raceway. 18 raceways.
Inlet Water Valve	0.5 in	1	each	\$	43.46			7 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve	0.5 in	1	each	ş Š	43.46			7 Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
Outlet Water Valve Outlet Gas Valve	1.0 in	1	each	\$	67.23	54		O Price from ValveStore.com (http://www.valvestore.com/prodinfo.asp?number=551032)
	0.5 in	1		ş S	8.00			6 Price from http://www.ancorp.com/line.aspx?id=819
Flanges	0.5 III	1	each	Ş	8.00	162	\$ 1,29	6 Price from http://www.ancorp.com/line.aspxrid=619
Gas Capture Subassembly								
Compressor	45 kgmol/hr	45	kgmol/hr	٠,	9,233.00	1	\$ 414.24	1 Using H2A Unit cost
PSA				Ś	26,895	1		2 Using H2A scaling
Raceway Collection Pipe	108 ft	1	ft	\$	1.00	108		8 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
naceway concension ripe	100 10	-		Ÿ	1.00	100		altered) and 2 to 1 molar ratio of hydrogen to oxygen. Pricing from PVC Plastic Corp.
Main Collection Pipe	3120 ft	1	ft	\$	6.18	3120	\$ 19,28	2 Sized for Peak Hydrogen production. Assuming Plastic Gas piping, 100 ft/s velocity, uniform pipe diameter (can be
Con Contact Disc	50.6				6.40	50	ć 20	altered) and 2 to 1 molar ratio of hydrogen to oxygen. Pricing from PVC Plastic Corp.
Gas Capture Pipe	50 ft	1	ft	\$	6.18	50	\$ 30	9 altered) and 2 to 1 molar ratio of hydrogen to oxygen. Pricing from PVC Plastic Corp.
Organism Feed Subassembly								
Transfer In Pump	150 gpm	150	gpm	\$	10,252	3	\$ 20.75	5 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
Nutrient Metering Pumps	130 Shiii	1468	Gal/Hr.	\$	2,594	1		4 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
	150 anm							4 Est. Based on Perry's Chemical Handbook, Plant Design and Economics 5 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
Mixing Pump	150 gpm	150	gpm	\$	10,252	3		
Nutrient Tank	21 gal	10	gal	\$	30.00	3	\$ 9	0 10 gallon Cylindrical Process Tank, Part #0275-085 (http://www.watertanks.com/products/0275-085.asp)
Raceway Slurry Collection Pipe	108 ft	1	ft	\$	1.00	108	\$ 10	8 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Main Slurry Collection Pipe	3120 ft	1	ft	\$	4.31	3120	\$ 13,44	7 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Recycle-Feed Transfer Pipe	180 ft	1	ft	\$	6.18	180	\$ 1,11	2 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Consumables								
Initial Nutrients	1 lb	1	lb	\$	0.20	1.112714485		0 NFC Company, Chicago, IL (800) 734 4515
Initial Water	5720312 gal	1	gal	\$	0.00	5720311.865		4 H2A Feedstock Costs
Initial Acetate	7793 kg	1	kg	\$	0.60	7792.757824	\$ 4,63	7 Chemical Journal of Korea. Assumes consumption to be four times more to account for full growth conditions.
Recycle Subassembly								
Rotary Drum filter	25,741 gph	3750	gph		7,000.00	7		O Information from Dana Kent at Advanced Aquaculture Inc. on Hydrotech Drum Filter
Transfer Out Pump	150 gpm	150	gpm	\$	10,252	3		5 Est. Based on Perry's Chemical Handbook, Plant Design and Economics
Main Slurry Feed Pipe	3120 ft	1	ft	\$	4.31	3120		7 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Raceway Slurry Feed Pipe	108 ft	1	ft	\$	1.00	108	\$ 10	8 Pricing based off of Estimates from PVC Plastic Corp. Assumes 10 ft/second flow rate and Density of 1g/ml
Fermentation Subassembly Tank	6173 gal	1	gal	\$	2.00	24,693	ć 40.20	6 This is a scaled cost based on the capital costs from NREL Report TP-510-32438
Slurry Piping - 0.5"	500 ft	1	ft	Ś	0.52		\$ 45,36	O Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
Slurry Piping - 0.3	5077 ft	1	ft	Ś	1.00	5.077		7 Sized using Continuity Equation. Assumed a velocity of 1 ft/sec.
,		4		-	198.50	- , -		
Pump	6173 gal/day			\$		1		9 http://www.grainger.com/Grainger/items/1P795
Inlet Valves	1 in	1	each	\$	67.23	4		9 http://www.valvestore.com/products.asp?dept=1485
Outlet Valves	0.5 in	1	each	\$	46.85	4	\$ 18	7 http://www.valvestore.com/products.asp?dept=1485
Control System								
Control System Control Room	160 ft2	1	ft2	\$	50.00	160	Ś RAN	O comes from price quote of \$50/ft2 from http://www.buyerzone.com/industrial/modular_buildings/prefab_guide.html
Control Room Wiring Panel	200 112	1			3,000.00	1		O Consultation with Innomation Systems Inc.
Raceway wiring Panel		1		\$	146.00	54		4 Information from Tessco Technologies Inc.
Computer and Monitor		1			1,500.00	1		O Information from Emerson Process Management
Labview Software		1			4,299.00	1		O Information from Emerson Process Management
Level Indicators		1		\$	714.00	54		O Omega Engineering Inc. LVR51 Liquid Level Float Transmitter + DPi32 Meter
Pressure Sensors		1		Ś	345.00			Omega Engineering Inc. PX209 Pressure Trnasducer + DPI32 Meter
Hydrogen Area Sensors		1			7,600.00			Honeywell 7866 Gas Analyzer (http://www.lesman.com/unleashd/catalog/analytical/analyt_hwhydrogengas.htm)
Air Temperature Meter		1		\$	599.00			O Omega DP81T Meter
Air Temperature Indicator		1		\$	38.00			O Omega TH-10-44000 Thermistor Probe
Water Temperature Indicator		1		\$	-		\$ -	Comes with the PH sensor
		1		\$	435.00			O Omega Engineering Inc. PHE - 6510 PH electrode + DP24 - PH Meter
pH level Indicator		1		\$	-		\$ -	Comes with H2 Sensor
pH level Indicator Oxygen Area Sensors					5,500.00	1		0 Information from Emerson Process Management
Oxygen Area Sensors		1					,-50.0	
Oxygen Area Sensors Nutrient Flow Valve		1 1			5,500.00	1	\$ 5.500.0	O Information from Emerson Process Management
Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve		_		\$	5,500.00 5,500.00	1 1	,	O Information from Emerson Process Management O Information from Emerson Process Management
Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve Hydrogen Flow Meter	406380 ft	1	ft	\$	5,500.00 5,500.00 0.02		\$ 5,500.0	0 Information from Emerson Process Management
Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve	406380 ft 505080 ft	1	ft ft	\$ \$	5,500.00	1	\$ 5,500.0 \$ 7,883.7	
Oxygen Area Sensors Nutrient Flow Valve Water Flow Valve Hydrogen Flow Meter Instrument Wiring		1 1 1		\$ \$ \$	5,500.00 0.02	1 406380	\$ 5,500.0 \$ 7,883.7 \$ 9,798.5	0 Information from Emerson Process Management 7 Information from Waytek Inc. at waytekwire.com

28.3 Lignocellulosic Fermentation/MEC Integration

The output from a lignocellulosic fermentor would be primarily a mix of acetic acid and ethanol with lesser amounts of other organic acids and glucose. NREL fermentor research on the corn stover H_2 fermentor resulted in the following byproduct:

acetic acid	26.0 mM
succinic acid	5.6 mM
lactic acid	1.8 mM
formic acid	0.6 mM
ethanol	14.0 mM

Subsequently, research at Penn State operated the MEC on this product mix. ⁹⁹

The fermentation integration evaluated was that of lignocellose fermentation with MEC. This integration occurs in series providing little overlap in equipment. The process diagram is shown in Figure 28-7.

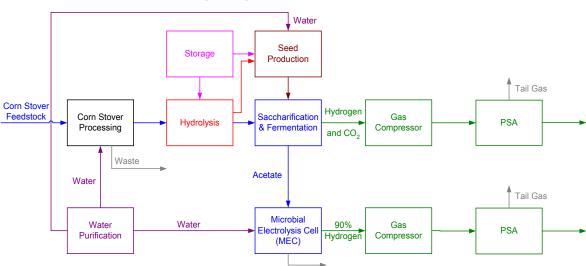


Figure 28-7. Process Diagram for Fermentation-MEC Integration Integrated Lignocellosic Fermentation with MEC

The MEC component of this integrated system as defined in Part III has been sized to consume 100% of the lignocellose fermentation waste acetate and other organics. We have assumed no extra labor will be needed for the integrated system. Because the hydrogen volumes are large and the output gas compositions are different in each case system, separate gas capture systems are used for the fermentor and MEC. The Bill of Materials for the Integrated Fermentation-MEC is shown in Figure 28-8.

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⁹⁹ Logan, Bruce. "Electrochemically Assisted Microbial Fermentation of Acetate." ZFH-8-77623-01. NREL. Colorado. January 2009.

Figure 28-8 Rill of Materials for Integrated Fermentation-MEC

Figure 28-8. l			grate			<i>.</i>
Description	Install Factor	Size Req'd Units		Unit cost	Qty Req'd	Total Cost
Corn Stover Prep Subassembly Bale Transport Conveyor	1.62		\$	400,000	2 \$	800,000
Bale Unwrapping Conveyor	1.19		Ş	150,000	2 \$	300,000
Belt Press Discharge Conveyor Shredder Feed Conveyor	1.89 1.38		Ş	50,000 60,000	1 \$	50,000 240,000
Truck Scales	2.47		<i>~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~</i>	34,000	2 \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$ \$	68,000
Truck Unloading Forklift	1		\$	18,000	4 \$	72,000
Bale Moving Forklift Corn Stover Wash Table	1 2.39		ş S	18,000 104,000	4 \$ 2 \$	72,000 208,000
Shredder	1.38		Ş	302,000	4 \$	1,208,000
Concrete Feedstock-Storage Slab Polymer Feed System	2.2 2.28		Ş	450,655 30,000	1 \$	450,655 30,000
Wash Table Pump	3.87		\$	20,000	2 \$	40,000
Wash Water Pump	5.19		Ş	15,000	2 \$	30,000
Clarifier Underflow Pump Clarified Water Pump	13.41 7.07		Ş	6,000 15,000	1 \$	6,000 15,000
Belt Press Sump Pump	2.92		\$	19,000	1 \$	19,000
Clarifier Thickener	1.51		\$	135,000	1 \$	135,000
Belt Press Magnetic Separator	1.25 1.3		Ş	100,000 10,335	1 \$	100,000 10,335
Wash Water Tank	2.8		\$	50,000	1 \$	50,000
Clarifier Thickener Tank	3.04		\$	135,000	1 \$	135,000
Pretreatment/Hydrolysis Subassembly						
Hydrozylate Mix Tank Agitator	1.2		\$	28,421	1 \$	28,421
Hydrozylate Mixing Tank Hydrozylate Cooler	1.2 2.1		Ş	32,237 23,266	1 \$ 1 \$	32,237 23,266
In-line Sulfuric Acid Mixer	1		\$	2,542	1 \$	2,542
Sulfuric Acid Pump	2.8		\$	8,289	1 \$	8,289
Sulfuric Acid Tank Lime Solids Feeder	1.4 1.3		Š	9,441 3,900	1 \$ 1 \$	9,441 3,900
Lime Unloading Blower	1.4		š	99,594	1 \$	99,594
Lime Dust Vent Baghouse	1.5		ş	140,707	1 \$	140,707
Lime Storage Bin Hydrolysis Tank Pump	1.3 2.8		\$\$\$\$\$\$\$\$\$\$\$\$	136,370 69,516	1 \$ 1 \$	136,370 69,516
Methane Boiler	1.3		\$ \$	200,000	1 \$	200,000
			-	,	•	,
Fermentation Subassembly Fermentation Tank	1.2		Ś	493,391	5 \$	2,466,955
Fermentation Agitator	1.2		\$	19,676		196,760
Fermentation Cooler	2.1		\$	6,780	5 \$	33,900
Fermentation Recirculation Pump Lignin Wet Cake Screw	2.8 1.4		Ş	13,666 16,837	5 \$ 5 \$ 5 \$ 1 \$	68,330 84,185
Acetate Product Storage Tank	1.4		\$	160,829	1 \$	160,829
Acetate Transfer Pump	1.3		\$	53,737	1 \$	53,737
Pneumapress filter HX - 1	1.4 1.3		Ş	1,285,736 22,346	4 \$ 1 \$	5,142,942 22,346
HX - 2	1.3		\$\$\$\$\$\$\$\$\$\$\$\$	194,618	1 \$	194,618
FTC	1.3		\$	6,781	5 \$	33,905
Seed Production Subassembly						
Seed Hold Tank Seed Hold Tank Agitator	1.2		\$	160,829	1 \$	160,829
Seed Hold Transfer Pump	1.2 1.4		Š	12,492 22,050	1 \$ 1 \$	12,492 22,050
1st Seed Fermentor	2.8		\$	14,700	2 \$	29,400
2nd Seed Fermentor 3rd Seed Fermentor	2.8		\$	32,600	2 \$	65,200
4th Seed Fermentor	2.8 1.2		Š	81,100 39,160	2 5	162,200 78,320
5th Seed Fermentor	1.2		\$	146,549	2 \$ 2 \$ 2 \$ 2 \$ 2 \$	293,097
4th Seed Agitator 5th Seed Agitator	1.2		\$	11,645	2 \$	23,289
4th Seed Agitator 4th Seed Fermentor Coil	1.2 1.2		Š	10,291 4,658	2 \$ 1 \$	20,582 4,658
5th Seed Fermentor Coil	1.2		<i>~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~</i>	28,238	1 \$	28,238
Seed Transfer Pump	1.4		Ş	53,737	2 \$	107,474
MEC Subassembly				0 = :	4.435.00 6	57 400 T
MEC Tanks Brush Cathode	1.3 1.2		\$\$\$\$\$\$\$	0.51 14.60	1.13E+08 \$ 27436736 \$	57,488,911 400,686,098
Brush Anode	1.2		\$	7.92	7868218 Ś	62,316,288
Power Supply	1.3		ş	350,000.00	53 \$	18,550,000
Process Water Circulating Pump MIC - 1	2.8 1.3		ş S	8,818 88,542	1 \$ 1 \$	8,818 88,542
MIC - 2	1.3		\$	554,634	1 \$	554,634
Cooling Water Pump/MEC Pumps	2.8			242,216	12 \$	2,906,592
]						
Storage Subassembly CSL Storage tank Agitator	1.2			2,143	1 \$	2,143
CSL Pump	2.8			6,188	1 \$	6,188
CSL Storage Tank	1.4			61,949	1 \$	61,949
CSL/DAP Day Tank CSL/DAP Pump	1.4 2.8			28,470 6,188	1 \$ 1 \$	28,470 6,188
CSL/DAP Pump CSL/DAP Day Tank Agitator	1.2			12,348	1 \$	12,348
DAP Solids Feeder	1.3			3,900	1 \$	3,900
DAP Unloading Blower DAP Vent Baghouse	1.4 1.5			49,014 9,595	1 \$ 1 \$	49,014 9,595
DAP Vent Bagnouse DAP Storage Bin	1.3			34,255	1 \$	34,255
Sulfuric Acid Pump	2.8			13,814	ı š	13,814
Sulfuric Acid Storage Tank Propane Storage Tank	1.2 1.4			60,470 30,825	1 \$ \$ 1 \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ 1 \$ \$ \$ \$ 1 \$ \$ \$ \$ 1 \$ \$ \$ \$ 1 \$ \$ \$ \$ 1 \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ \$ 1 \$ \$ \$ \$ \$ \$ \$ 1 \$	60,470 30,825
Make-up Water Pump	2.8			8,735	1 \$ 1 \$	8,735
Process Water Circulating Pump Process Water Tank	2.8 1.4			8,818 168,502	1 \$ 2 \$ 2 \$	17,635 337,004
	1.4			108,502	2 \$	337,004
Gas Capture Subassembly Compressor Fermentor	1.3	1704 kgmol/hr	. ė	9,233	1,704 \$	15,729,564
FC-1	1.3	1704 Kgiliol/III	\$	29,623	1,704 \$ 1 \$	29,623
FIC -1	1.3		\$	57,651	1 \$	57,651
FIC -2 Compressor MEC	1.3 1.3	1929 kgmol/hr	\$	311,057 9,233	1 \$ 1929 \$	311,057 17,812,305
PSA Fermentor	1.3	Tara KRIIIOI/III	ڊ	9,233	1 \$	1,527,494
PSA MEC	1.3				1 \$	302,154
Hydrogen Flow Meter	1.3		\$	5,500	1 \$	5,500.00
				System	Initial Cost \$	593,317,371

28.3.1 Flow Chart

The combined system mass flows and flow properties are diagramed in Figure 28-9. Details of these components and the reactions are included in the Part II discussions. A detailed Mass and energy balance is included in Part IV, Appendix A.

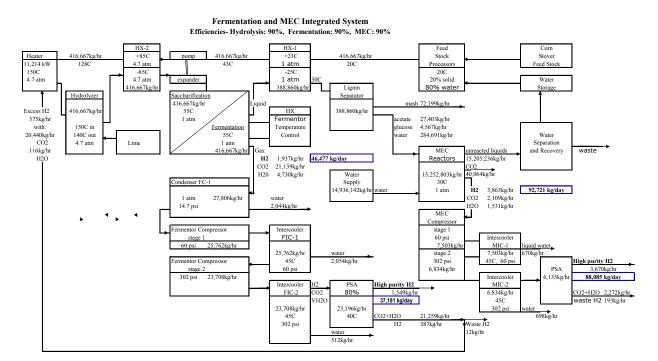


Figure 28-9. Fermentor/MEC Mass Balance Flow Chart

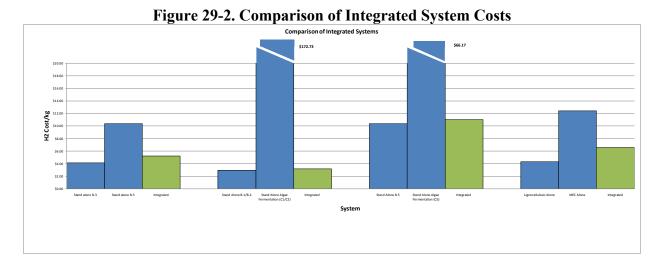
29. Results and Discussion for Integrated Systems

The hydrogen production costs for the previously described system combinations are discussed below. By comparing the hydrogen production costs from the integrated systems to the individual systems we can determine if there is any benefit to systems integration. A cost comparison for the integrated systems is shown in Figure 29-1.

Figure 29-1. Integrated Systems Results

Systems	Capital Costs	H2 Production (kg/day)	H2 Cost (\$/kg)
Stacked Photobio Beds			
Stand alone B-3	\$39,485,240	10,000	\$4.17
Stand alone B-5	\$34,196,970	10,000	\$10.36
Integrated	\$41,485,500	10,600	\$5.25
Photobio-Fermentor Integration			
Stand Alone B-1/B-2	\$21,880,470	10,000	\$2.99
Stand Alone Algae Fermentation (C1/C2)	\$37,142	7	\$172.73
Integrated	\$22,272,680	10,007	\$3.21
Photobio-Fermentor Integration			
Stand Alone B-5	\$34,196,970	10,000	\$10.36
Stand Alone Algae Fermentation (C5)	\$86,211	13	\$66.17
Integrated	\$34,591,120	10,013	\$11.04
Lignocellulosic Fermentor and MEC			
Lignocellulosic Alone	\$44,944,078	37,181	\$4.33
MEC Alone	\$558,689,165	88,055	\$12.43
Integrated	\$593,317,371	125,266	\$6.61

The cost change between the stand-alone systems and the integrated systems is shown in Figure 29-2.



30. Integrated System Conclusions and Recommendations

Integrating hydrogen producing systems can yield greater hydrogen production per area of land, however, it is not necessarily the most cost effective method of producing hydrogen for the following reasons:

- The increase in capital costs for the stacked photobioreactor beds and the photobioreactor plus fermentor, while less than the systems alone, are still substantial enough to outweigh the increase in hydrogen output.
- For the Fermentor/MEC combination, the high cost of H₂ from the MEC makes the combination uneconomic. This is partly due to the current immature and unoptimized status of the MEC, and the results could be markedly improved with additional MEC developments and cost optimization.

31. Part IV Appendix A: Integrated Fermentor/MEC Mass/Heat Balance

Processes				<u>egrated</u>							<u> </u>		
			61	Mass flow	1 "	mole flow	T	Tave	ФТ	Ρ.	Ср	h	dq/dt
	10		%	kg/day	kg/hr	kgM/hr	°C	°C	°C	psi	kJ/kg °C	kJ/kg	kJ/hr
Feedstock	Corn stover		20.0%	2,000,000	83,333		20			14.7			
Inputs		cellulose	36.7%	734,000	30,583								
		hemicell	27.4%	548,000	22,833 29,917								
		Lignin,etc total	35.9% 100.0%	718,000 2,000,000	83,333								
	water	total	80.0%	8,000,000	333,333		20			14.7			
	total slurry		100.0%	10,000,000	416,667		20			14.7			
IIV 4							20.0			117	4.400		
HX-1	from feedstock to HX-2			10,000,000 10,000,000	416,667 416,667		20.0 43.3	31.7	23.3	14.7	4.180		40,655,319
	from fermentor			9,332,641	388,860.06		55.0	31.7	23.3	14.7	4.182		40,000,019
	to LigSep			9,332,641	388,860		30.0	42.5	-25.0	14.7	4.102		-40,655,319
LINZ &								12.0	20.0	60.0	1.000		10,000,010
HX-2	from HX-1 primary			10,000,000	416,667		43.3	05.0	05.0	68.8	4.206		440 004 050
	to hydrolyzer heater			10,000,000 10,000,000	416,667 416.667		128.5	85.9	85.2 85.0	68.8	4.215		149,281,250
	from hydrolyzer to sacchrification			10,000,000	416,667		140.0 55.0	97.5	05.0	00.0	4.215		-149,281,250
				10,000,000	410,007		33.0	31.5					-149,201,230
Hydolyzer	heating of slurry from I	HX-2		10,000,000	416,667		128.5						
Heater				10,000,000	416,667		150.0	139.3	21.5	68.8	4.290		38,387,188
	heating of CO2 from P			490,873	20,453		45.0						
	CO2/H2mass			490,873	20,453		150.0	97.5	105.0	14.7	0.913		1,960,729
	heating of H2O from P			2,783	116		45.0	07.5	105.0	447	1.070		02.005
	H2O/H2mass Total heat input re		ting ∐2 ∗T	2,783	116		150.0	97.5	105.0	14.7	1.970		23,985 40,371,902
	Waste H2 burner h		effic =)				ı	1	1		1	40,371,902
	H2 LHV kJ/kg =		90%	8,994	375					14.7			40,371,902
	TIZ LITV KU/Kg =	119,705	30 /6	10,000,000	416,667					14.7			40,371,302
				10,000,000	410,001								
Total heating from HX-1	+ HX-2 + Heater												230,308,471
Hydrolyzer	In from Heater			10,000,000	416,667		150.0			68.8			
, ,	inputs	cellulose	36.7%	734,000	30,583					4.68	Ī		
		hemicell	27.4%	548,000	22,833					atm			
		Lignin,etc	35.9%	718,000	29,917								
		water	80.0%	8,000,000	333,333								
		total		10,000,000	416,667								
efficiency=	output	complex sugars	6	1,153,800	48,075		140.0						
90%		xylan		128,200	5,342								
		Lignin,etc		718,000	29,917								
		organics		2,000,000	83,333								
		water		8,000,000	333,333								
	Endothermic heat above	total	ı	8,000,000 10,000,000	333,333 416,667		10.0						
	Endothermic heat absorto HX-2	total		10,000,000	416,667		10.0			68.8			
	to HX-2	total		10,000,000	416,667 416,667		140.0			68.8			
Saccharification	to HX-2 from HX-2	total		10,000,000 10,000,000 10,000,000	416,667 416,667 416,667		140.0 55.0			68.8			
Saccharification in fermentor	to HX-2	total		10,000,000	416,667 416,667		140.0			68.8			
	to HX-2 from HX-2	total orption ΦT		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667		140.0 55.0 55.0			68.8			
in fermentor	to HX-2 from HX-2 to fermentation	total proption ⊕T		10,000,000 10,000,000 10,000,000	416,667 416,667 416,667	267	140.0 55.0			68.8			
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation	total orption ΦT		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075	267 (glucose)	140.0 55.0 55.0			68.8			
in fermentor Fermentor	to HX-2 from HX-2 to fermentation	total total total simple sugars Lignin,xylan,etc		10,000,000 10,000,000 10,000,000 10,000,000 10,000,000 1,153,800 846,200	416,667 416,667 416,667 416,667 416,667 48,075		140.0 55.0 55.0			68.8			
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation	total prytion ot total simple sugars Lignin,xylan,etc water		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333		140.0 55.0 55.0			68.8			
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification	total rption total simple sugars Lignin,xylan,etc water reactants		10,000,000 10,000,000 10,000,000 10,000,000 11,153,800 846,200 8,000,000 10,000,000	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667		140.0 55.0 55.0			68.8			
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen	total total total simple sugars Lignin,xylan,etc water reactants tation		10,000,000 10,000,000 10,000,000 10,000,000 10,000,000 1,153,800 846,200 8,000,000 10,000,000 207,676	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653	(glucose)	140.0 55.0 55.0 55.0			68.8			
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification	total total total simple sugars Lignin,xylan,etc water reactants tation H2		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937	(glucose)	55.0 55.0 55.0 55.0			68.8			
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen	total total total simple sugars Lignin,xylan,etc water reactants station H2 CO2		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139	(glucose) 961 480	140.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen	total rption ot total simple sugars Lignin,xylan,etc water reactants tation H2 CO2 V H2O		10,000,000 10,000,000 10,000,000 10,000,000 11,53,800 846,200 8,000,000 10,000,000 207,676 46,476.6 507,339.5 113,542	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731	(glucose) 961 480 263	55.0 55.0 55.0 55.0			14.7			
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total protion otal simple sugars Lignin,xylan,eto water reactants tation H2 CO2 V H2O total gas		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807	(glucose) 961 480	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	from HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen	total protion otal total simple sugars Lignin,xylan,etc water reactants tatation H2 CO2 V H2O total gas slurry total		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 3416,667 8,653 1,937 21,139 4,731 27,807 388,860	(glucose) 961 480 263	140.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total proprion ot T total simple sugars Lignin,xylan,etc water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,etc		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 21,139 4,731 27,807 388,860 35,258	(glucose) 961 480 263	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total protion otal total simple sugars Lignin,xylan,etc water reactants tatation H2 CO2 V H2O total gas slurry total		10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 28,845	(glucose) 961 480 263	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total proprion otal total simple sugars Lignin,xylan,etc water reactants station H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Acetate	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 21,139 4,731 27,807 388,860 35,258	(glucose) 961 480 263	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total protion otal simple sugars Lignin,xylan,eto water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,eto Acetate Glucose	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 4,808	(glucose) 961 480 263	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency =	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out	total protion otal simple sugars Lignin,xylan,eto water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,eto Acetate Glucose L-H20	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 31,937 21,139 4,731 27,807 388,860 35,258 28,845 4,808 319,949	(glucose) 961 480 263	55.0 55.0 55.0 55.0						
in fermentor Fermentor efficiency = 90%	from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out slurry out to HX-1 total mass out	total protion dT total simple sugars Lignin,xylan,etc water reactants tatation H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Acetate Glucose L-H2O total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 28,845 4,808 319,949 388,860 416,667	(glucose) 961 480 263	55.0 55.0 55.0 55.0 55.0			14.7	14.496		
in fermentor Fermentor efficiency =	from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1	total protion otal simple sugars Lignin,xylan,eto water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,eto Acetate Glucose L-H20	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 4,808 319,949 388,860 416,667 1,937	(glucose) 961 480 263	55.0 55.0 55.0 55.0				14.496 0.953		
in fermentor Fermentor efficiency = 90% Condenser	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1 total mass out gases in	total proprion otal simple sugars Lignin,xylan,etc water reactants station H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Acetate Glucose L-H2O total total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 28,845 4,808 319,949 388,860 416,667	(glucose) 961 480 263	55.0 55.0 55.0 55.0 55.0			14.7			
in fermentor Fermentor efficiency = 90% Condenser	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1 total mass out gases in	total proprion otal total simple sugars Lignin,xylan,etc water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Acetate Glucose L-H20 total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 35,258 4,808 319,949 388,860 1,937 1,937 21,139	(glucose) 961 480 263	55.0 55.0 55.0 55.0 55.0 55.0			14.7	0.953		
in fermentor Fermentor efficiency = 90% Condenser	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1 total mass out gases in from fermentor	total protion otal simple sugars Lignin,xylan,etc water reactants station H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Acetate Glucose L-H2O total H2 CO2 V H2O total H2 CO2 V H2O total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 22,807 388,860 319,949 388,960 416,667 1,937 21,139 4,731 21,139 4,731 1,937	961 480 263 1,704	55.0 55.0 55.0 55.0 55.0 55.0 55.0 55.5 55 55 55 55 55	50	-10	14.7 14.7 14.7 14.7 14.7	0.953 1.912 14.496		-280,719
in fermentor Fermentor efficiency = 90% Condenser	from HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermen gas out slurry out to HX-1 total mass out gases in from fermentor	total protion otal simple sugars Lignin,xylan,etc water reactants station H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Glucose L-H20 total H2 CO2 V H2O total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 319,949 388,860 416,667 1,937 21,139 4,731 27,807	961 480 263 1,704	55.0 55.0 55.0 55.0 55.0 55.0 55.5 55 55 55 55 55 55 45	50	-10	14.7 14.7 14.7 14.7 14.7 14.7	0.953 1.912 14.496 0.953		-201,350
in fermentor Fermentor efficiency = 90% Condenser	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1 total mass out gases in from fermentor	total total simple sugars Lignin,xylan,eto water reactants tation H2 CO2 V H2O total gas slurry total Lignin,xylan,eto Acetate Glucose L-H20 total H2 CO2 V H2O total H2 CO2 V H2O total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 319,949 388,860 416,667 1,937 21,139 4,731 27,807 1,937 21,139 2,686,5	961 480 263 1,704	55.0 55.0 55.0 55.0 55.0 55.0 55.0 55.5 55 55 55 55 55			14.7 14.7 14.7 14.7 14.7	0.953 1.912 14.496		-201,350 -51,367
in fermentor Fermentor efficiency = 90% Condenser	to HX-2 from HX-2 to fermentation in from sacchrification H2O reacted in fermer gas out slurry out to HX-1 total mass out gases in from fermentor	total protion otal simple sugars Lignin,xylan,etc water reactants station H2 CO2 V H2O total gas slurry total Lignin,xylan,etc Glucose L-H20 total H2 CO2 V H2O total	;	10,000,000 10,000,000 10,000,000 10,000,00	416,667 416,667 416,667 416,667 416,667 48,075 35,258 333,333 416,667 8,653 1,937 21,139 4,731 27,807 388,860 319,949 388,860 416,667 1,937 21,139 4,731 27,807	961 480 263 1,704	55.0 55.0 55.0 55.0 55.0 55.0 55.5 55 55 55 55 55 55 45	50	-10	14.7 14.7 14.7 14.7 14.7 14.7	0.953 1.912 14.496 0.953		-201,350

Processes			%	Mass flow kg/day	kg/hr	mole flow kgM/hr	°C	T ave	<t °C</t 	P psi	Cp kJ/kg °C	h kJ/kg	dq/dt kJ/hr
Compressor	in	H2	/0	46,477	1,937	961	45		J	14.7	norng 0	norng	NO/111
stage 1		CO2		507,340	21,139	480	45			14.7			
F-1		V H2O		64,477	2,687	149	45			14.7			
		total		618,293	25,762	1,590	45			14.7			
	out	H2		46,477	1,937	961	190.8			60			
		CO2		507,340	21,139	480	190.8			60			
		V H2O total		64,477 618,293	2,687 25,762	149 1,590	190.8			60			
								_					
Intercooler	Gas in	H2		46,477	1,937	961	190.8			60	14.496		
FIC-1 Primary		CO2 V H2O		507,340 64,477	21,139 2,687	480 149	190.8 190.8			60 60	0.953 1.912		
Tilliary		total		618,293	25,762	143	130.0			00	1.312		
	Gas out	H2		46,477	1,937	960.6	45	117.9	-146	58	14.496		-4,092,88
		CO2		507,340	21,139	480.3	45	117.9	-146	58	0.953		-2,935,68
		V H2O		15,169	632.1	35.1	45	117.9	-146	58	1.912		-176,19
		total gas		568,986	23,708								-7,204,76
	Liquid out	L H2O		49,307	2,054		45		-146	58	4.200		-915,40
	4-4-14	V-L Phase cha	ange heat	4 407 070	40.470							-2222	-4,565,04
Secondary	total out water in			1,187,279 3,642,123	49,470 151,755		20				4.180		-12,685,209
Georiaary	water out			3,642,123	151,755		40	30	20		4.180		12,685,20
Compressor	in	H2		46,477	1,937		45			58			
stage 2	itt	H2 CO2		507,340	21,139		45 45			58			
F-2		V H2O		15,169	632		45			58			
		total		568,986	23,708	1,476	,,,						
	out	H2		46,477	1,937	960.6	218			302			
		CO2		507,340	21,139	480.3	218			302			
		V H2O		15,169	632	35.1	218			302			
		total		568,986	23,708	1,476.0							
FIC-2	Gas in	H2		46,477	1,937		218			302			
Primary		CO2		507,340	21,139		218			302			
		V H2O		15,169	632		218			302			
	0	total		568,986	23,708	000.0	15	404.45	470	200	44.400		4.050.000
	Gas out	H2 CO2		46,477 507,340	1,937 21,139	960.6 480.3	45 45	131.45 131.45	-173 -173	300 300	14.496 0.953		-4,853,629 -3,481,348
		V H2O		2,876	120	480.3	45 45	131.45	-173	300	1.912		-3,481,348
		total gas		556,692	23,196	0.7	70	101.10	110	500	1.012		-8,374,596
	Liquid out	L H2O		12,293	512		45		-173	300	4.200		-270,646
		V-L Phase cha	ange heat									-2222	-1,138,14
	total out			568,986	23,708								-9,783,386
Secondary	water in			2,808,964	117,040		20	20	00		4.180		0.700.000
	water out			2,808,964	117,040		40	30	20		4.180		9,783,386
PSA	in	total		556,692	23,196	000.0	45			300			
fermentor		H2 CO2		46,477	1,937	960.6	45			300			
		V H2O		507,340 2,876	21,139 120	480.4 6.7	45 45			300 300			
	out	H2 outlet	80%	37,181	1,549	0.7	45			300			
		H2 loss	20%	9,295	387	192.1	45			300			
		CO2		507,340	21,139	480.4	45			300			
		CO2/H2 mass	ratio	54.6									
		V H2O		2,876	120	6.7	45			300			
		VH2O/H2 mass waste gas out	s ratio	0.31 519.511	21.646	679.2							
	Rumerus	waste gas out se of waste H2=	97%	519,511	21,046	6/9.2							
LigninConsester		I	0170	0 220 644 1	200 000								
LigninSeparator	in from HX-1 (from fermentor)	Lignin etc	1	9,332,641 846,200	388,860 35,258		30			14.7	1		
	(monit lennientor)	Acetate		692,280	28,845		30			14.7			
		Glucose		115,380	4,808								
	1	L-H20		7,678,781	319,949								
		total		9,332,641	388,860								
	out - mash	Lignin, etc	100%	846,200	35,258		30			14.7			
	1	Acetate	5%	34,614	1,442								
	1	Glucose	5%	5,769	240								
	1	LH2O/lignin	100%	046 000	25 250								
	1	LH2O total	1	846,200 1,732,783	35,258 72,199								
	out - liquid	Acetate	95%	657,666	27,403		30			14.7	†		
		Glucose	95%	109,611	4,567		30	I					
	to MEC	Glucose	3370	109.011	4.507								
	to MEC	H20-L	3376	6,832,581	284,691								

Processes			%	Mass flow kg/day	kg/hr	mole flow kgM/hr	°C	T ave	9T °C	P psi	Cp kJ/kg °C	h kJ/kg	dq/dt kJ/hr
MEC water addition			/0	339,082,263	14,128,428	Ng/W/TII	Ü	Ü	U	Poi	norny C	No/NY	NU/III
MEC	from LigSep	Acetate		657,666	27,403	456.3	30						
0.9V system		Glucose		109,611	4,567	25.4							
		total substrate		767,277	31,970	481.7							
	Motor od ditions	H20-L		6,832,581	284,691		-						
	Water addition: Acetate	total input H2O + substrat		7,599,858 346,682,121	316,661 14,445,088		ł						
	dilution (g/L) =	Total H20 need		345,914,844	14,443,000		ł			1			
90%	2.213	Water Addition	<u>-</u>	339,082,263	14,128,428		ł			1			
reaction	2.2.10	total water		345,914,844	14,413,119		Ì						
completion	total input	•		346,682,121	14,445,088								
	reactant vol.=	91,524,080 gall											
	reacted acetate+gluc	ose	90%	690,549	28,773								
	reacted water	luo		414,314	17,263	958.3							
	output-gas	H2		92,721	3,863	1,916.5	30			14.7			
aamalatiaa	calculation	CO2 total CO2 in H2	5%	1,012,142 50,607	42,173 2,109	958.3 47.9	30 0.05001			14.7			
completion	(process chart)	H2O-V	3/0	36,752	1,531.3	85.0	30			14.7			
	(process criait)	total cathode ga	as	1,141,615	47,567	2,049	30			14.7			
	output-liquid waste	Acetate	10%	65,767	2,740	2,043	30			1			
	4	Glucose	10%	10,961	457		30						
		H20-L		345,463,778	14,394,324								
		total liquids		345,540,506	14,397,521								
	total output			346,682,121	14,445,088								
CO2 Vented from MEC			95%	961,535	40,064								
Compressor	in	H2		92,721	3,863	1,916	30			14.7			
MC-1		CO2	5%		2,109	48	30			14.7			
		V H2O		36,752	1,531.3	85.0	30			14.7			
		total		180,080	7,503	2,049	30			14.7			
	out	H2		92,721	3,863	1,916	204			60			
		CO2		50,607	2,109	47.9	204			60			
		V H2O total		36,752	1,531	2,049	204			60			
				180,080	7,503	2,049							
Intercooler	Gas in	H2		92,721	3,863		204			60			
MIC-1		CO2		50,607	2,109		204			60			
Primary		V H2O total		36,752 180,080	1,531 7,503		204	<u> </u>		60			
	Gas out	H2		92,721	3,863	1,916	45	124.3	-159	58	14.496		-8,882,141
	Out out	CO2		50,607	2,109	47.9	45	124.3	-159	58	0.953		-318,543
		V H2O		20,679	861.6	47.8	45	124.3	-159	58	1.912		-261,287
		total		164,007	6,834								-9,461,971
	Liquid out	L H2O		16,072	670		45		-159	58	4.200		-324,584
		V-L Phase cha	inge heat									-2222	-1,488,040
	total out			180,080	7,503								-11,274,595
Secondary	water in			3,237,113	134,880		20	20	00		4.180		44.074.505
	water out			3,237,113	134,880		40	30	20		4.180		11,274,595
Compressor	in	H2		92,721	3,863		45			58			
MC-2		CO2		50,607	2,109		45			58			
		V H2O		20,679	862	0.040	45			58			
	out	total		164,007	6,834	2,012	45			58			
	out	H2 CO2		92,721 50,607	3,863 2,109	1,916 48	267 267			302 302			
		V H2O		20,679	862	48	267			302			
		total		164,007	6,834	2,012	201	-		302			
Intercooler	Gas in	H2		92,721	3,863	-,	267			302			
MIC-2	Jas III	CO2		50,607	2,109		267			302			
Primary		V H2O		20,679	862		267			302			
,		total		164,007	6,834								
	Gas out	H2		92,721	3,863	1,916	45	156	-222	300	14.496		-12,432,757
		CO2		50,607	2,109	48	45	156	-222	300	0.953		-445,880
		V H2O		3,921	163.4	9.1	45	156	-222	300	1.912		-69,347
		total gas		147,249	6,135		ļ .						-12,947,984
	Liquid out	L H2O	Ц.,	16,758	698		45		-222	300	4.200		-473,726
	tatal and	V-L Phase cha	inge heat	404.00=	0.004							-2222	-1,551,548
	total out			164,007	6,834		20				1.100		-14,973,258
Casandar				4,299,057	179,127		20				4.180		
Secondary	water in				170 127		40	30	20		∆ 180		14 973 259
,	water out	luo		4,299,057	179,127	1011	40	30	20	200	4.180		14,973,258
Secondary PSA MEC		H2 CO2			3,863 2,109	1,914 48	45	30	20	300 300	4.180		14,973,258

Part V: Discussion of Project Results

32. Summary of Results and Conclusions

This report consists of technoeconomic boundary analyses conducted for thirteen different biological hydrogen production systems. Eight were stand-alone systems:

- Five photosynthesis systems using algae and bacteria
- A fermentation system for waste algae
- A fermentation system for lignocellulose
- A Microbial Electrolysis Cell (MEC)

Five integrated systems were examined, each combining two of the above systems:

- A vertically stacked photosynthesis system using algae and PNS bacteria
- Three systems combining photobiological and fermentor systems
- A lignocellulose fermentation system combined with an MEC to process the organic byproduct of the fermentor

32.1 Photosynthesis systems

Each photosynthesis system used a series of large ponds or beds for organism growth and subsequent hydrogen production. The reactor beds were covered with a non-porous transparent cover to capture the H_2 and other gaseous products. Multiple configuration approaches were considered including single bed, dual bed, and chemostat configurations. The best single configuration for reach system was selected for more detailed study. Cost analysis suggests that large shallow reactor beds with thin film LDPE covers are the most economic approach. Such reactor configurations were selected for all photobiological H_2 production.

The five photosynthesis systems were:

- B-1: *Chlamydomonas reinhardtii* mutant with O₂ tolerant hydrogenase
- B-2: Cyanobacterium mutant with O₂-tolerant hydrogenase
- B-3: *Chlamydomonas reinhardtii* with mutated sulfate permease
- B-4: *Chlamydomonas reinhardtii*, immobilized on a porous mat and sulfur deprived
- B-5: Rhodobacter sphoeroides RV Purple Non-Sulfur (PNS) Bacteria

The B-1, B-2 and B-5 systems were used in a chemostat II configuration, which is able to continuously generate H₂ while the organisms are regenerated using a portion of the solar radiation. The B-3 system alternated between H₂ generation (3 days) and algae regeneration (4 days). The B-4 system was immobilized on a polypropylene film, thus minimizing the algae's energy requirements. This system operated cyclically, alternating 3 days production and 1 days regeneration.

For the hydrogen production calculations, the following key assumptions were made affecting solar-to-hydrogen (STH) energy efficiency for the upper bound of organism functioning:

1. PAR (Photosyntheticaly Active Radiation): 44% for B-1 through B-4 and 71% for B-5

- 2. Antennas: Mutants are developed with highly truncated antennas for maximal solar utilization (mutants have been developed with moderately truncated antennas but these have not produced significant amounts of hydrogen)
- 3. Light saturation: Mutants are developed that do not have ETR (Electron Transfer Rate) limitations in sunlight up to maximum intensity, thus allowing 12.2% STH energy efficiency. (Current mutants are saturated at low sunlight levels, limiting STH efficiency to 2-3%)
- 4. Chemostat II: A continuously operating Chemostat II is feasible, allowing simultaneous growth and H₂ production. (This continuous operation has not yet been demonstrated in comprehensive experiments)

Near term STH energy conversion efficiencies were also estimated for the photobiological systems. The key assumptions listed above for the upper bound cases generally apply with the exception of an imposition of light saturation affects (ie. ETR limitations). These near term efficiencies are somewhat subjective and are higher than performance currently demonstrated in the lab but much lower than upper bound performance.

Figure 32-1summarizes the solar-to-hydrogen energy conversion efficiency assumed for both upper bound performance and near term performance.

Figure 32-1. Photobiological System STH Energy Efficiency 100

STH Efficiency	B1	B2	В3	B4	В5
Upper Bound	9.2%	9.2%	5.2 %	2.25%	3.5%
Near Term	2%	2%	1.3%	1.5%	1.5%

32.2 Algae Fermentation Systems

Fermentation systems were designed to carry out dark fermentation of waste organisms as would be generated in the B-1 through B-5 systems. The maximum potential output from glucose is 4 moles H₂ per mole glucose. The fermentation converts the organisms into H₂, CO₂, acetic acid, and other organic compounds. The algae fermentation process has been experimentally demonstrated at lab scale by NREL using NREL-developed bacteria consortia. These initial tests at NREL partially converted cell starches, and subsequently, using the same consortium, additionally converted lipids. The high starch algae (sulfur deprived for 21 hours and 32% glucose) yielded 1.7 moles H₂ per mole glucose, or H₂ mass of 0.618% of algae mass. The low starch algae (sulfur deprived for 142 hours and 6% glucose) yielded 2.3 moles H₂ per mole glucose, or H₂ mass of 0.155% of algae mass. With additional experimental developments, near term future mass conversion rates are expected to be 0.4wt% from sulfur depleted algae.

For this study, the fermentor unit was sized based on the waste algae output from the photosynthesis systems. With this relatively small feedstock, the ferment output was low, resulting in high H₂ production cost.

 $^{^{100}}$ STH Efficiency =Solar to Hydrogen conversion efficiency = ratio of hydrogen net energy produced (lower heating value) to total solar energy incident on reactor bed.

For the algae fermentor production calculations, the following key assumptions were made:

1. Mass conversion rate of sulfur deprived algae was 0.4% H₂ mass/algae mass. (Current test achievements include: 0.154% for sulfur deprived 142 hrs and 0.613% for sulfur deprived 21 hrs)

Only an upper bound performance estimate was made for the fermentation system since the system is at a much more developed level than the photobiological system.

32.3 Lignocellulose Fermentation System

The lignocellulose fermentation system used corn stover as a feedstock to generate hydrogen via a dark fermentation process. The process is quite complex and involves extensive feedstock pre-processing, hydrolysis, saccharification, and fermentation. Portions of the process design and capital costs were based on an NREL corn stover-to-ethanol plant cost analysis. The unique 150°C hydrolysis process used for this study is one that has been demonstrated by NREL. The unique organisms for the saccharification process and for the fermentation-to-H₂ process have been developed by NREL at lab scale. The saccharification process utilizes organisms to convert the hydrolysis products into simple sugars in a short time. The subsequent fermentation process uses the same bacteria to produce H₂ and CO₂ gas plus simple organic liquids

For the lignocellulose fermentor production calculations, the following assumptions were made:

- 1. Acid hydrolysis to break down biomass to hemicellulose and cellulose components of complex sugars can be effectively carried out at a temperature of 150°C and pressure of 4.7 atm. with an efficiency of 90% conversion of the components.
- 2. Saccharification and fermentation can be effectively carried out sequentially in the same reactor vessel at a temperature of 55°C, at atmospheric pressure, and using 40 hr batch cycle with an efficiency of 90% conversion.

The saccharification process utilizes bacteria to convert the hydrolysis products into simple sugars in a short time. The subsequent fermentation process uses the same bacteria to produce H_2 and CO_2 gas plus organic liquids, requiring approximately 40 hours. Efficiency for these processes in combination was 90% conversion to H_2 and simple liquid organic byproducts.

Costs of 37 tonne/day H_2 production were initially calculated assuming zero value of the byproducts. These byproducts are essentially: 692 tonnes of organic acid and alcohol liquids plus 846 tonnes of lignin and xylan solids. The liquid byproducts comprising 51% acetate and 21% ethanol have intrinsic value, but would require a subsequent separation process such as distillation. Taking credit for the value of the large amount of byproduct would substantially reduce net H_2 costs. A more rigorous assessment of this effect should be conducted. As an alternative to byproduct recovery, the liquid organics can be processed in an MEC to produce additional hydrogen.

In addition to the liquid byproducts, the extracted lignin solids can be used as a low grade fuel for industrial processes.

Like the algae fermentation system, only an upper bound performance estimate was made for the lignocellulosic fermentation system.

32.4 Microbial electrolysis Cell (MEC) System

The MEC has been developed at Penn State University to break down simple liquid organics such as acetic acid and ethanol mixed with water into H₂ and CO₂, with the gasses being separated by the electrolysis process.

For the electrolysis process, the anode microbes generate a voltage which is supplemented with an external voltage to generate an electrolysis current. A lower external voltage results in higher efficiency, but increases reaction times, thus increasing system size and cost. It was determined that for lowest cost H₂, the system should be operated at a higher than normal voltage (0.9V) to minimize capital plant costs. The very low concentration of the input acetic acid (~2g acetate/Liter of water as opposed to the fermentor at 200g/L) resulted in a very large system, i.e., 96,000,000 gallons of total reactor volume for 88 tonnes H₂/day. These volumes and the required high area anodes and cathodes were based on specifications from lab tests by Penn State. The anode used was a carbon brush with the microbe layer and the cathode was a stainless steel brush. The details of utilization of these electrodes in a large scale reactor tank have not been fully worked out. Since the MEC separates most of the H₂ from the CO₂, its PSA requirements are greatly reduced and there is reduced loss of H₂ in the PSA process.

Key assumptions for the MEC system were:

- 1. Conversion efficiency of acetate to H₂ is 90% of the theoretical 4 moles of H₂/mole acetate (lab tests have achieved as high as 95%)
- 2. The lab-scale system design will function equally well for very large scale reactors.
- 3. Acetate feedstock for the stand-alone MEC was \$0.60/kg, (which is a significant component of the resultant H₂ cost).

Only an upper bound performance estimate was made for the MEC system given its currently very low stage of development.

32.5 Integrated Stacked Photosynthesis System

This system employs two different photosynthesis systems having different, but overlapping, PAR wavelength bands. The narrower band system is stacked on top of the wider band system so that the lower system can utilize photons not utilized by the upper system. For this case, the more efficient (4 photons/ H_2), but narrower band *Chlamydomonas reinhardtii* was above the less efficient (11 long wavelength photons/ H_2), but wider band (PAR = 0.71) PNS bacteria. For the top bed, the B-3 system was used, since the B-1 and B-2 mixtures of O_2 and O_2 and O_3 and O_4 raised safety concerns for this application and the B-4 mat and high cell density absorbed too much sunlight. The stacked system has the benefit of reduced land area requirement.

32.6 Integrated Photosynthesis and Fermentor System

This system used the algae or bacteria waste from the photosynthesis beds as feedstock to an algal/organism fermentor. The B-1, B-2 and B-5 systems were chosen as the best adapted for the integration, since, in chemostat operation, they will be filtering waste algae from a slip stream of water to maintain bed concentration. In the B-3 and B-4 system, no waste algae is removed due to the need for the system to respire enough glucose to keep the system anaerobic. In all cases, the quantity of feedstock was so low that very little H_2 was produced as compared with the 10 tonne/day photosynthesis beds. For the B-1 and B-2 integrations, output was \sim 7kg/day and for the B-5 integration, output was \sim 18 kg/day. An additional benefit of the B-5 integration was that the fermentor produced acetic acid byproduct, providing 3% of the B-5 acetic acid requirement.

32.7 Integrated Lignocellulosic Fermentor and MEC

The baseline lignocellulosic fermentor and baseline MEC were sized to allow integration of the two such that the organic liquid byproduct of the fermentor could be used as the entire feedstock for the MEC. This byproduct has been shown in NREL experiments to be 51% acetic acid and 21% ethanol, with the remainder being other organic acids. Thus, the 2,000 tonnes/day corn stover plus water produced 37 tonnes H_2 /day from the fermentor and 88 tonnes H_2 /day from the MEC.

32.8 Gas Processing

For each of these systems, the reactor gaseous outputs were ducted to compression and gas separation systems. The compressors were two stage units, using intercoolers to reduce gas temperature and to condense water vapor, thus minimizing compression power requirement. The final separation was carried out with PSA (Pressure Swing Adsorption) units that would produce 99.9% pure H_2 .

32.9 Hydrogen Production Cost Comparisons

Given the systems and performance assumptions listed above, the feasibility, performance, capital cost, and resultant $k + kg + H_2$ were evaluated for each system and integrated system. System hydrogen production costs are summarized in Figure 32-2.

Figure 32-2. H₂ Production Costs

	H_2	Hydrogen	Cost, \$/kg
System	Production kg/day	Near Term Performance	Upper Bound Performance
Photobiological H ₂ Production			
B-1: Algal O ₂ -tolerant Hydrogenase	10,000	\$8.15	\$2.99
B-2: Cyanobacterium O ₂ -tolerant Hydrogenase	10,000	\$8.15	\$2.99
B-3: Algal Sulfate Permease	10,000	\$10.48	\$4.17
B-4: Immobi lized Algal, Sulfer deprived	10,000	\$8.44	\$6.02
B-5: PNS Bacteria	10,000	\$13.95	\$10.36
Fermentation of Waste Algae/Photobacteria			
C-1 or C-2 (Effluent from B-1 or B-2)	7		\$172.73
C-5 (Effluent from B-5)	19		\$66.17
Fermentation of Lignocellulose			
System with no byproduct credit	37,181		\$4.33
System with byproduct sales (\$0.12/kg acetate byproduct)	37,181		\$2.09
MEC - Microbial Electrolysis Cell (Acetic Acid Feedstock)	88,055		\$12.43
Integrated Systems			
Integrated Photobiological - Stacked System (B-3 over B-5)	10,600		\$5.25
Integrated Photobiological/Fermentor			
B1-C1 or B2-C2 Integration	10,007		\$3.21
B5-C5 Integration	10,019		\$11.04
Integrated Lignocellulosic Fermentor/MEC	125,266		\$6.61

For the pure photobiological systems, the upper bound performance B-1/B-2 system¹⁰¹ achieved the lowest hydrogen cost, however, these results are predicated on major improvements in organism mutations achieving truncated antenna reductions, elimination of cell light saturation due to Electron Transfer Rate (ETR) limits, and satisfactory chemostat II operation. The B-3 and B-4 system costs are slightly higher and the systems are more complex, but the components have been more completely demonstrated. The B-5 system has the highest cost of the photobiological systems due the larger amount of photons needed (11 to 15 vs. 4) and the high

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 $^{^{101}}$ While the B-1 and B-2 pathways utilize different organisms, all system engineering parameters are identical. Consequently, predicted hydrogen cost is the same.

cost of the acetic acid feedstock. This system definition also assumed a satisfactory Chemostat II

Not surprisingly, the photobiological systems achieving near term STH energy efficiency are observed to be substantially higher cost than those achieving upper bound STH efficiency. The cost difference is a function of both required reactor area and scaling affects of non-bed components, thus the cost difference cannot be determined by simply ratioing STH efficiencies.

The algae/bacteria fermentation systems have high costs due to the low organism feedstock input resulting in low H₂ output. A large part of the resulting H₂ cost is due to the labor costs, (94-96% of total cost) since we are analyzing it as a stand-alone system. The cost contribution of the labor drops drastically when integrated with the Photobiological system. The current results are based on a projected fermentation output of highly sulfur-deprived organisms and do not exploit fully the organic components of the algae feedstock. It is expected that future bacteria and processing developments can facilitate more extensive conversion of the starch, lipid and protein content of the algae into H₂. Note that lignocellulose was not added to the algal fermentor to supplement the feedstock due to different bacterium needed and significant transportation costs from lignocellulosic sources to the high solar intensity photobiological sites.

The lignocellulosic fermentation achieved a moderately low H_2 cost, using bacteria and processing that has been proven in lab environments, but not in large scale demonstrations. There is also high potential for cost reduction from sales of the 51% acetic acid content liquid byproduct. If the byproduct had a market value of \$0.12/kg (as compared to the market price of $\sim $0.60/kg$ for acetic acid), the net H_2 cost would be reduced to near \$2.00/kg.

For the MEC system, the moderately high H₂ cost resulted from the very dilute acetic acid/water reactant, and necessitated a very large reactor volume and correspondingly very large anode and cathode areas. This high capital cost was coupled with high acetate market price, which could potentially be reduced by lowering acetic acid purity, which is not marketed, but is available as a fermentor byproduct. The immaturity of the full scale system concepts and components indicated that there is extensive potential for future cost reductions. Cost saving could also arise from higher concentration of electrolyte and higher pressure operation.

For the integrated stacked photobiological system, the H_2 cost is between the cost of the individual stand-alone systems. This indicates that there is no cost benefit to integration as a scaled-up version of the lowest cost non-integrated configuration is most preferable.

For the integrated photobiological algae/fermentor system, the resulting H_2 costs are higher than the stand-alone photobiological system, also indicated that integration is not preferred.

For the integrated fermentor/MEC system, the MEC's H₂ production cost is reduced significantly due to supply of a "free" feedstock. However, due to high MEC capital costs, the cost of the combined system is still significantly higher than the fermentor alone.

33. Recommendations for Future Work

Key recommendations for future work are summarized below:

Photobiological Systems

- Conduct research to further reduce the truncated antenna of mutants
- Conduct research to eliminate or alleviate the current Electron Transfer Rate (ETR) limitations for organisms and resulting light saturation
- Conduct sensitivity testing on advanced mutants to more fully assess the effects of algae photon utilization rate saturation
- Demonstrate the Chemostat II operation at larger scale
- Evaluate alternative reactor bed concepts
- Consider the use of an alternative immobilization mat for use in the B-4 system. As currently postulated, B-4 uses a fibrous, high surface area polypropylene mat on which to cultivate algae. This mat has been shown to work well with other algal organisms and can be purchased at low cost as opposed to having to be fabricated on-site (at an anticipated high cost). However, alternate mats, perhaps made of alginate, offer several advantages: they can be used as a nutrient source for the algae and/or used as feedstock for the fermentor when the photobiological system is integrated with an algal fermentor. For these reasons, consideration of alternate B-4 systems is warranted.
- Conduct more comprehensive systems designs, addressing details of mixing, pH control, bed temperature control, and CO₂ absorption

Future Algae Fermentation Systems

- Evaluate feedstock algae pre-treatment processes (e.g. hydrolysis and saccharification) to significantly increase the algae-to-hydrogen conversion rate (by greater conversion of lipids and other components)
- Consider stand-alone large-scale hydrogen production using high glucose content, rapid growing, denser concentration algae as a substrate, grown specifically for fermentation
- Use non-sulfur deprived algae, greatly increasing the easily fermentable glucose content
- Reduce fermentation time from 72 hours to at least the 40 hour batch time characteristic of the lignocellulosic fermentation

Lignocellulose Fermentation Systems

- Conduct further analysis to verify the benefit of the lignocellulose fermentation liquid organic byproduct sale to dramatically reduce the cost of hydrogen. This would include evaluation of potential byproduct component selling price reductions due to increases in worldwide supply from fermentation processors
- Conduct further analysis to address the separation of byproduct components (acids, ethanol, etc.), as in a distillation process

MEC Systems

- Through research and analysis, develop optimized production process and components for low capital cost systems, addressing issues such as:
 - Increased solution density
 - o Higher pressure operation
 - Low cost cathodes and anodes
 - o Cathode and anode optimization for large reactors
- Determine the extent of ion transport loss increases as reactor size grows to production scales

Integrated Systems

- Postulate additional synergistic integrated system combinations to achieve reduced hydrogen cost
- Analyze integration of reactor bed configurations (dual beds, other) that may not be optimal for stand-alone photobiological reactors, but are advantageous when combined in an integrated system

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