

Milestone Report

**Updated Cost Analysis of
Photobiological Hydrogen
Production from
Chlamydomonas reinhardtii
Green Algae**

Milestone Completion Report

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**Updated Cost Analysis of Photobiological Hydrogen Production
From *Chlamydomonas reinhardtii* Green Algae**

Wade A. Amos
National Renewable Energy Laboratory

Milestone Report for the U.S. Department of Energy's HCFIT Program
Analysis Task

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INTRODUCTION

In 1999 NREL completed a preliminary cost analysis of photobiological hydrogen production from *Chlamydomonas reinhardtii* (Amos, 1999). At the time, NREL researchers, in cooperation with researchers at the University of California-Berkeley, were able to produce hydrogen using a wild-type algae in a laboratory batch reactor system. Cells were first cultured, then switched to a sulfur-deficient environment to produce hydrogen. The researchers have now managed to produce hydrogen continuously using a series of two flow reactors. This is a critical process advancement. This study takes a more detailed look at the effects that cell density, light adsorption and light saturation have on algal hydrogen production. The previous study had looked mainly at incident light intensities, batch cycles and light adsorption without directly attempting to model the saturation effects seen in algal cultures.

While research has continued on *Chlamydomonas reinhardtii*, the question asked most often with regards to algal hydrogen production is “how good does it get.” The previous study identified reduced antennae size, increased hydrogen production rates, continuous hydrogen production and lower reactor costs as critical factors in the cost of algal hydrogen production. However, if algal hydrogen production under the best conditions cannot begin to approach the U.S. Department of Energy (DOE) cost goal of \$2.60/kg for renewable hydrogen, does it make sense to continue funding the research? For this reason, the current study focuses on the future cost of hydrogen from algae and shows that in some cases the hydrogen selling price does approach the DOE cost target.

One other aspect of algal hydrogen production is also included in this study: performance estimates based on actual solar data. A previous NREL report looked at solar-thermal hydrogen production from methane (Spath & Amos, 2002). The same solar conditions, economic assumptions and storage methods that were used in that study were used in this study to determine the cost of algal hydrogen production under real-world conditions.

Based on this analysis, the estimated future selling price of hydrogen produced from algae ranges \$0.57/kg to \$13.53/kg, depending upon where you define the system boundaries. The base-case assumes a continuous hydrogen production system with a reactor cost of \$10/m², a pressure-swing adsorption (PSA) unit, compression to 20 MPa, and enough storage to reliably supply 300 kg/d despite bad weather conditions. For this system, the hydrogen selling price is \$13.53/kg. If the system can be connected to a hydrogen pipeline and the production isn't limited by storage capacity, the hydrogen selling price drops to \$5.52/kg. If one removes the compression and assumes a PSA is not needed—hydrogen production at ambient pressures—the selling price drops to \$3.68/kg. Finally, if one then assumes a lower photo-bioreactor price of \$1/m², the selling price may be as low as \$0.57/kg—below the DOE target.

CYCLIC HYDROGEN PRODUCTION

In 1999, researchers at NREL, working with researchers at University of California-Berkeley, discovered that *Chlamydomonas reinhardtii* could be forced to produce hydrogen under sulfur-free anaerobic conditions. The laboratory procedure was to grow the algae in light with a normal sulfur-containing growth media, then centrifuge and wash the cells in growth media that did not

contain sulfur. The cells would then be added to the sulfur-deficient media and after a transition period of 24-48 hours, the cells would start producing hydrogen. Over the course of 4 days, the hydrogen production would slowly drop and eventually stop, presumably due to other effects of the sulfur deprivation.

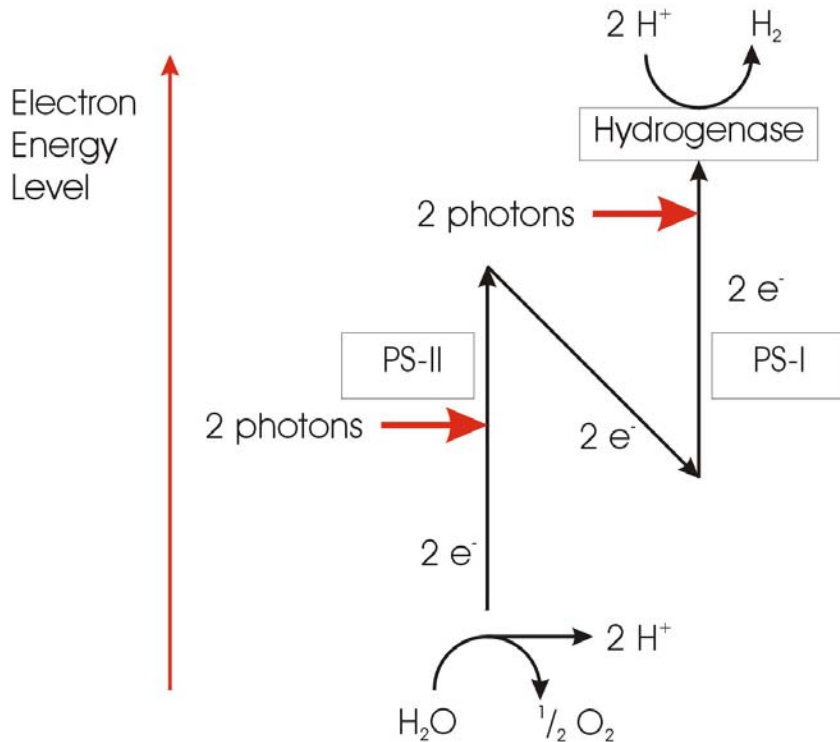
During the start of the transition, the algae's oxygen production would drop due to the effects of sulfur deprivation. Eventually the oxygen consumption of the cells would exceed their ability to produce oxygen. At this point, the flasks would be sealed the cells would start to consume any residual oxygen in solution and eventually the flasks would go anaerobic. The addition of acetate to the growth media accelerated the transition by providing a carbon source that the cells could consume through aerobic oxidation. After going anaerobic, there would be another delay while the cells synthesized the hydrogenase enzyme required for hydrogen production. Once the solution was anaerobic and the hydrogenase enzyme had been synthesized, the cells could start producing hydrogen.

During hydrogen production, oxygen production does not completely stop. The effect of sulfur-deprivation is to slow the first step of photosynthesis, where electrons are pulled from water in photosystem II (PS-II) to produce oxygen. It was discovered that complete removal of sulfur had an adverse effect on hydrogen production because PS-II would completely shutdown and not produce any electrons for transfer to the hydrogenase to produce hydrogen. Instead, the requirement is that PS-II be *slowed* to the point where any oxygen produced is consumed by the cells for normal respiration and no excess oxygen is produced. The sulfur deprivation also stops the cell growth in the culture. Figure 1 shows how electrons are pulled from water and raised to a higher energy level in PS-II. The electrons then drop to a lower energy level while the cells capture some of this energy for metabolic activities, before being given another boost in energy while passing through photosystem I (PS-I) in the algae.

There are several options for the high-energy electrons leaving PS-I. The electrons can be recycled through PS-I to produce ATP energy for the cell, they can be diverted for cell growth and starch production, or they can be dumped to hydrogenase to produce hydrogen. Note that recycling electrons does not remove them from the cell, so if electrons continue to enter from PS-II, the only options are cell growth, starch production or hydrogen production. Cell growth and starch storage are hindered by sulfur deprivation, so hydrogen production remains as the main route for dumping electrons from the organism under anaerobic conditions. In other words, the reason a wild-type organism produces hydrogen is to rid itself of electrons fed in through PS-II.

Eventually, the sulfur deprivation has other adverse effects on the cells and hydrogen production stops after approximately 4 days—sooner if no sulfur at all is present in the sulfur-deficient growth solution. One option is to “regenerate” the cells by giving them sulfur again and exposing them to light to obtain the energy to recover.

Figure 1 – Electron Pathway through PS-II and PS-I for Hydrogen Production

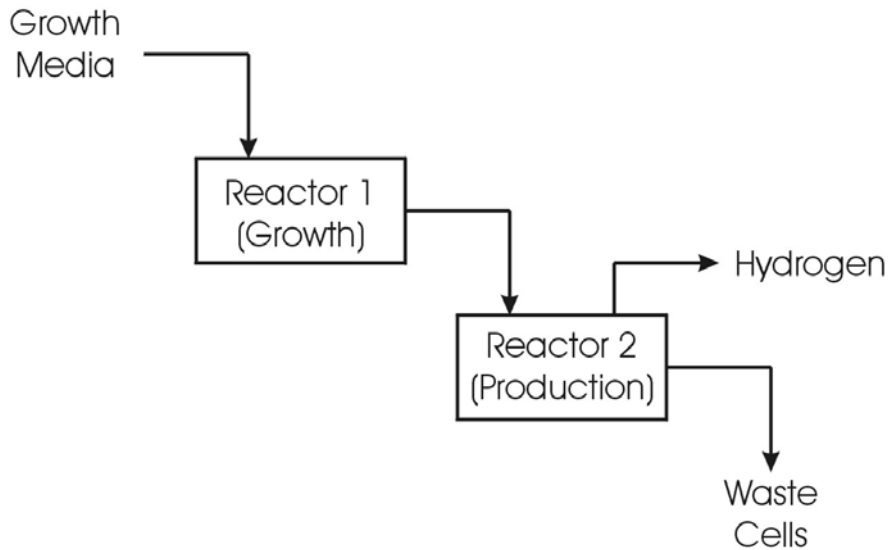


CONTINUOUS HYDROGEN PRODUCTION

One of the obvious improvements to the above system is to find a way to operate the system continuously, without the need to transfer the cells into a sulfur-deficient medium. In 2002, NREL researchers developed a system using two continuous-flow reactors for producing hydrogen continuously for periods of up to several weeks.

The continuous hydrogen production process involves using two continuously-stirred tanks. Figure 2 shows the tank configuration. In Reactor 1, cells are cultured in media containing minimal levels of sulfur. PS-II is slowed and oxygen production remains lower than oxygen consumption for cellular respiration, but by bubbling the solutions with carbon dioxide and a small amount of oxygen, the cells are able to remain in Reactor 1 indefinitely, obtaining some energy from photosynthesis and some energy through respiration of acetate in solution.

Figure 2 – Continuous Hydrogen Production



Cells from Reactor 1 are transferred to Reactor 2, which is maintained under anaerobic conditions. Cells entering Reactor 2 already have suppressed PS-II systems, so they will not cause Reactor 2 to go aerobic. Any residual oxygen is quickly consumed by the algae in Reactor 2. Finding themselves under anaerobic conditions, the cells will start producing hydrogenase and subsequently, hydrogen. The transition step that consumes the oxygen in solution in the batch system is avoided by having Reactor 2 already anaerobic. At the same time, some cells are continuously removed from Reactor 2. The effect is that the cells are removed from Reactor 2 before they completely stop producing hydrogen. Successful operation has been shown with a dilution rate of 0.5/day, which is equivalent to an average residence time of 2 days for the cells. Because Reactor 2 is a continuously-stirred reactor (like Reactor 1), the average residence time is 2 days, but some individual cells removed from the reactor may have been there longer or shorter times. With an average residence time of 2 days, one would expect a hydrogen production rate lower than the initial production rate of the batch system, but higher than the production rate at the end of a batch production cycle. The net effect of Reactor 2 is to add new fresh cells with a high production rate while also removing older cells near the end of their useful production cycle. It may be possible that a plug-flow reactor (PFR) would be more efficient.

The cells removed from Reactor 2 could be regenerated, like in the batch system. As in any biological system, some cells will need to be removed to prevent build-up of inert biological materials that cannot be re-consumed by new cells.

IDEAL SYSTEM

As mentioned in the introduction, the primary area of concern at this stage of research is whether there is any chance that the technology can compete economically with other hydrogen production technologies. Addressing these economic concerns requires identifying the limiting factors for the design of the system. In algal hydrogen production, these limiting factors may be biological limits—such as how fast the organism can physically process photons from sunlight,

solar considerations—such as average light intensities in the culture, engineering considerations—such as what reactor materials can be used, and scientific considerations—do I have the knowledge to do the required level of genetic engineering at this point?

The *ideal* algal hydrogen production system would meet the following criteria:

- 1). It would have no cell wasting—the cells would naturally maintain the same cell density without a net increase in cell mass and new cells would obtain nutrients through cryptic growth off dead cells.
- 2). The pond depth would be just enough to maximize light adsorption, but no deeper.
- 3). The cells would have a reduced antennae size so that they would adsorb only as many photons as they could convert to hydrogen and no more. This would allow the additional photons to pass deeper into the algal solution and be adsorbed by cells further down in the liquid. All the incident photons would thereby be absorbed and converted to hydrogen.
- 4). All electrons passing through PS-II would be used for hydrogen production with no side-reactions.
- 5). The cells would produce hydrogen at the maximum rate at which they could process electrons without any concerns with oxygen production and inhibition.
- 5). The cells would be contained in a cheap, durable translucent reactor material that fully transmitted all required wavelengths, would have a low hydrogen permeation rate to contain the hydrogen, and would not allow algae cells to fasten to the inner surface and block the sunlight.

SATURATION IN ALGAL CULTURES

One factor limiting hydrogen production in algae is a phenomenon called light saturation. Whether producing oxygen or hydrogen, the gas production rate increases almost linearly at low light concentrations, but quickly levels out and approaches a maximum value, well before reach full sunlight intensity is reached. This is caused by the fact that algae are able to absorb far more photons than they can collect and transfer into PS-I. If the light-collecting antennae can be reduced in size, light will penetrate deeper into the cell culture. It is believed that if the antennae size can be reduced to a size that matches the cell's ability to process the photons, it will not adversely affect the health of the algae cells. The University of California-Berkeley is actively developing mutants with reduced antennae size. By screening mutants for reduced antennae size and then identifying the DNA sequences that were modified, the researchers plan to identify the genes controlling antennae size. This information can then be used to optimize the antennae size in *Chlamydomonas reinhardtii* as well as other photosynthetic organisms.

Modeling saturation in algae greatly affects the predicted hydrogen production rates in algae cultures. In the previous NREL study, saturation was accounted for by comparing the hydrogen production rates of cultures under similar lighting conditions. In this study, the effects of saturation are modeled directly to determine the effect of cell concentration and antennae size on hydrogen production.

MODELING SATURATION AND HYDROGEN PRODUCTION

Estimating hydrogen production while accounting for saturation and differences in light intensity requires a comparison of the number of photons available with the amount of algae present in the culture. The number of photons absorbed by the culture was estimated by using Beer's law to calculate light intensities at different depths in a pond of algae. Beer's law states that absorbance, A , is a function of concentration, C , light path length, b , and a constant, E_{ta} .

$$A = C \cdot b \cdot E_{ta}$$

Absorbance is defined as the negative log of the incident light intensity divided by the light intensity at the given path length.

$$A = -\log(I/I_0)$$

The absorbance of an algal culture can be measured using a spectrometer. For this analysis, it was assumed that algae followed Beer's law, but this was not confirmed. The following data was used for modeling light absorbance: $A = 1.7$ units, $b = 1$ cm, $C = 0.34$ g/L.

To determine the light intensity and photons absorbed in the solution, the pond depth was divided into 0.2 mm deep layers. The % transmitted light was calculated at each depth using the equation:

$$I / I_0 = \% \text{ transmittance} = 10^{-E_{ta} \cdot X \cdot C}$$

Where X is the depth into the liquid and C is the cell concentration in g/L. For a given light intensity, the number of photons transmitted per m^2 was calculated. To determine the number of photons, the intensity of full sunlight was assumed to be 1000 W/m^2 , with 50% of that being photosynthetically active radiation (PAR). An average wavelength of 550 nm (average of 400-700 nm) was assumed for calculating the average energy per photon. This resulted in a photon density of $2.3 \times 10^{-3} \text{ ein/m}^2/\text{s}$ hitting the surface of the liquid. At the bottom of each 0.2 mm layer, the % transmitted light was multiplied by the number of photons hitting the surface. The difference in transmitted photons between one layer and the layer above it is the number of photons absorbed per m^2 in that 0.2 mm layer. In hydrogen production, it takes 2 electrons to form one molecule of hydrogen and it takes two photons per electron to pass the electrons from water through PS-II and PS-I. Therefore, the potential hydrogen production based on the photons absorbed is the number of photons absorbed times a yield coefficient of 0.25, or $5.75 \times 10^{-4} \text{ mol H}_2/\text{m}^2/\text{s}$ at the surface.

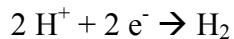
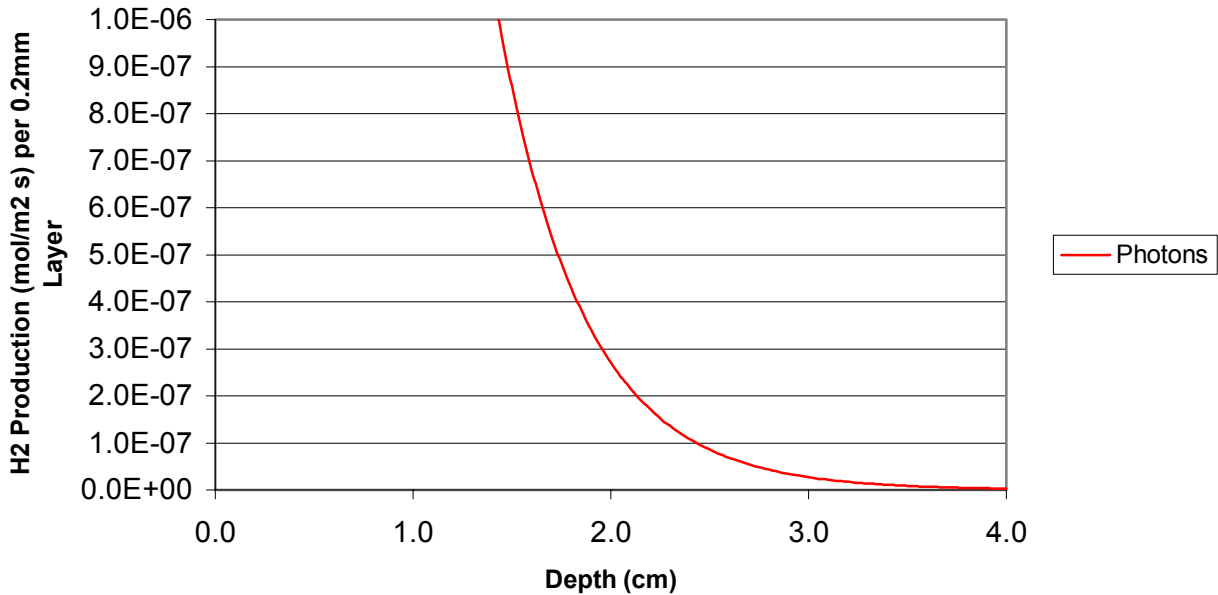


Figure 3 shows the potential rate of hydrogen production based upon the number of PAR photons absorbed in a 0.2 g/L culture for depths of up to 4 cm for a wild-type algae.

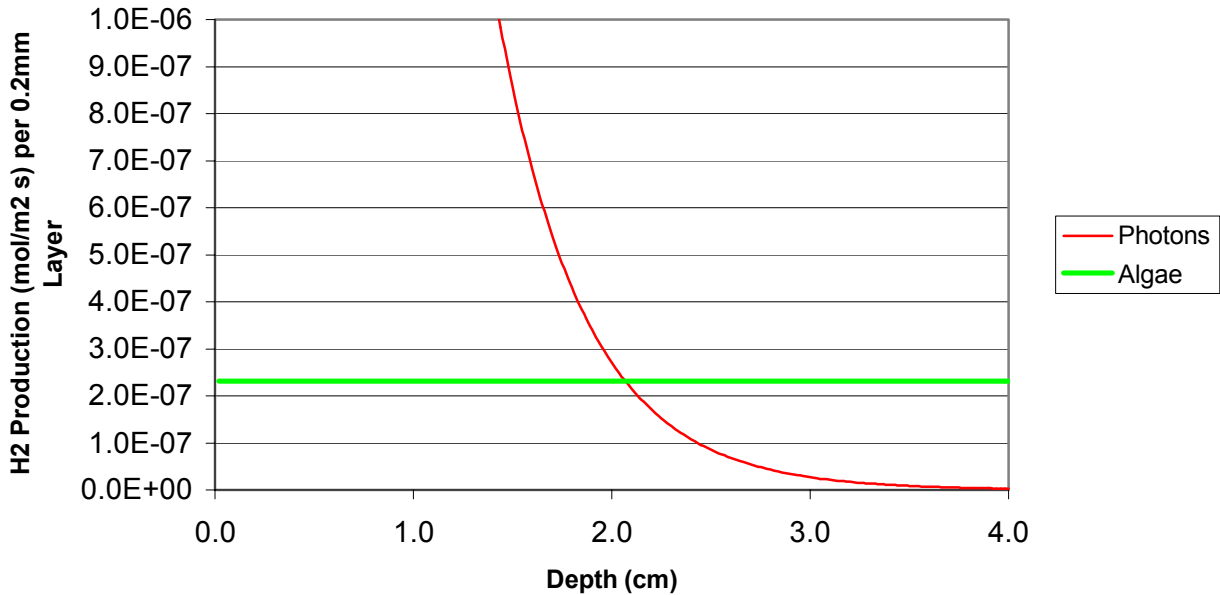
Figure 3 – Potential Hydrogen Production Based Upon PAR Photons Available



To determine the number of photons that can be processed by the culture (i.e., saturation), the volume of the 0.2 mm layer was calculated, (100 cm x 100 cm x 0.02 cm = 200 cm³ or 0.2 liters). This was multiplied by 0.2 g/L, which represents a typical dilute cell concentration used in the lab. The result is 0.04 g of cells in each 0.2 mm x 1 m² layer of the culture. If we then assume most biological organisms can transfer 1 electron per gram cell dry weight of cells per day to an external electron acceptor (Gossett, 1995), we get a maximum hydrogen production rate of 2.3×10^{-7} mol H₂/m²/s per 0.2 mm layer of cells at 0.2 g/L cell concentration.

Figure 4 shows the algal production limitation superimposed on the photon availability curve from Figure 3. Until a depth of about 2 cm into the solution, the number of photons available for hydrogen production far exceeds the algae's ability to process them into hydrogen. The photons absorbed in excess of the algae's production capability are not put to productive use, resulting in low light-to-hydrogen conversion efficiency.

Figure 4 – Algal Production Limitation Compared to Photons Absorbed



At a depth of about 2.0 cm, the number of photons available becomes the limiting factor; there is enough algae to process the full number of photons being absorbed, but the light intensity near the bottom of the solution has dropped to a lower level. Figure 5 shows how much hydrogen will be produced in each 0.2 mm layer of algae at the given depth. Near the surface, the hydrogen production is constant because there are plenty of photons and the algae mass is limited in its ability to process them. Below 2 cm, the photons become limiting and the production in deep layers drops off down to 4 cm where almost all of the photons have been absorbed. Figure 6 is a log plot of Figure 5; the photons available drops logarithmically and the production per 0.2 mm layer drops with the photons available in the deeper sections of the pond.

Figure 5 – Algal Hydrogen Production Based Upon Biological and Photon Limits

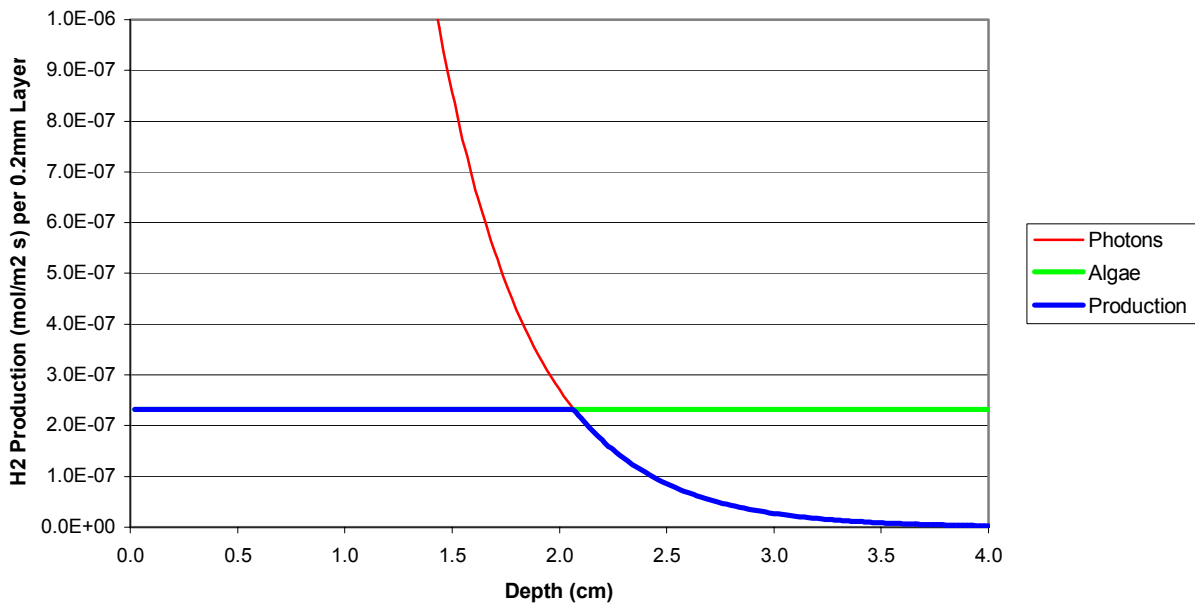
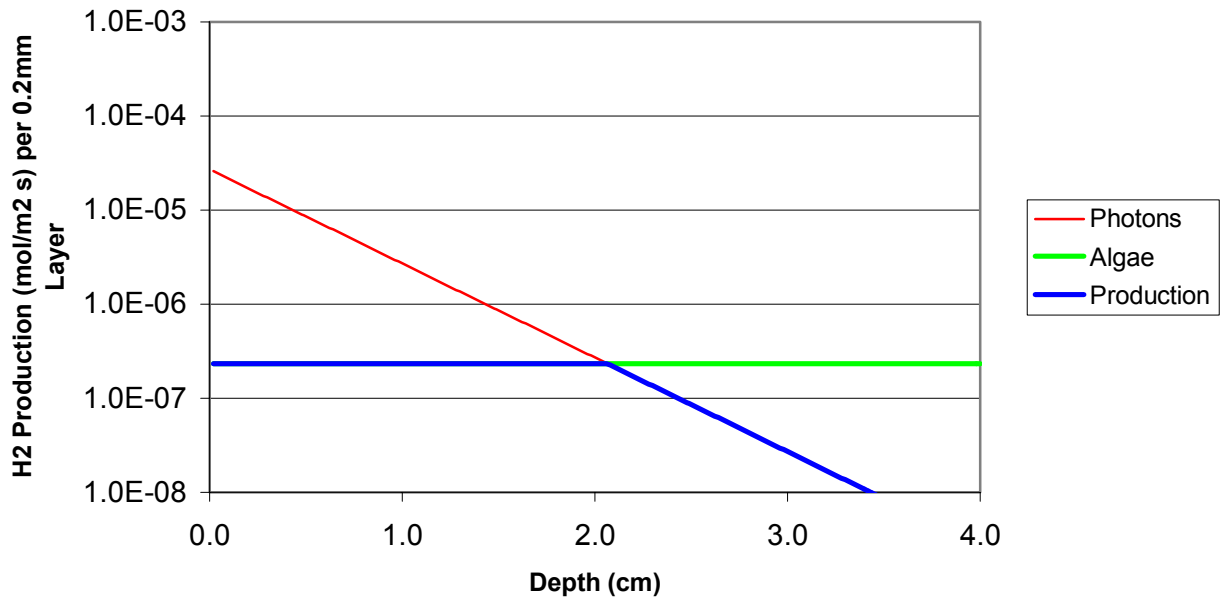


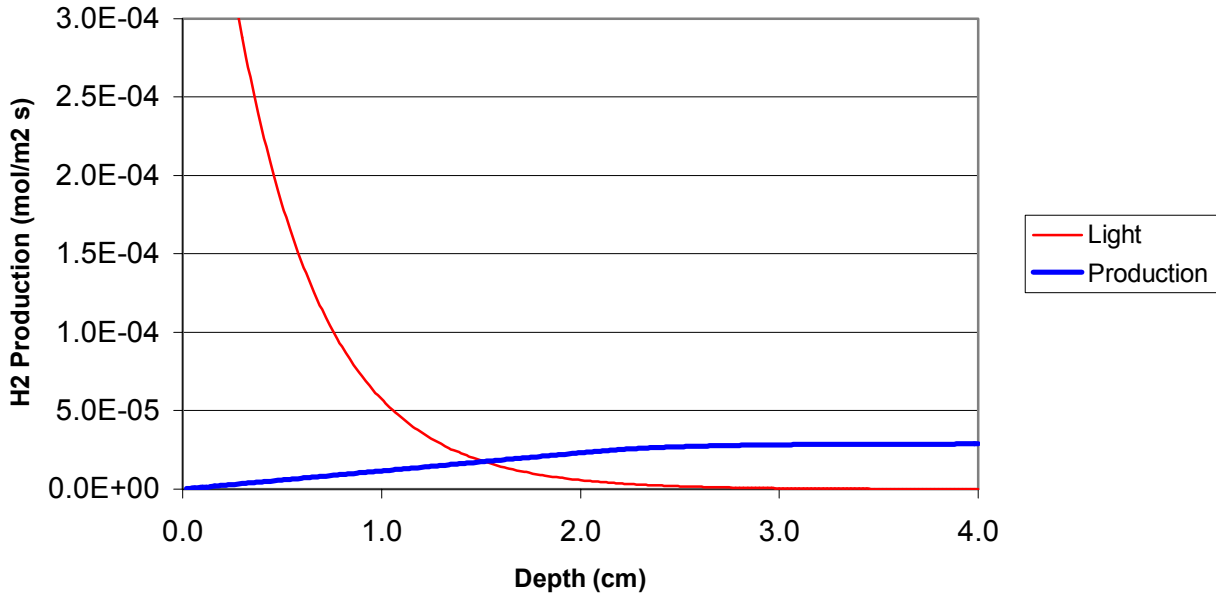
Figure 6 – Log Plot of Algal Hydrogen Production



Keep in mind that the hydrogen production in Figures 3-6 are the hydrogen production *per layer* of cell culture. The cumulative or net hydrogen production represents how much hydrogen can be produced for the entire 1 m x 1 m section of the pond. This hydrogen production rate is plotted in Figure 7, along with the light intensity. As you can see, the production increases linearly with pond depth and then eventually levels off once the light intensity becomes the

limiting factor. (The difference in magnitude for the hydrogen production in Figure 7 compared with the previous figures is due to the fact that the cumulative production represents many 0.2 mm layers added together.)

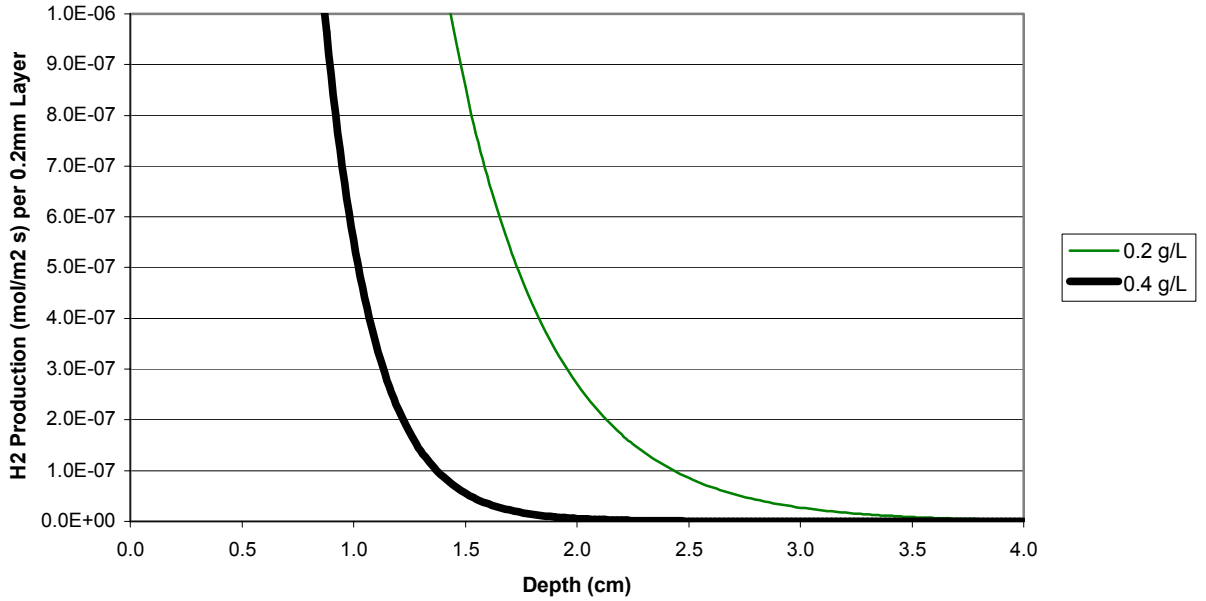
Figure 7 – Net Hydrogen Production per Square Meter of Pond



DIFFERENT CELL CONCENTRATIONS

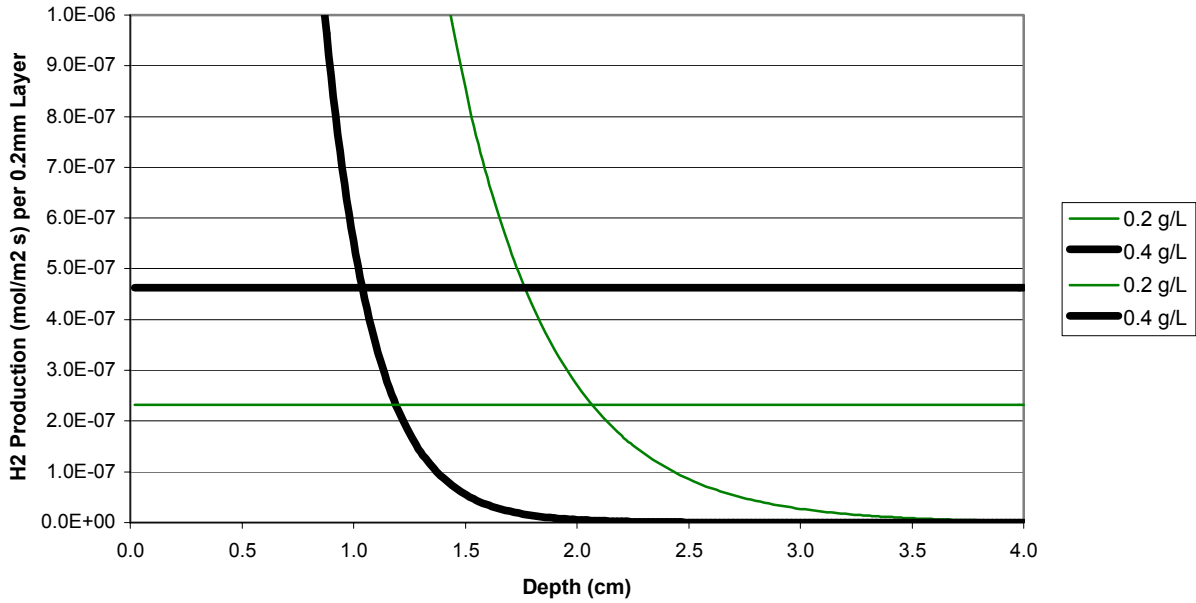
Figures 3-7 represented a culture with a cell concentration of 0.2 g/L, which is relatively dilute. Bacterial cell concentrations of 5 to 10 g/L are not uncommon in wastewater treatment and fermentations. The effect of cell concentration on light penetration is predictable: the higher the cell concentration, the more light that will be absorbed at any given depth and the lower the light intensity at the bottom of the culture. Figure 8 shows what happens to the available photons when the cell concentration is doubled from 0.2 to 0.4 g/L. Less light makes it to the bottom layers of algae and therefore there are fewer photons available to produce hydrogen at any given depth. In the case of the 0.4 g/L culture, almost all of the light is absorbed 2.0 cm below the surface.

Figure 8 – Potential PAR Photons Available for Different Cell Concentrations



However, because the cell concentration in the culture is twice as high, the same 0.2 mm layer of cells contains twice the cell mass and can therefore process twice the number of photons to produce twice as much hydrogen per layer. Figure 9 shows the higher possible hydrogen production rate because of the increased cell mass.

Figure 9 – Increased Biological Hydrogen Production at Higher Cell Concentrations



If one looks at the photon limitation and the biological algae limitation, one can generate Figure 10, which compares the hydrogen production rate per layer. What is seen is that the higher cell concentration has higher hydrogen production rates in the upper layers, but the more dilute concentration allows the light to penetrate deeper before the hydrogen production drops off. Figure 11 is the log plot of the same data.

Figure 10 – Algal Hydrogen Production for Higher Cell Concentrations

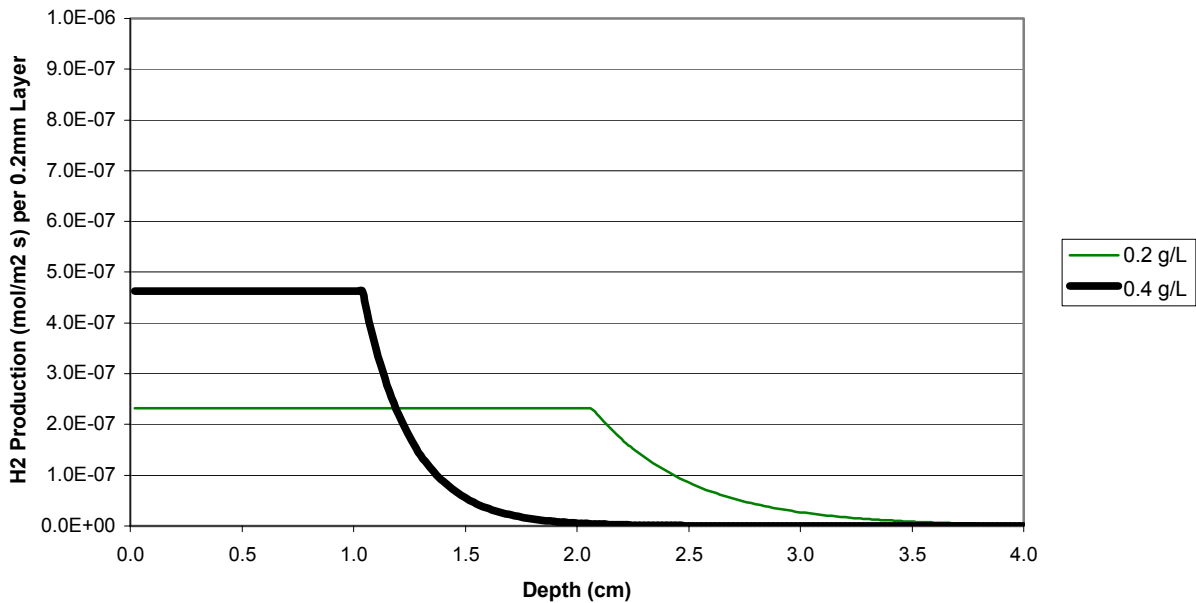
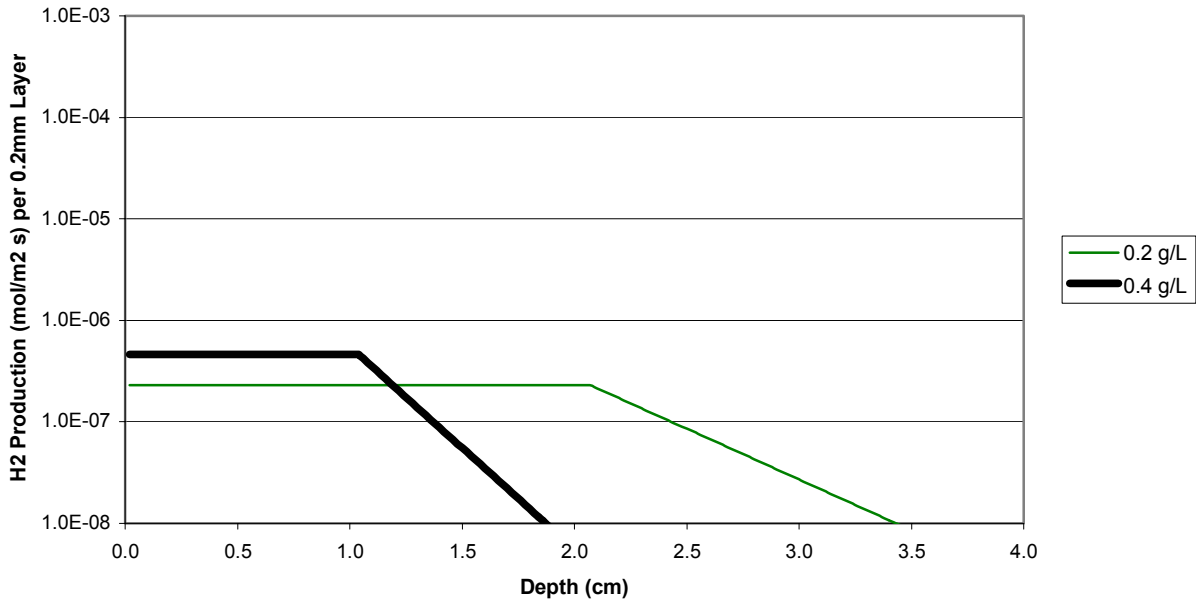


Figure 11 – Log Plot of Algal Hydrogen Production



One thing to keep in mind is that the area under the depth vs. production curve in Figure 10 is the cumulative or net hydrogen production per m^2 . In Figure 10, you can see that the area under the two curves out to 4 cm is almost exactly the same. This is also shown in Figure 12, which is the cumulative or net hydrogen production for different pond depths. The interesting fact is that the model predicts that both cell cultures will produce the same amount of hydrogen per m^2 if the pond is deep enough. However, if you have a pond depth of only 1 cm, the dilute 0.2 g/L pond will only have about half the production of the 0.4 g/L culture. If the pond is more than 4 cm, the total hydrogen production will be the same.

Figure 12 – Net Algal Hydrogen Production for Higher Cell Concentrations

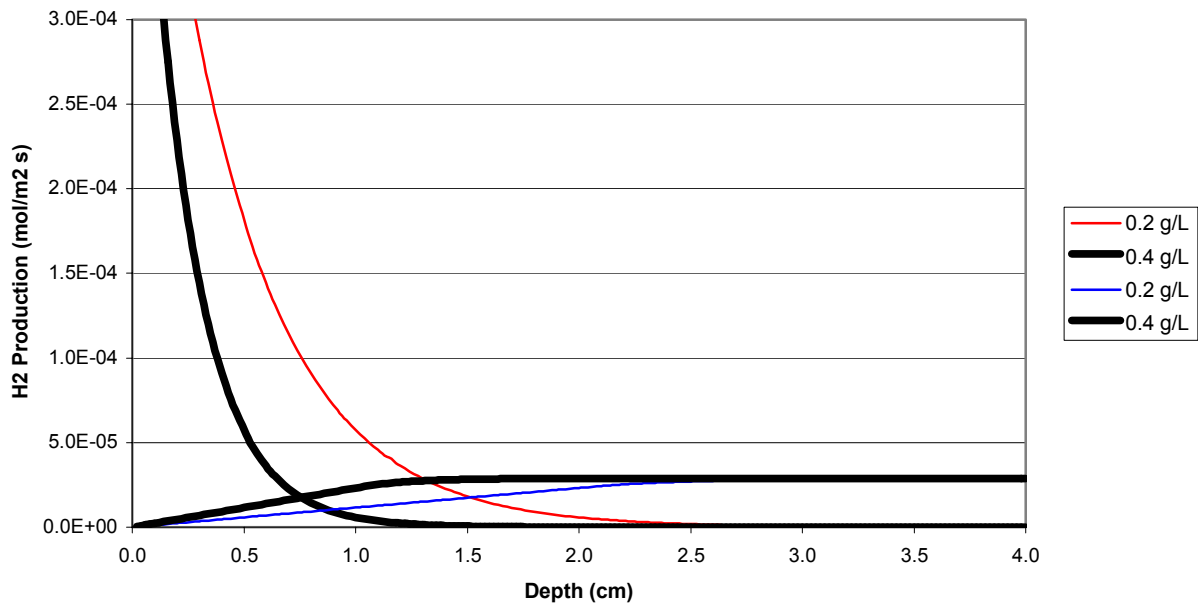
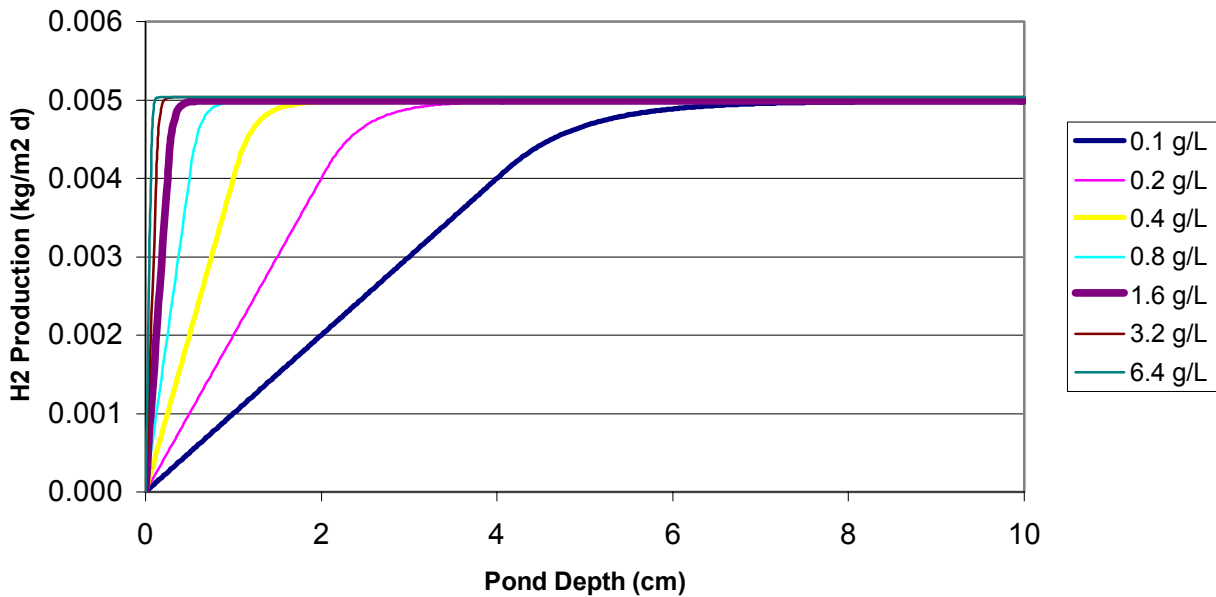


Figure 13 shows the hydrogen production for a number of different cell concentrations. Note the units in this graph have been changed to kg H₂/m²/d. (The numerical value of one “day” assumes 24 hours of sunlight so it can be normalized to the available daylight for any given region—the kg H₂/m²/d does not assume a diurnal cycle.) From this graph, one can see that a pond depth of 10 cm will work for almost any culture; a deeper pond will not result in any increase in hydrogen production. However, a more shallow pond can be used for the more concentrated cultures without any loss in hydrogen production capacity.

Figure 13 – Algal Hydrogen Production Rates for Various Cell Concentrations and Pond Depths



TRUNCATED ANTENNAE SIZE

The analysis up to this point has shown that hydrogen production can be limited by the photons available or the capacity of algae to process the photons into hydrogen. Another observation is that the number of photons absorbed is much higher than the algae’s ability to process the photons. If we can reduce the number of excess photons absorbed and let them reach deeper into the liquid, we should be able to produce more hydrogen. This is exactly the goal of truncated antennae size research being conducted at UC-Berkeley. By reducing the size of the algae’s light collecting antennae, but not affecting the organism’s ability to process the photons to produce hydrogen, one gets deeper light penetration for the same cell concentration, which means more photons are available at the lower depths for hydrogen production. This is shown in Figure 14. The mutant identified here allows 10 times more light transmission than the wild type organism. While 10 times light penetration may seem high, merely growing the algae under high light intensities can achieve 4 times higher light penetration. Also notice that the light now penetrates 8 cm into the liquid, as compared to 4 cm for the wild-type. Both types of cells are assumed to be at 0.2 g/L cell concentrations.

Figure 14 – Increased Light Penetration with Truncated Antennae Mutants

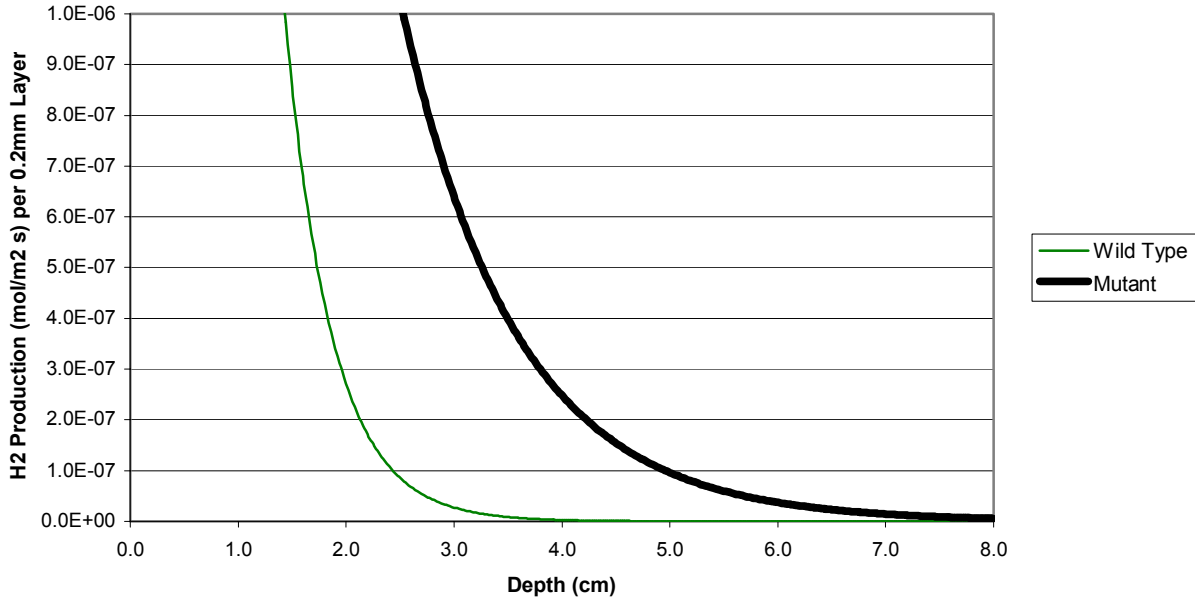


Figure 15 superimposes the algae limitation curve on top of the mutant and wild-type photon curves. Since the cell concentration is the same in both cases, there is only one line for the biological limit. With the mutant, the light available doesn't become limiting until you reach 4 cm into the liquid. It also means that instead of the hydrogen production starting to drop off at 2 cm, it doesn't start dropping off until 4 cm into the liquid. This increased light penetration directly results in a higher net hydrogen production, as shown in Figure 16. The required pond depth is twice as much because of the better light penetration, but the net hydrogen production per m² is twice as high for the same production area and same incident light level. Also note that the increased production potential of the mutant can't be differentiated until the two production curves start to diverge at 2 cm of depth. Near the surface, both cultures are saturated with all the photons they can process. At 2 cm of depth the wild-type has absorbed most of the photons, but there's still plenty of light in the mutant culture at a depth of 2 cm.

Figure 15 – Biological Production Limits on Wild-Type and Mutant Algae

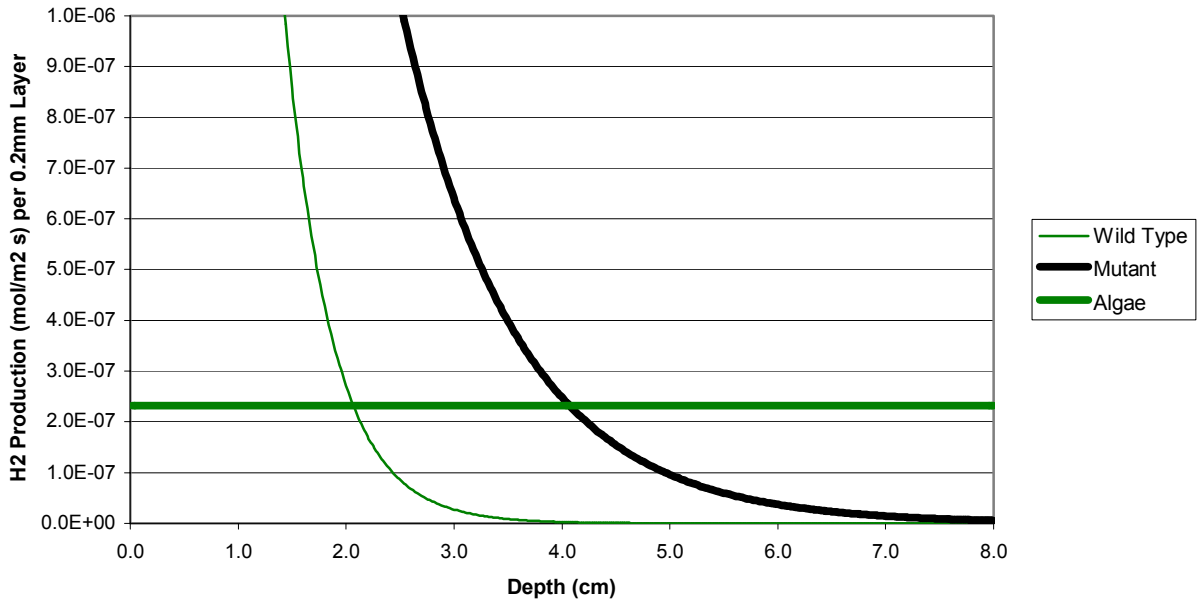
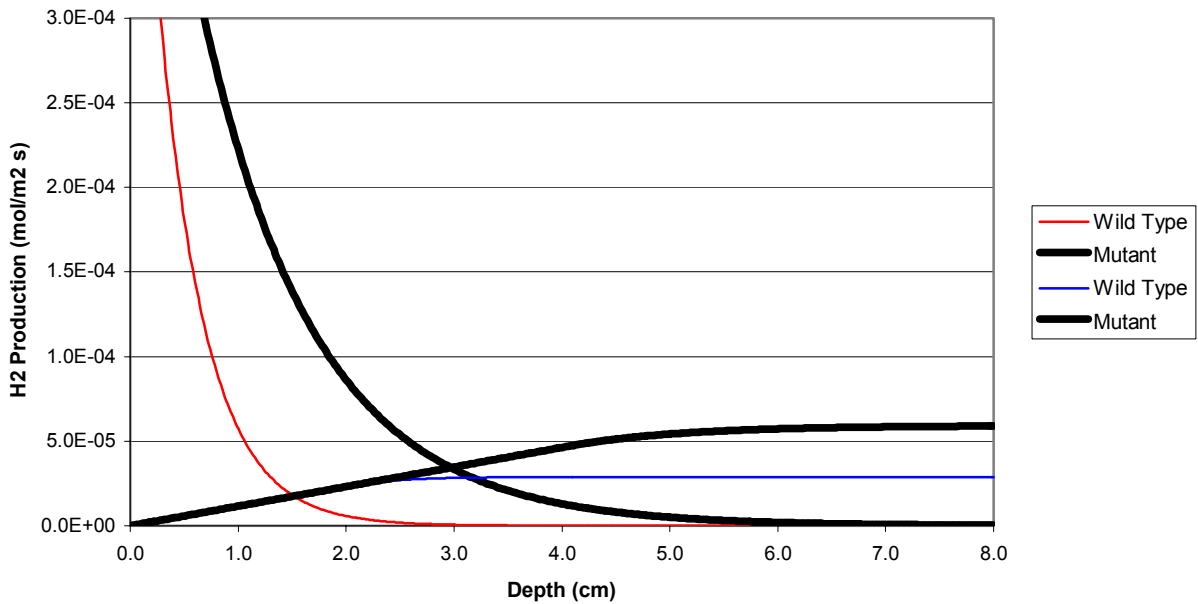


Figure 16 – Comparison of Net Hydrogen Production for Mutant and Wild-Type Algae



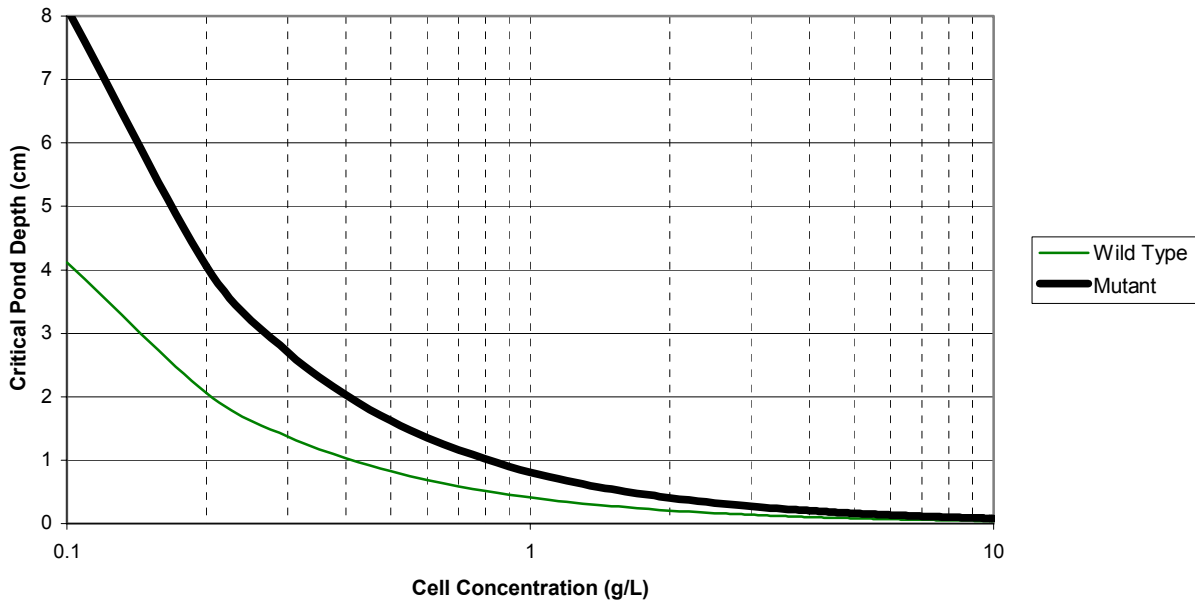
CRITICAL POND DEPTH

Figures 12 and 16 show that different pond depths are needed in order to maximize hydrogen production depending upon the cell concentration and antennae size. For each combination of

antennae size and cell concentration, there will be a critical minimum pond depth required in order to achieve the maximum hydrogen production. Until the photons become limiting, the hydrogen net production rate per m^2 continues to increase steadily. Once one reaches the depth where the potential hydrogen from photons equals the algae's potential to produce hydrogen, the hydrogen production rate starts to drop. If you assume the critical depth to be the depth where the two limits are equal you can plot how the required depth changes with concentration and antennae size. (Another method would be to plot a line where the photons drop to some percentage of the incident light level.) Figure 17 shows the critical depth for both a wild-type organism and a truncated antennae mutant. Because of the higher light penetration of the mutant, the deeper the pond is needed for any given cell concentration. Likewise, a more dilute solution requires a deeper pond because of the better light penetration. *However, note that for any given antennae size, if you pond is deep enough, you will get the same net hydrogen production rate per m^2 , no matter what the cell concentration.* You just need a deeper pond with the dilute culture. This point is not immediately obvious.

(Note this analysis assumes the light absorbance of the culture obeys Beer's law. This is not necessarily the case and has not been verified. NREL plans to collect more data to confirm this relationship.)

Figure 17 – Critical Pond Depth for Mutant and Wild-Type Algae



INCIDENT LIGHT INTENSITY

As mentioned previously, the high light intensity near the surface of the algal culture doesn't result in increased hydrogen production because the algal cells are already converting all of the photons they possibly can into hydrogen. All of the photons that are absorbed in excess of what the algae can process are wasted and result in lost efficiency with respect to the light utilization

This begs the question of what happens if the incident light intensity hitting the surface of the liquid is reduced? If one cuts the incident light level by 50%, does the hydrogen production drop by 50%? The answer is *no*.

Figure 18 shows the photons available for hydrogen production at 1 sun and at 0.1 suns. As expected, the culture being illuminated by a partial sun always has fewer photons available at any given depth. However, if you look at the critical depth, it is about 2 cm for 1 sun and 1 cm for 10% of a sun. If the critical depth is only on half of that of a normal sun, than the hydrogen production will also be about one half the normal value. This is shown also shown in Figure 19, which plots the net hydrogen production per m^2 . As you can see, the light intensity starts much lower and drops quicker in the 0.1 sun case, but for a 90% reduction in sunlight, the algal hydrogen production only drops by about 40%. The reason for this is because both cultures are saturated and therefore produce the same amount of hydrogen in the top 1 cm of the pond. After this depth, the production at 0.1 suns starts to drop off and then the full sun case drops off after 2 cm. Because the top 1 cm has enough photons to be saturated in either case, the production remains high at partial illumination.

Figure 18 – Photons Available for Hydrogen Production at Lower Light Intensities

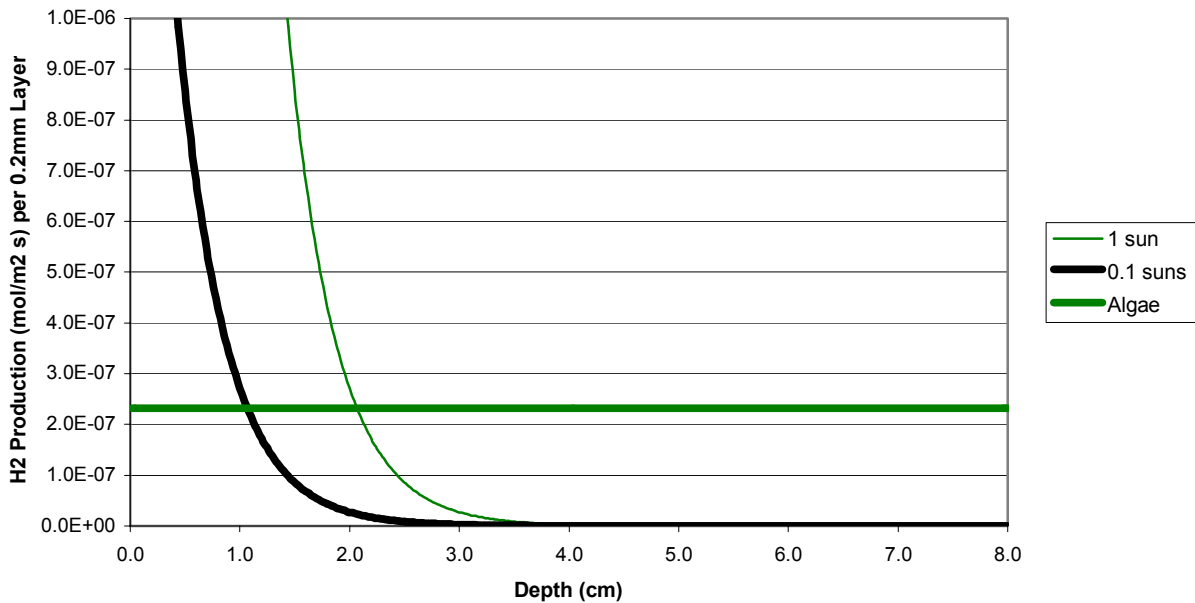
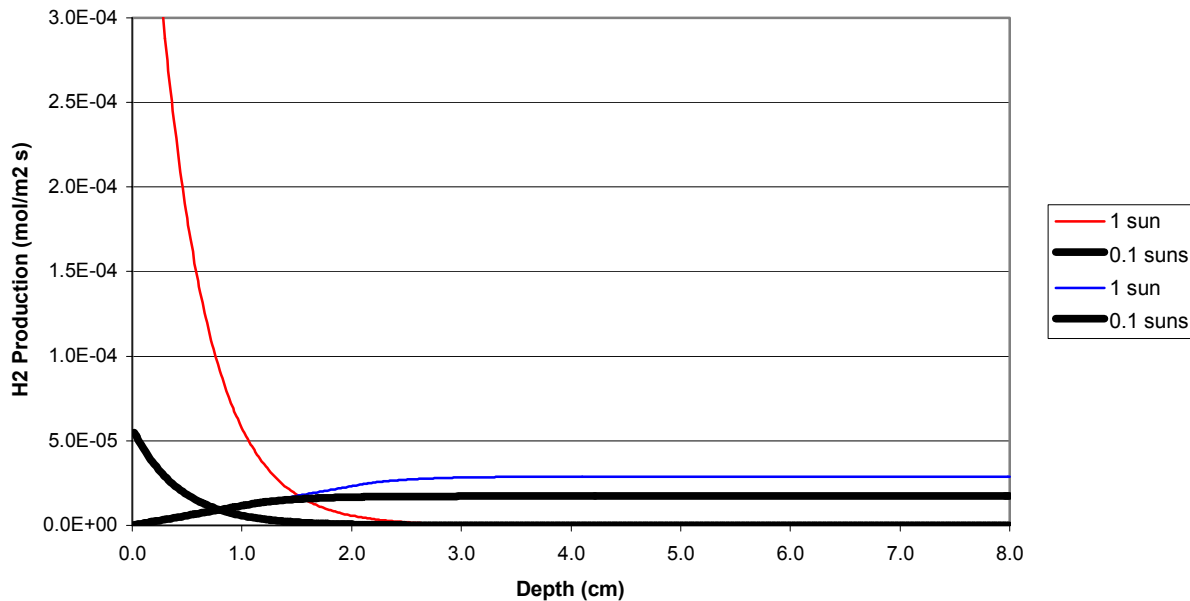


Figure 19 – Algal Hydrogen Production at Lower Light Intensities



The effect of lower light intensity has two important implications. First, if hydrogen production remains significant at low light intensities, it means that areas with lower light intensity or cloudy conditions may still have the potential to produce significant amounts of hydrogen. Second, it means that it may be possible to boost the efficiency of light utilization by collecting sunlight and then “diluting” it to lower levels and still maintain relatively high hydrogen production levels. For instance, one m² of collection area could be used to illuminate 10 m² of production units while maintaining greater than 50% of the same production rate per m². That means for the same 1 m² of collection area, you could get 10 m² x 50% or 5 times the normal hydrogen production rate as a conventional pond system.

HYDROGEN PRODUCTION CURVE

In the laboratory, data is collected under standard conditions to help analyze the results. However, nature rarely provides standard or “ideal” conditions in the outside world. For this reason, it becomes important to determine how a laboratory system might perform when subjected to real-world conditions.

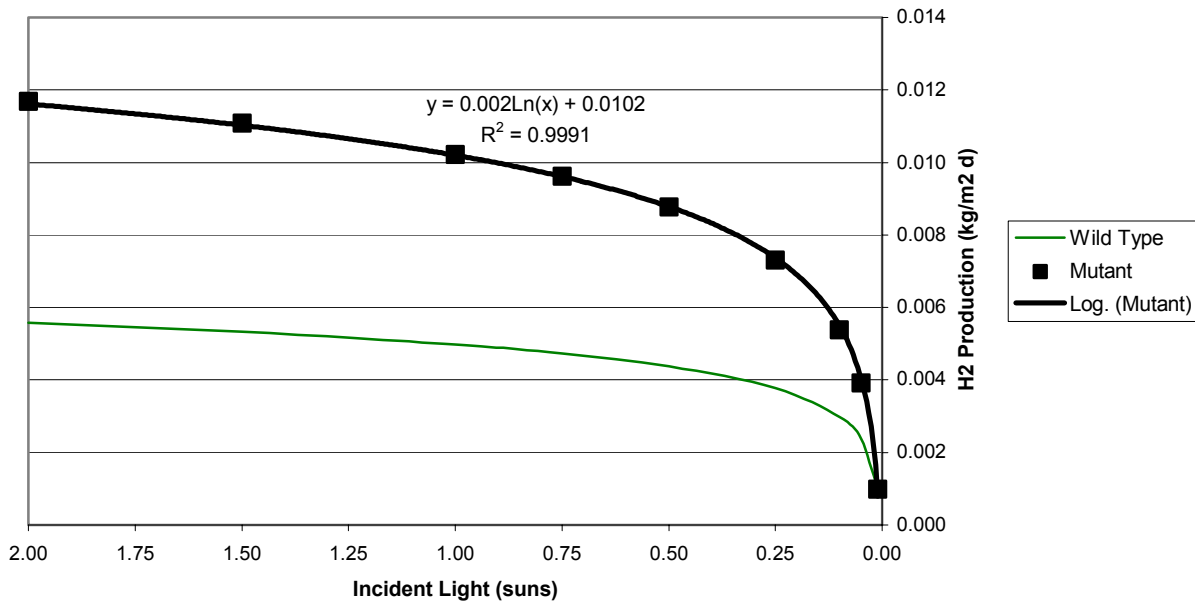
The first step for converting data for use in a production model is to pick a set of design parameters for an algal hydrogen production system. Over the course of this study, a standard concentration of 0.2 g/L has been used. This will be the concentration used for the process design. Next, if we examine Figure 15, we can see that at 0.2 g/L, the critical depth for the mutant strain of algae producing 10 times the wild-type light transmission is about 4 cm with the light intensity dropping almost to zero at 8 cm. We will pick a pond depth of 10 cm for the process design using the mutant algae strain. This assures nearly maximum possible production of hydrogen per m². For higher cell densities, the critical pond depth would be lower, so a 10 cm pond maximizes production for 0.2 g/L or any higher cell concentration.

Given these conditions: a 0.2 g/L culture with a 10 cm pond depth and a mutant that transmits 10 times more light than normal, we can calculate the hydrogen production rate of our system for a range of light incident intensities. Figure 20 shows what the curve looks like for both a wild-type and the truncated antennae mutant. Note that the units in this graph are kg H₂/m²/d. The production rate curve is logarithmic and for the given design parameters has the following relationship between hydrogen production and light intensity:

$$\text{Production (kg H}_2\text{/m}^2\text{/d)} = 0.0102 + 0.002 \ln(I_0)$$

where I₀ is the incident light intensity in suns.

Figure 20 – Algal Hydrogen Production Versus Incident Light Intensity



SOLAR INSOLATION DATA

Once we have a relationship between light intensity and hydrogen production, we can use hourly insolation data for a specific location to see how a solar production system might perform, taking into account weather patterns and diurnal cycles. NREL previously conducted a study on the solar-thermal decomposition of methane to produce hydrogen and carbon black (Spath & Amos, 2002). In that study, solar insolation data from Phoenix, Arizona, was used. This study uses the same solar data.

Insolation data is reported as an hourly average in W/m². For every hour over an entire year, the average light intensity was entered into the above equation and then multiplied by the chosen a pond area to obtain the hourly hydrogen production rate. By adding up the hourly production

rates for the entire year, it was possible to calculate exactly how much hydrogen could be produced for a given pond area.

For the purposes of this analysis, it was assumed that the cell mass was constant. No cells were removed from the system and all new growth obtained their nutrients from cryptic growth off dead cell mass. In a real system, the build-up of inert material would require that some cells eventually be purged from the system.

STORAGE ISSUES

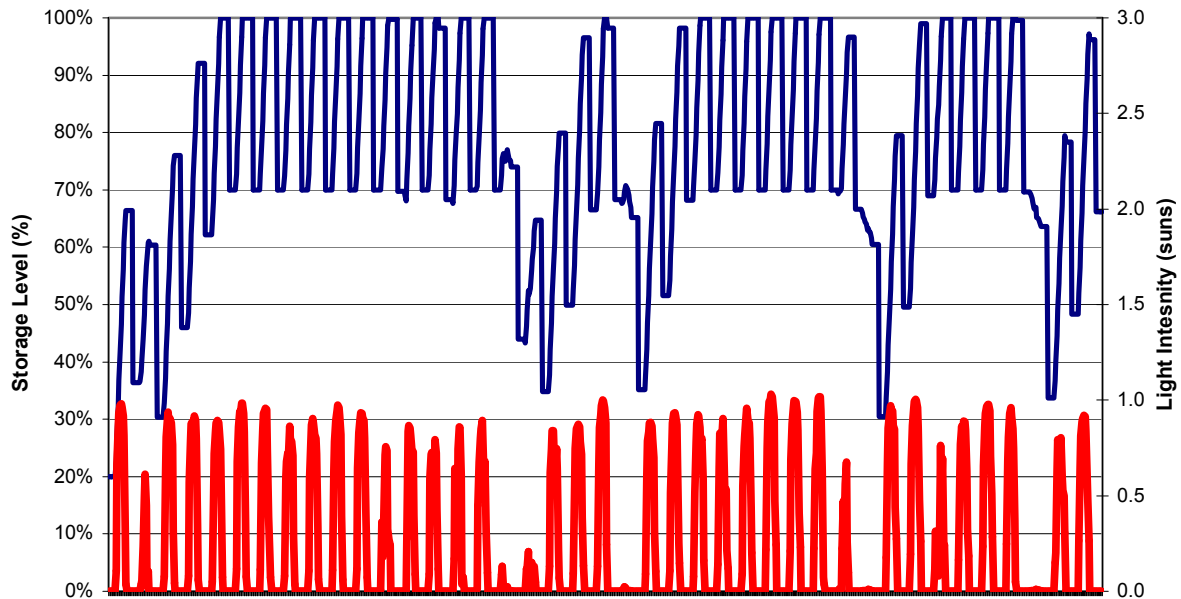
One concern with all intermittent solar systems is how the system will handle the loss of light at night and during cloudy periods. Unless the system is sited near an existing hydrogen pipeline, some type of backup system or storage is required to meet a constant demand for hydrogen at an isolated location, such as a refueling station. In the previous solar-thermal study, we looked at three system designs: a stand-alone system with sufficient storage to make it through the longest cloudy period; a system with an electric heater for the thermal cracking of hydrogen; and a system without storage that supplies a hydrogen pipeline.

Storage requirements of intermittent solar systems must be determined using real solar data. While the need for storage to get one through the night is obvious, the maximum amount of storage to maintain reliable daily delivery of hydrogen is generally determined by one or two periods of especially cloudy weather during the year. It was also determined from the previous study that these periods of poor sunlight are not seasonal and occurred several times throughout the year. As a result, the storage requirements were quite high due to the need to supply storage several days in a row without any hydrogen production.

Another problem associated with storage is that when the hydrogen storage tanks get full, all additional hydrogen production that day will be lost—there is simply no where to put the hydrogen. Initially it might seem that this would be a rare occurrence, but because you are trying to keep the hydrogen tanks full in case of poor weather, they are generally kept at 70% of maximum capacity or more. Increasing the onsite storage will give one slightly more additional storage, but generally a large increase in storage capacity is required to significantly affect the net amount of hydrogen produced. Figure 21 shows how the hydrogen storage capacity varies from day to day during January and February. The hydrogen is drawn down each morning then hydrogen goes into storage during the day. Almost every day the maximum capacity of the storage system is reached, requiring shutdown of the system. During several points over the two-month time, the storage levels get down to 30%, so it would not be practical to reduce the onsite storage or else one would run out of hydrogen on those days. Light intensity is shown at the bottom of Figure 21. In the economics section, the amount of lost production due to storage limitations will be highlighted.

If a system is connected to a pipeline, there are two benefits that improve the economics. First, there is no need for high-pressure storage—the hydrogen is dumped directly into the pipeline as it's produced and the pipeline itself provides some storage due to changes in operating pressure. Second, production is no longer limited by storage capacity so the yearly hydrogen production is higher.

Figure 21 – Affect of Weather on Storage Levels



REACTOR COST

In the previous study on algal hydrogen production, the reactor cost significantly affected the price of the hydrogen produced. Estimates of reactor materials costs range from a few cents per m^2 to \$100 or more. The main reason for this is that different material requirements were assumed. While there are some commercial reactors that grow algae under artificial light to produce food additives or supplements, these represent high-value materials so the reactor can be more expensive. For food additives, certain FDA requirements must be met, which further increases the cost of the reactor. Algal hydrogen production does not need to meet FDA requirements and it is also possible that if selective growth pressures can be determined for the specific cultures of interest, no sterilization will be required.

The previous study reviewed the retail price of different transparent and translucent materials that could be used to construct a bio-reactor for algal hydrogen production. These prices are shown in Table 1. It is reasonable to assume that if glass or Plexiglas is used, the reactor cost could approach \$100/ m^2 . However, if one assumes that something like polyethylene film with a hydrogen-impermeable coating is used, the cost could be \$1.00/ m^2 or less. For this study, \$100/ m^2 , \$10/ m^2 and \$1/ m^2 were used. It was assumed that 10% land would be required in addition to the area used for the ponds themselves.

Table 1 – Retail Cost of Transparent & Translucent Materials

| Material | Cost (\$/m²) |
|--------------------|--------------------------------|
| Glass | \$51.61 |
| Plexiglas | \$15.47 |
| Clear PVC | \$5.56 |
| Blue Tarp | \$0.46 |
| 4 mil polyethylene | \$0.19 |
| 1 mil polyethylene | \$0.05 |

HYDROGEN PURIFICATION

One question asked with regards to algal hydrogen production was how much purification of the hydrogen would cost. It is assumed that the hydrogen produced would be relatively pure, except for some water vapor and possibly some carbon dioxide. It certainly wouldn't contain any contaminants of major concern, such as carbon monoxide or high levels of sulfur. However, for the sake of completeness, a PSA capital cost with the associated compression was included in the base case. Cases were also run without a PSA unit.

HYDROGEN COMPRESSION

For the cases that include hydrogen storage, compressor capital charges and electricity consumption are included. For the pipeline case, compression to 2 MPa was included. Note that all compressors must be sized for peak hydrogen flow, which can be significantly higher than the average flow. For comparison to other hydrogen production systems, the capacity factor and storage-to-production ratio of the stand-alone 300 kg/d system were 25.5% and 3.33:1, respectively. The capacity factor for the pipeline system was 39.5%--about one third of the potential hydrogen production was lost due to the storage limitation. Because of the high cost of storage and compression, one case was run without including any compression or storage.

HYDROGEN PRODUCTION RATES

Two stand-alone daily hydrogen production rates were chosen: 300 kg/d and 600 kg/d. These represent the flow rates at which hydrogen can be *reliably* supplied. In other words, the peak production rates are slightly higher and include some storage. The pipeline only case uses the same pond area as the 300 kg/d system, but does not have a storage limitation, so it supplies 446 kg/d, on average. A 300 kg/d production rate represents the amount of hydrogen required for one refueling station pump supplying 100 cars per day.

CAPITAL COSTS

Table 2 shows the capital cost breakdown for the 300 kg/d stand-alone system with 110,000 m² of pond area, 0.2 g/L cell concentration, a truncated antennae mutant, 10 cm pond depth, and a \$10/m² bio-reactor cost for a site in Phoenix, Arizona.

Table 2 – Algal Hydrogen Production Capital Costs

| | |
|---------------------------------|--------------------|
| Algae Ponds | \$1,100,000 |
| PSA Compressor | \$359,000 |
| PSA Unit | \$121,000 |
| Storage Compressor | \$578,000 |
| High-Pressure Storage | \$913,000 |
| Total Equipment Cost | \$3,071,000 |
| Engineering & Construction | \$1,423,000 |
| Contractor Fees & Contingency | \$674,000 |
| Total Capital Investment | \$5,168,000 |

OPERATING COSTS

The yearly operating costs for the same system are listed in Table 3. These costs include electricity for mixing, periodic washing of the pond covers, maintenance, electricity for the compressors, PSA operating costs, and labor for one person to spend 25% of their time onsite. The algal hydrogen production system shouldn't require full-time onsite supervision.

Table 3 – Algal Hydrogen Production Operating Costs

| | Annual Cost | \$/kg |
|--------------------------------|--------------------|----------------|
| Mixing/Pumping Electricity | \$12,000 | \$0.11 |
| PSA Compressor Electricity | \$6,000 | \$0.06 |
| Storage Compressor Electricity | \$18,000 | \$0.16 |
| Labor | \$24,000 | \$0.22 |
| PSA Operating Cost | \$4,000 | \$0.03 |
| Maintenance & Washing | \$55,000 | \$0.50 |
| Capital-Related Charges | \$1,360,000 | \$12.44 |
| Hydrogen Sales | \$1,480,000 | \$13.53 |

HYDROGEN SELLING PRICE

A discounted cash flow analysis assuming a 15% return on investment was performed to determine the minimum hydrogen selling price for several different system designs. The stated selling prices all assume ongoing improvements are successful. The selling price associated with the current state of development in algal hydrogen production would be significantly higher. The minimum hydrogen selling prices for the different systems are shown in Table 4, along with the associated capital costs and annual operating costs.

Table 4 – Capital Costs, Operating Costs and Hydrogen Selling Prices for Different Algal Hydrogen System Configurations

| System Design | Capital Cost | Annual Operating Cost | Minimum Hydrogen Selling Price |
|---|----------------|-----------------------|--------------------------------|
| 300 kg/d, \$10/m ² , PSA, high-pressure storage | \$5.2 million | \$119,000 | \$13.53 |
| 600 kg/d, \$10/m ² , PSA, high-pressure storage | \$9.1 million | \$214,000 | \$11.96 |
| 300 kg/d, \$10/m ² , PSA, pipeline delivery | \$3.2 million | \$131,000 | \$5.92 |
| 300 kg/d, \$10/m ² , high-pressure storage | \$5.0 million | \$115,000 | \$12.93 |
| 300 kg/d, \$10/m ² , pipeline delivery | \$2.9 million | \$127,000 | \$5.52 |
| 300 kg/d, \$10/m ² , ponds only, no compression | \$1.9 million | \$101,000 | \$3.68 |
| 300 kg/d, \$1/m ² , ponds only, no compression | \$0.2 million | \$51,000 | \$0.57 |
| 300 kg/d, \$1/m ² , PSA, high-pressure storage | \$3.5 million | \$70,000 | \$8.97 |
| 300 kd/d, \$1/m ² , PSA, pipeline delivery | \$1.5 million | \$81,000 | \$2.83 |
| 300 kd/d, \$100/m ² , PSA, high-pressure storage | \$22.2 million | \$614,000 | \$439.00 |
| High-pressure storage only | \$3.0 million | \$24,000 | \$7.75 |
| Pipeline delivery, no storage limit | \$1.1 million | \$47,000 | \$2.04 |

DISCUSSION

The base case design for the algal system produced hydrogen for a minimum hydrogen selling price of \$13.53/kg. This price included a 15% return on investment, included the required hydrogen storage for periods of low sunlight and assumed a reactor cost of \$10/m². By doubling the pond area and production rate, the hydrogen selling price drops to \$11.96/kg due to economies of scale and reduced labor charges per kg of hydrogen.

One question was whether or not the pressure swing adsorption would be required. In the analysis, the capital and operating costs associated with PSA purification were included, but the same hydrogen production was assumed in all cases. The reason for this is that low contaminant levels are expected and some excess hydrogen from storage could be used for purging the PSA beds. Removing the PSA capital and operating costs dropped the hydrogen selling price to \$12.93/kg, so the PSA itself doesn't increase the costs greatly, but if the hydrogen recovery is low, the hydrogen selling price will increase.

The major contributor to the hydrogen selling price is the compression and storage required to make it through the periods of poor sunlight. The compression and storage alone contribute \$7.75/kg to the hydrogen selling price. The solar-thermal decomposition study performed by NREL came to the same conclusion. To present a fair comparison of the cost of production without storage, one option was to site the production facility on an existing hydrogen pipeline. This not only eliminated the high-pressure storage, but allowed a higher average daily production rate because there was not storage limitation. The minimum selling price without storage, but with compression to pipeline pressure was \$5.52/kg with the \$10/m² reactor cost.

One other question to be answered by this economic analysis is what the actual hydrogen production looks like without the complications of compression and storage. If one considers

only the cost of the production ponds, the hydrogen selling price would be \$3.68/kg for a reactor costing \$10/m². For a reactor costing \$1/m², the hydrogen selling price drops at \$0.57/kg, showing the importance of the reactor cost. If the storage cost is included with the \$1/m² reactor cost, the hydrogen selling price becomes \$8.97/kg. For the higher reactor cost of \$100/m², the hydrogen selling price goes up to \$439.00/kg—again indicating the importance of reactor cost.

CONCLUSIONS

Although there are several cases where the minimum hydrogen selling price approaches or reaches the DOE targets, this analysis assumes a very high algal hydrogen production rate—much higher than what has been demonstrated in the lab. In addition, some simple assumptions were made regarding the absorption of light by the algae. While future improvement in the hydrogen production rate are hard to predict, the optical properties of these cultures can be verified through data collected in the lab or through literature searches.

There are two other major factors that will affect the eventual cost of the algal hydrogen production. The first is the cost of the photo-bioreactor. Because of the sheer size of the hydrogen production ponds, the bioreactor cost must be minimized. However, until more information is provided on what materials are appropriate for use in the photo-bioreactors, it is hard to estimate how low the reactor cost might be. For this reason a wide range of reactor prices was used in this analysis.

The second major cost factor is the storage required for a stand-alone system. For any intermittent renewable, compression and storage will be major factors, whether an algal production system, a solar-thermal production system, or a wind system. Since conventional high-pressure compression and storage are mature technologies, any cost reductions in this area would come through improved or new technology.

The current areas of research include truncated antennae mutants, oxygen-tolerant hydrogenases and increased hydrogen production rates. All of these factors are important to the economics of algal hydrogen production. The truncated antennae size allows deeper light penetration into the growth ponds and higher hydrogen production rates. An oxygen-tolerant hydrogenase is important if oxygen production exceeds the oxygen consumption of the algae at higher hydrogen production rates. Finally, demonstrating higher and higher hydrogen production rates is a vitally important factor in the economics. This analysis assumes a production rate that matches the typical rate of electron transfer for bacteria or other micro-organisms. It might be possible through genetic engineering to even increase this maximum electron transfer rate and produce even more hydrogen.

The previous analysis of algal hydrogen production looked at a batch system and used incident light intensities and an average number of hours of daylight to estimate the hydrogen production. In this analysis, saturation effects are included and actual solar insolation data is used to estimate the hydrogen production. These are improvements over the previous analysis.

The major recommendation would be to collect more information on photo-bioreactor costs. Critics of algal hydrogen production often cite the high reactor cost as the major roadblock.

However, if some of the materials lower down on the list of materials in Table 1 are acceptable, the installed reactor cost may be close to $\$1/\text{m}^2$ and therefore closer to the DOE goal.

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