DOE/GO/10170--T9

Process Study:
The Dual-Bed Hydrogen Production Process
as being developed by
The Florida Solar Energy Center

Prepared by:

J. Philip DiPietro
Edward G. Skolnik

Energetics, Incorporated

Prepared for:

Sentech, Incorporated
Under
Subcontract Number 96DE-GFO01-EN1003
Prime Contract Number DE-FC36-96GO10170

June, 1997

Analysis of the Dual-bed Hydrogen Production Process

Clovis Linkous of the Florida Solar Energy Center is developing a "dual-bed" hydrogen production process[i]. The idea is to break the water splitting process into two separate chemical reactions, each with roughly ½ the electrochemical potential of direct water dissociation. This enables the dual-bed process to utilize a much broader range of sunlight photons than conventional photoelectrochemical (PEC) systems. However, it requires twice as many photons per unit of hydrogen produced. The purpose of this analysis is to evaluate and quantify the trade-offs presented by the dual bed process and determine if it holds economic potential as a hydrogen production technology.

Process Description

Figure 1 is a schematic of the dual bed process. It works as follows: An aqueous solution containing a redox mediator (M) is charged to a reactor. (A redox mediator is a species that is capable of reversible charge transfer.) The reactor is a shallow box with five opaque sides and a transparent top. The bottom of the reactor is coated with a photoactive catalyst. Sunlight photons travel through the transparent roof and the aqueous solution and strike the photoactive catalyst, creating charged active sites and driving the following general reaction:

$$4H_2O + 4M \text{ --> } 2H_2 + OH^- + 4M^+ \qquad \{1\}$$

Hydrogen gas bubbles up through the solution and is captured. Liquid effluent from the first reactor, containing positively charged redox mediator, is pumped to the second reactor. The second reactor is similar to the first, but its bottom is coated with a different photoactive material that catalyzes the following general reaction:

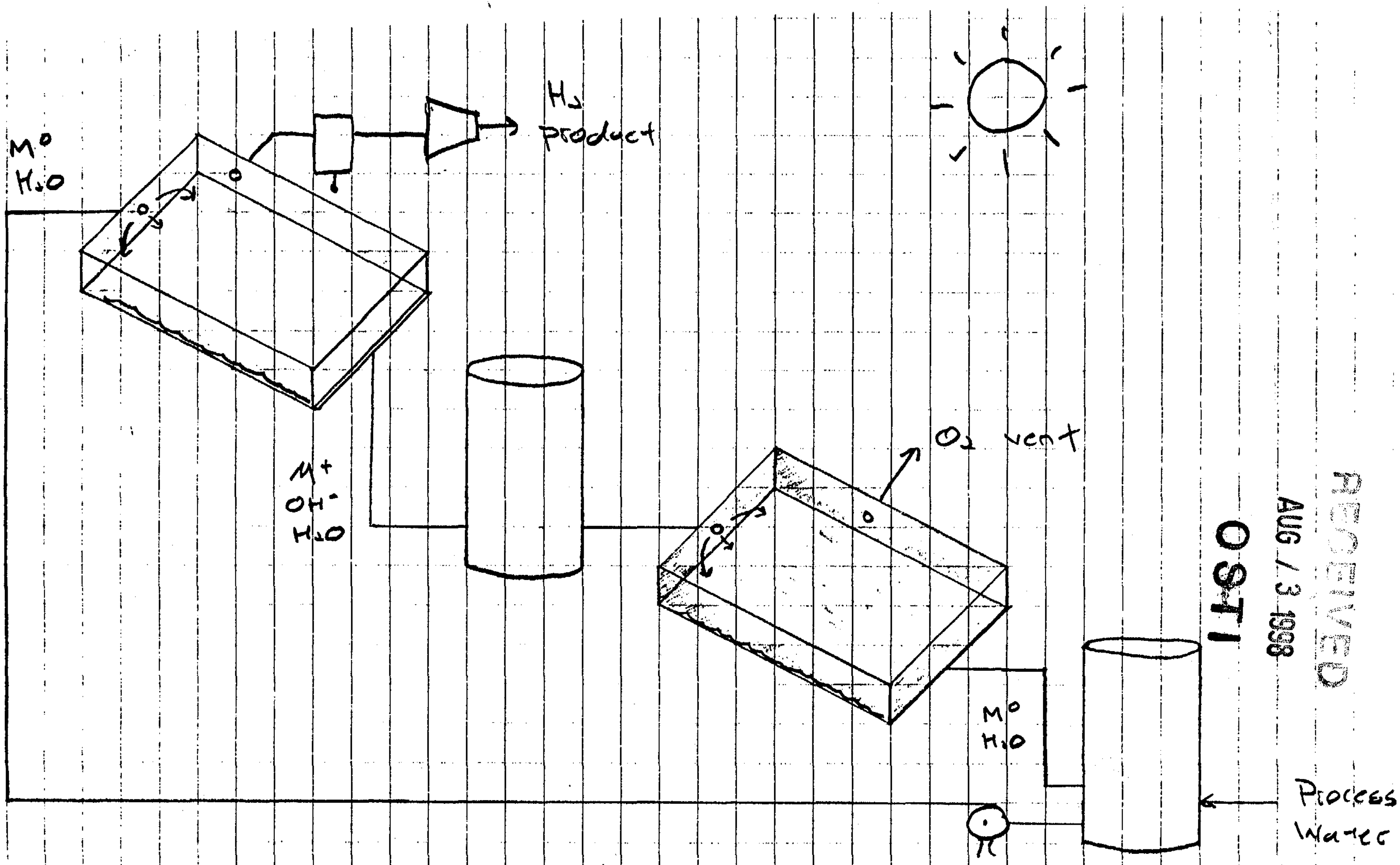
$$4H_20 + 4M^+ \text{ --> } O_2 + 2H_20 + 4M + 4H^+ \qquad \{2\}$$

Oxygen bubbles up through the solution and is vented. The second reactor needs a glass top, not to capture oxygen, but to prevent dust, leaves, and debris from collecting in it. The redox mediator has been returned to its initial state, and the aqueous solution is recirculated to the first reactor. Buffer tanks between the reactors stabilize the concentration of reactants.

Solar Efficiency

The capital cost of a solar-based water dissociation system is roughly proportional to the solar collection surface area. Thus, the economics rely on how much hydrogen can be produced per unit of solar insolation.

Figure 1. Dual Bed Hydrogen Production Process



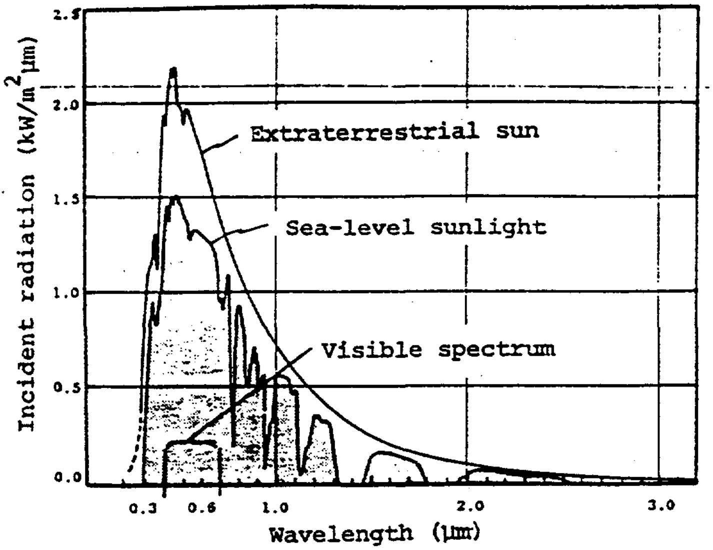


Figure 2. The intensity of solar radiation of various wavelengths reaching the top of the earth's atmosphere (extraterrestrial sun) and reaching the earth's surface (sea-level sunlight). Dips in the ground-level radiation are due to energy absorption by oxygen, ozone, water vapor, and carbon dioxide in the air.

Taken from Engineer's Guide to Solar Energy by Y. Howell and J. A. Bereny

Figure 2 shows the spectrum of solar energy at sea level. The y-axis represents the incident energy per area in kW, and the x-axis is photon wavelength in microns. The kW per area for a given photon wavelength equals the number of photons with that wavelength multiplied by their energy level. The energy of a photon is given by:

$$E = h * c / \lambda \qquad \{3\}$$

where:

E = photon energy (Joules)
c = speed of light (3×10^{17} nm/s)
h = Plank's constant (6.626×10^{-34} Js)
λ = cell maximum photon wavelength (nm)

Equation {3} reveals that a photon of wavelength 600 nm has twice as much energy as a photon with wavelength 1200 nm. Figure 2 shows that photons of wavelength 600 nm supply 4 times as much energy per unit area and time as 1200 nm wavelength photons. However, because they are higher energy, there are only twice as many 600 nm photons as there are 1200 nm.

Consider a plate-type PEC system utilizing a single-layer photovoltaic (PV) material. Each PV material has a characteristic potential; all photons absorbed by the material produce electric current of the characteristic potential. Photons that have too long a wavelength to produce the PV material voltage do not result in the generation of electricity. Photons that have a higher energy than is necessary, produce the characteristic voltage only; excess energy is dissipated.

The theoretical potential of the water dissociation reaction is 1.229 volts, but a potential that is greater than theoretical is needed. This overpotential must overcome internal losses within the PV material, overcome the voltage drop across the boundary between the PV material and the electrolyte solution, and force sufficient diffusion kinetics. 1.6 electron volts are generally regarded as the minimum potential required to drive a plate-type PEC system.

The electric potential produced by a photon is related to the photon wavelength as follows.

$$V = c * h / \{(F/A)*\lambda\} \qquad \{4\}$$

where:

V = electric potential (volts)
λ = photon wavelength (nm)
c = speed of light (3×10^{17} nm/s)
h = Plank's constant (6.626×10^{-34} Js)
F = Faraday's constant (96,486 joules/volt/mole of electrons)
A = Avogadro's number (6.022×10^{23} units per mole)

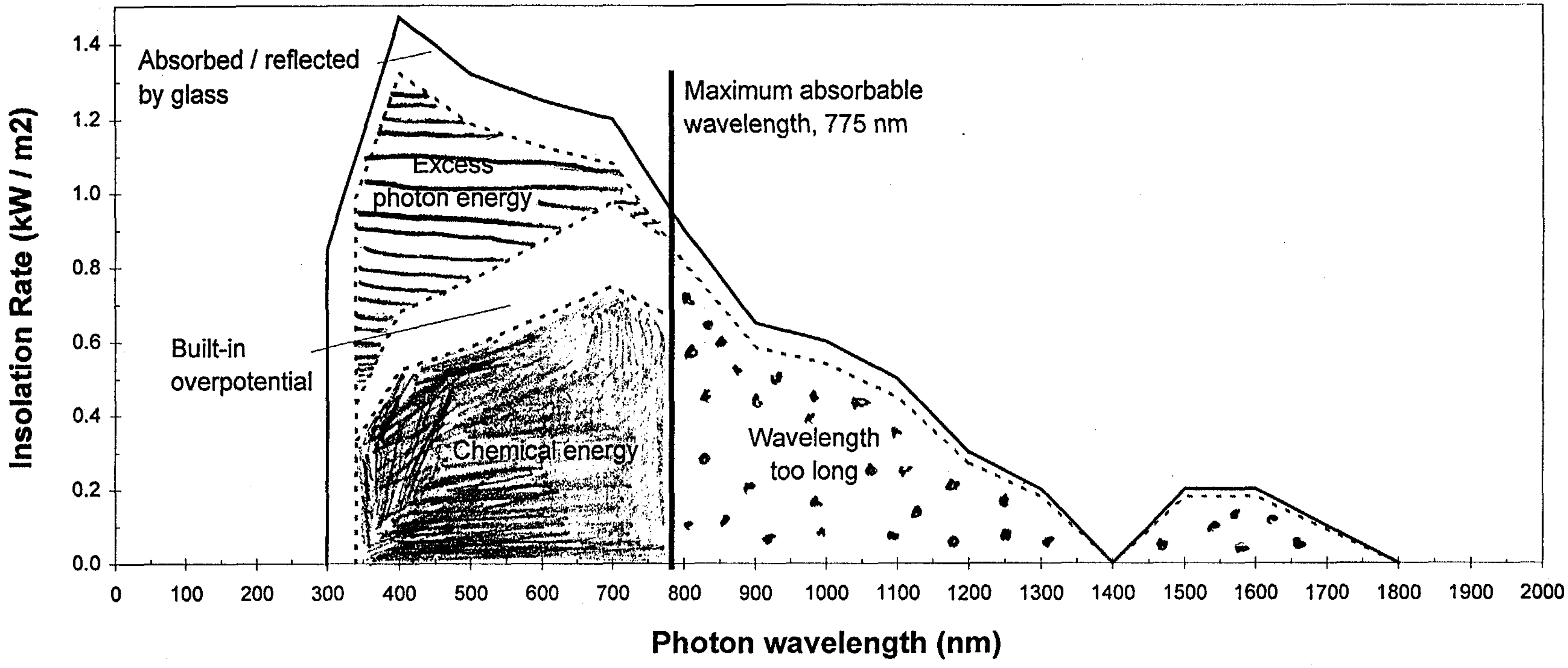
Solving for λ yields:

$$\lambda = 1{,}240 / V \qquad \{5\}$$

By equation {5}, for a PV material with a characteristic potential of 1.6 volts, the maximum wavelength that can be absorbed is 775 nm.

Figure 3 shows the fate of the spectrum of sunlight photons falling upon a plate-type PEC system with a single layer of PV materials having a band gap of 1.6 eV. Specifically it shows how much of the available solar energy is converted to chemical energy (hydrogen). The top line is the insolation to the unit and is based on the sea-level data shown in Figure 2. PEC systems require a glass cover to capture the evolved hydrogen, and some of the incident photons are reflected or absorbed by the glass. For this analysis, we assumed glass does not transmit photons below 340 nm, and has a transmittance of 90% across the rest of the spectrum. The vertical line cutting through the spectrum indicates the maximum absorbable wavelength (775 nm). Photons to the right of that line cannot be absorbed. Photons with a higher energy than is needed to produce 1.6 V (i.e., a wavelength below 775 nm) produce electric current, but the excess energy is not converted to electricity. As an example, for a photon with wavelength of 700 nm, 90% of the photon energy becomes electricity (700 / 775) and the excess 10% is dissipated. Figure 3 shows the losses due to excess photon energy increase with decreasing wavelength. Finally, there are energy losses due to built-in over potential. Twenty-three percent of the generated electric current is lost to over potential (1-1.23/1.6). The solar efficiency (i.e., kWh of hydrogen produced, lower heating value (LHV), per kWh of insolation) is shown to be 30%.

Figure 3. Disposition of photons incident upon a 1.6 V plate-type PEC system



Absorbed or reflected by glass	12%
Too high a wavelength	33%
Excess energy	17%
Built-in overpotential	9%
Chemical energy	30%
	100%

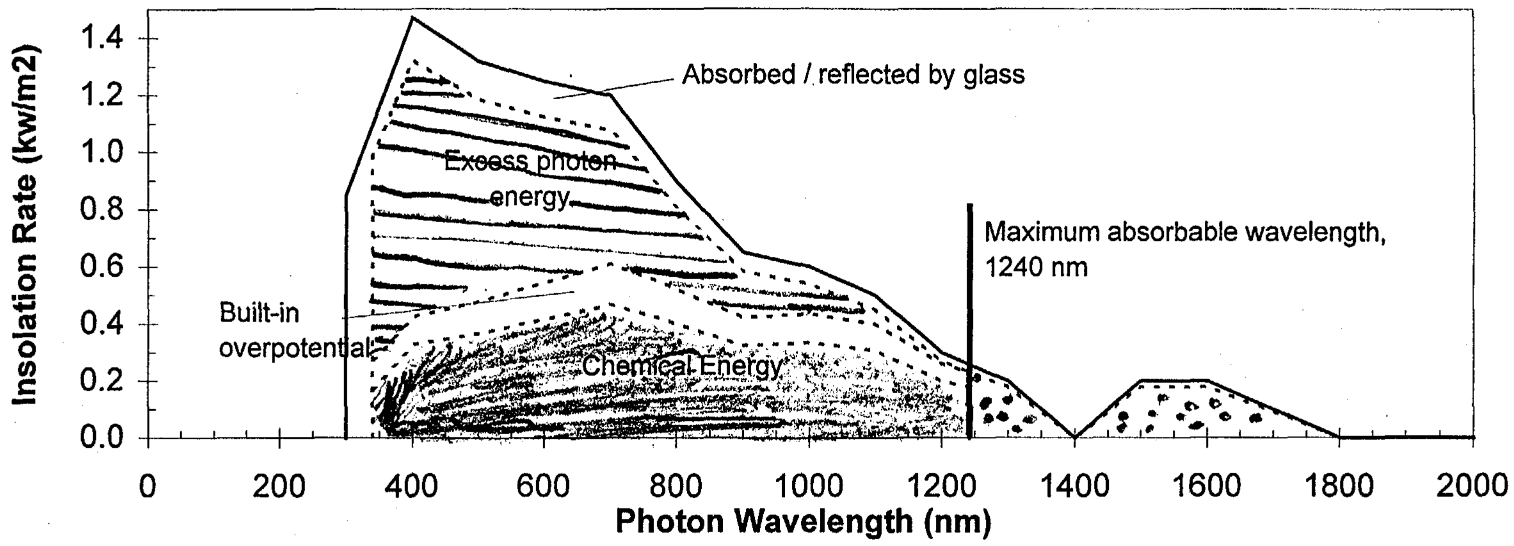
In the dual bed process, water dissociation is broken into two separate chemical reactions. Assume that each reaction contributes ½ of the overall water dissociation potential. This gives a theoretical electrochemical requirement of 0.615 Volts for each reaction (1.23/2). Assuming further that each reaction requires about the same built-in overpotential as do plate-type PEC systems, that is, 0.37 Volts (1.6-1.23), this gives a required photoactive material potential of about 1.0 Volts. The corresponding maximum photon wavelength is 1,240 nm.

Figure 4 shows the fate of the spectrum of incident photons on the dual bed process described above. Because the photoactive material has a lower characteristic voltage, the dual bed system is able utilize a much broader range of photons. However, because of the low reaction potential the losses due to excess energy are greater. Also, the dual bed process requires two reactions for each hydrogen molecule produced (compared to one for the plate-type systems), and we have assumed that each reaction requires the same absolute built-in overpotential (0.37 V). Thus, the losses due to built-in overpotential are twice as high for the dual bed system. These effects roughly cancel each other out, and the 1.0 volts dual bed system has a theoretical efficiency of 34%, slightly higher than the 30% of the 1.6 volts plate type PEC system. Note that because the reactions are assumed to be of equal potential, one figure can represent the solar efficiency of the two-reactor process.

It is likely that the two reactions will not share the water dissociation energy equally. In a side-by-side reactor design, the farther the reduction/oxidation reaction potentials are "out of balance," the larger the overall reactor surface area because the low-potential reactor will have a low solar efficiency due to excess energy losses. The dual bed reactors could be stacked on top of each other instead of being laid side-by-side. Figure 5 is a schematic of a tandem reactor design. The reactor is a shallow box with five opaque sides and a glass top, and contains a second glass plate roughly halfway down the reactor walls. The top of the interior glass plate is coated with hydrogen evolving catalyst and the bottom is coated with oxygen-evolving catalyst. Solution flows counter-currently above and below the glass plate. The top-layer reaction is the higher potential reaction (it is shown as the hydrogen-evolving reaction in Figure 5 but it could be either). Higher energy photons are absorbed by the top photoactive coating, and the lower energy photons pass through the top layer and are absorbed in the bottom layer. Figure 6 shows the fate of the spectrum of photons falling on a tandem-design dual-bed reactor in which the top layer reaction has a potential of 1.0 volts and the bottom layer reaction has a potential of 0.223 volts. Again, it is assumed that both reactions require a built-in overpotential of 0.37 volts.

Figure 6 shows the fate of the spectrum of photons that fall on a tandem design dual-bed reactor. The tandem reactor utilizes a higher percentage of the energy available in the high-energy photons than does the side-by-side design. The top layer contributes roughly 80% of the total potential energy to the overall water dissociation reaction, which is what one would expect based on the ratio of the reaction potentials (i.e., 1/1.23 - 80%). Interestingly, the tandem design increases the solar efficiency only marginally. The benefit of a tandem design is that it is better-suited reduction/oxidation reactions with disproportionate potentials and it expands the number of redox mediator photocatalyst material pairs that can be investigated.

Figure 4. Disposition of photons incident upon a 1.0 Volt dual bed system



Absorbed or reflected by glass	12%
Too high a wavelength	8%
Excess energy	36%
Built-in overpotential	10%
Chemical energy	34%
	100%

Figure 5. Dual Bed Hydrogen Production Process, Tandem Reactor Design

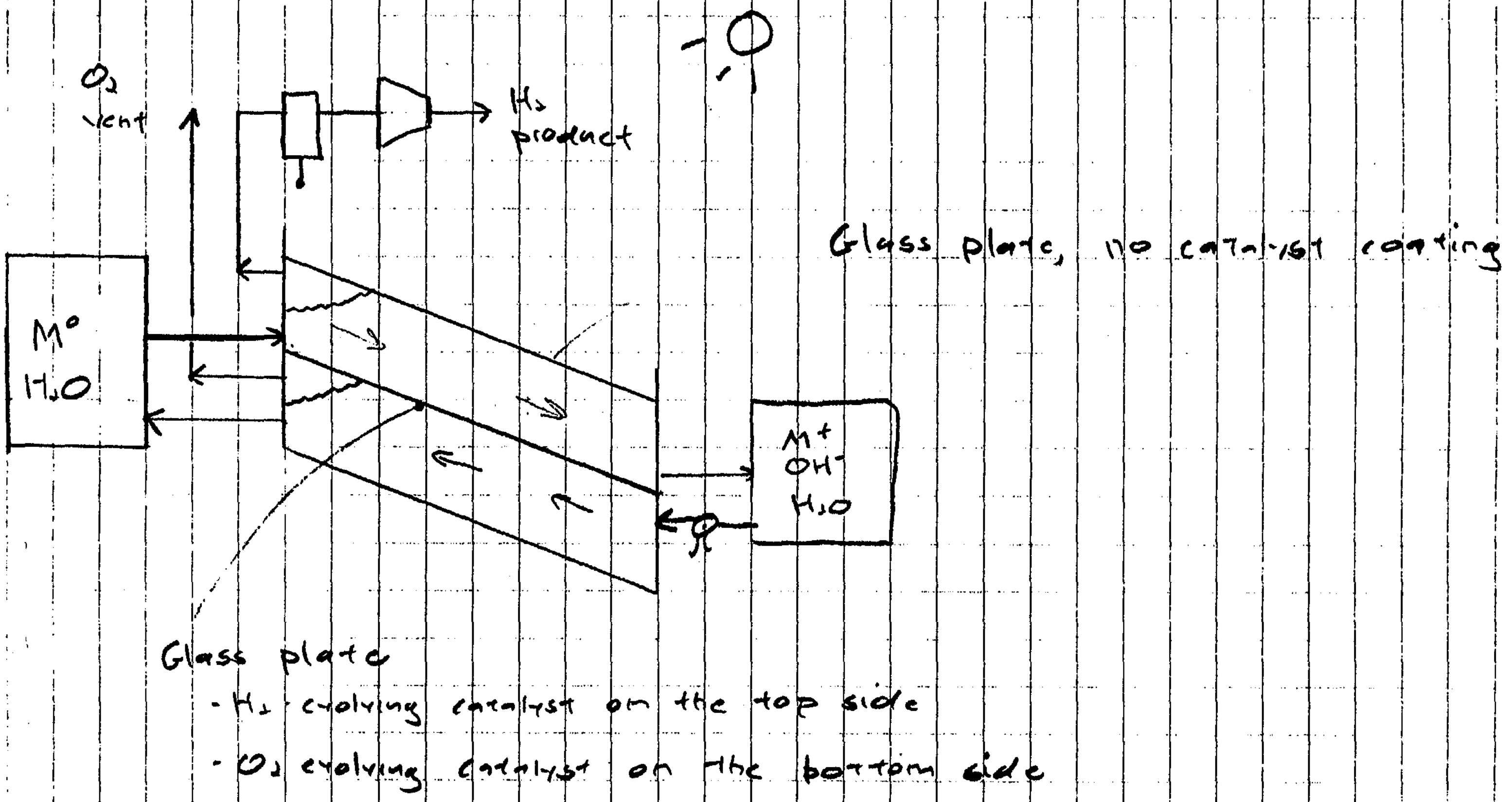
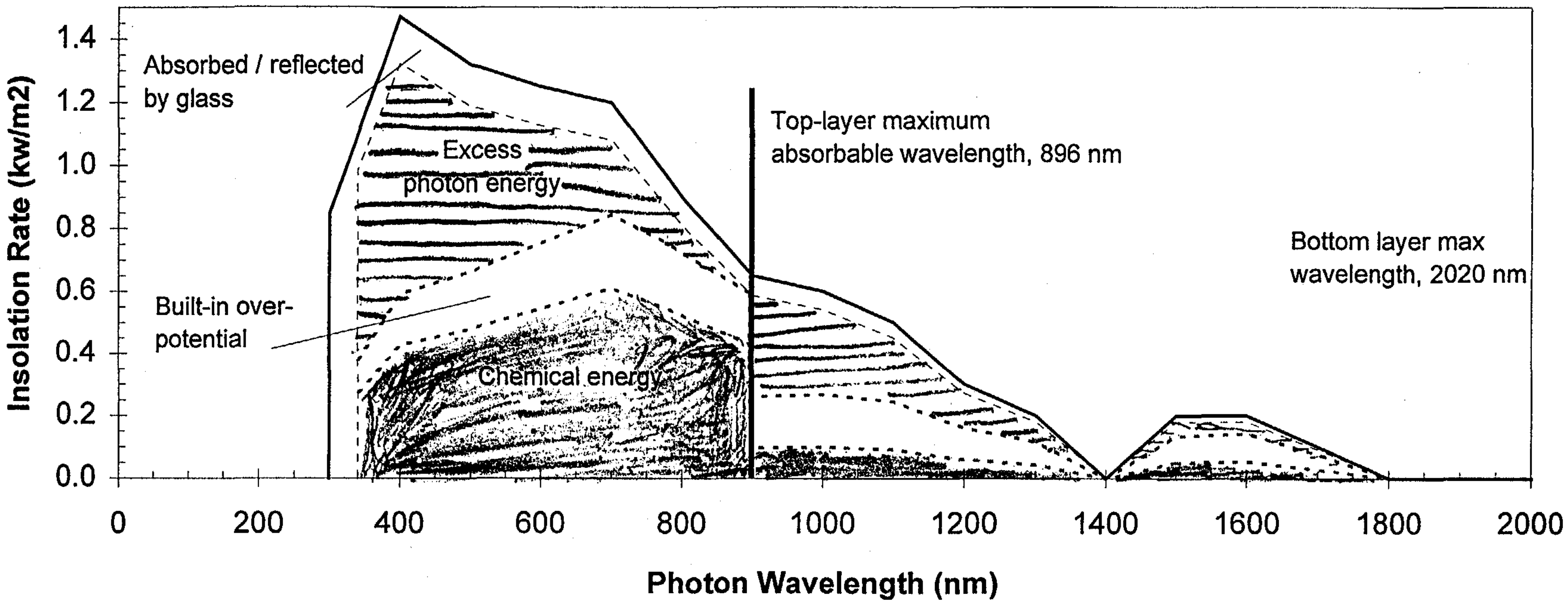


Figure 6. Disposition of photons incident upon a tandem reactor dual bed system



Absorbed or reflected by glass	12%
Too high a wavelength	2%
Excess energy	30%
Built-in overpotential	20%
Chemical energy	36%
	100%

Several loss mechanisms lower the achievable solar efficiencies below the theoretical values shown in Figures 3, 4 and 6. First, a portion of the photons of absorbable wavelength that fall on the PV material simply do not result in a charge (quantum efficiency). In addition, charges may recombine on the surface of the photoactive material before they are able to initiate the chemical reaction (charge recombination). Finally, the reaction products may recombine (back reaction). The back reaction is of particular concern for the duel bed process, because unlike plate-type PEC systems, the different reaction products are not spatially separated. Equation {6} presents the achievable solar efficiency as function of the theoretical efficiency multiplied by three correction factors for the loss mechanisms described above. Addressing these loss mechanisms is the primary thrust of the research, and although each mechanism cannot be eliminated, it is feasible that they can be minimized.

$$\eta_A = \eta_{Th} * \Phi * \eta_{CR} * \eta_{BR} \qquad \{6\}$$

where:

η_A Achievable Solar Efficiency
η_{Th} Theoretical Solar Efficiency
Φ Quantum Efficiency
η_{CR} Loss due to charge recombination
η_{BP} Loss due to back reaction

The solar efficiency of plate-type PEC systems can be significantly improved by using multi-layer PV materials. However, these materials are much more expensive than the simple coatings being considered for the dual bed process.

Cost Analysis

Table 1 presents the capital costs for a 15 MMSCFD hydrogen production plant. The cost of the dual-bed system is taken largely from a previous analysis of a plate-type PEC system[ii]. (1990 costs have been adjusted to 1996 levels based on the M&S index.) The PEC system that was analyzed produces dry hydrogen at 100 psig. All the component capital costs, indirect costs, and O&M costs are assumed to be the same except the dual bed system does not contain a photocatalyst plate. For the dual-bed process, the cost of the photoactive coating and the redox mediator inventory is assumed insignificant compared to the cost of the reactor structure and piping.

Importantly, using the cost estimates from the PEC system could understate the economic potential of the dual bed process because the dual bed process is more amenable to scale-up than is a plate-type PEC system. In addition, the PEC system analysis used fuel cells to power pumps and other equipment. Based on the daily capacity factor of 30%, combustion turbines (or grid electricity) would likely be more economic. Finally, because of the lower electrochemical potential of the dual bed process reactions, it may be better to use less expensive transparent covers that block out a larger portion of the high energy spectrum.

Table 1. Capital and Operating Cost Analysis of the Dual Bed Hydrogen Production System

Total Active Area	14.8	MM ft2	
Reactor Capital Cost			
Glazing	0.7	$/ft2	
Backing	0.7	$/ft2	
Foundation and Installati	2.2	$/ft2	
Ends & Assembly	0.3	$/ft2	
Piping, hydrogen	1.5	$/ft2	
Piping, solution	0.3	$/ft2	
Total reactor module	5.7	$/ft2	
System Capital Cost			
Reactor	83.9	MM$	
BOS	15.5	MM$	
Indirect cost	21.9	MM$	
Contingency	15.0	MM$	
Total capital cost	**136.3**	MM$	
Percent depreciable	78%		
Insolation rate	1	kW/m2	
Solar Efficiency	20.4%		
On-stream factor	95%		
Daily capacity factor	30%		
Daily H2 production	20	MMSCF	
Annual hydrogen prodn	2.4	MM MMBTu	
Hydrogen price	11.68	$/MMBtu	
Operating Revenue	27.9	MM$/yr	
O&M cost	1.7	MM$/yr	
Operating Income	26.2	MM$/yr	

Data taken from the report, Solar Photochemical Production of Hydrogen, TDA Research Inc., 1990

Table 2 presents an IRR analysis of a dual bed system based on the cost data presented in Table 1. We assume the facility requires one year to build. During that time no hydrogen production occurs. The facility then has a useful life of 20 years. We also assume that Quantum efficiency, charge recombination, and the back reaction together reduce the solar efficiency to 50% of theoretical, 17%. In Hydrogen Program systems analyses, the cost of hydrogen is considered in higher heating value (HHV) units. The first-principles analysis above gives solar efficiency in LHV. In order to be consistent with the Program convention we convert solar efficiency to HHV (17% is increased to 20.4%).

Tables 1 and 2 shows that a hydrogen price of 12 $/MMBtu is required to generate an after-tax IRR of 15% under the base case set of assumptions. There is a large range of uncertainty associated with both the capital cost of the reactor modules and the achievable solar efficiency. Figure 7 shows that the cost of hydrogen from a dual bed system varies between 7 and 30 $/MMBtu over a range of costs and efficiencies that could be reasonably expected.

Conclusions

Based on solar energy theory, the dual bed process could achieve solar efficiencies that are "in the ballpark" with plate-type PEC systems. More detailed assessment of practical loss mechanisms is needed to judge the processes potential.

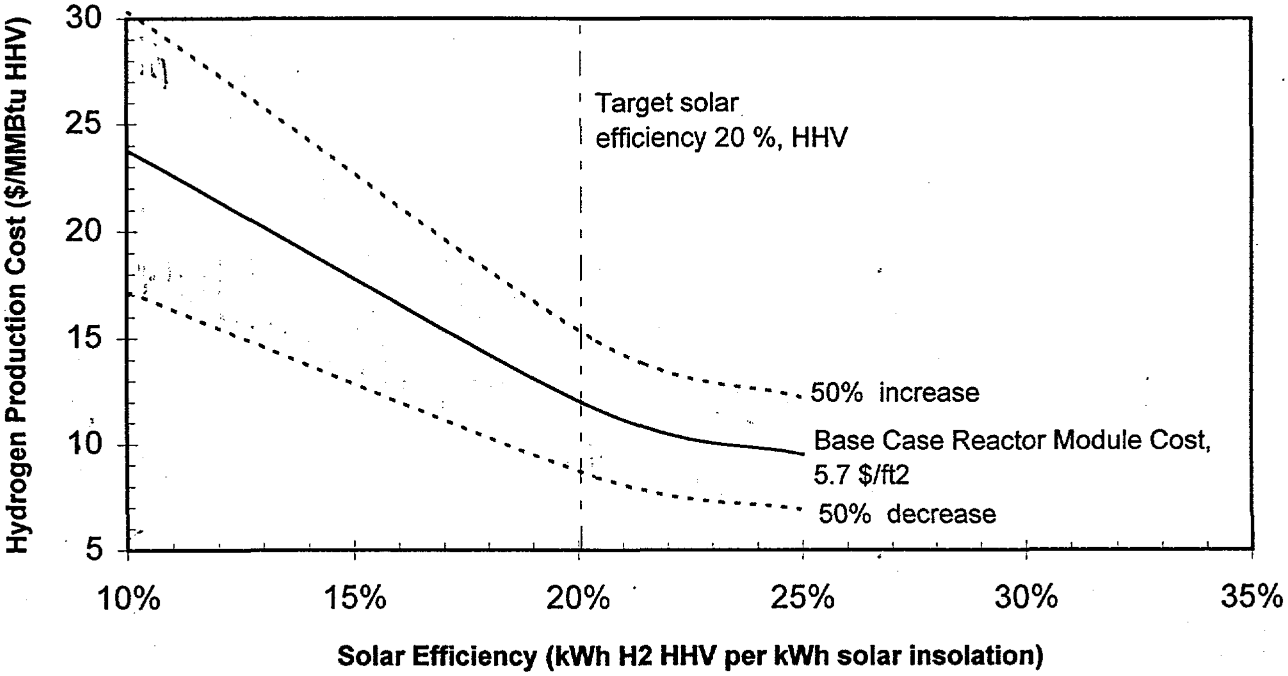
Even if the cost of the photoactive material is low compared to the cost of plate-type PEC material, because of the high cost of the reactor structure, the dual-bed solar efficiency must be higher than 10% (LHV basis) to be economically viable.

The dual bed technology has the potential to be competitive with other direct solar conversion approaches. Its success seems to depend on the identification of a good photoactive catalyst / redox mediator pair, and the minimization of charge recombination and back reaction loss mechanisms.

Table 2. IRR Analysis of the Dual-bed Hydrogen Production Process (MM$)

Year	Operating Income	Capital investment	Depreciation	Taxable Income	Taxes	After-tax income	Cash Flow
1		136.3					(136.3)
2	26.22		10.69	15.53	4.04	11.49	22.18
3	26.22		10.69	15.53	4.04	11.49	22.18
4	26.22		10.69	15.53	4.04	11.49	22.18
5	26.22		10.69	15.53	4.04	11.49	22.18
6	26.22		10.69	15.53	4.04	11.49	22.18
7	26.22		10.69	15.53	4.04	11.49	22.18
8	26.22		10.69	15.53	4.04	11.49	22.18
9	26.22		10.69	15.53	4.04	11.49	22.18
10	26.22		10.69	15.53	4.04	11.49	22.18
11	26.22		10.69	15.53	4.04	11.49	22.18
12	26.22		-	26.22	6.82	19.40	19.40
13	26.22		-	26.22	6.82	19.40	19.40
14	26.22		-	26.22	6.82	19.40	19.40
15	26.22		-	26.22	6.82	19.40	19.40
16	26.22		-	26.22	6.82	19.40	19.40
17	26.22		-	26.22	6.82	19.40	19.40
18	26.22		-	26.22	6.82	19.40	19.40
19	26.22		-	26.22	6.82	19.40	19.40
20	26.22		-	26.22	6.82	19.40	19.40
21	26.22	13.63	-	26.22	6.82	19.40	33.03
		total dep	106.88			**IRR**	**15.0%**
Salvage valu	10%						
Income Tax R	26%						

Figure 7. Hydrogen Production Cost from the Dual Bed Process versus Solar Efficiency and Reactor Module Capital Cost



---

i.Solar Photocatalytic H2 Production from Water Using a Dual-bed Photosystem, Clovis A. Linkous, Florida Solar Energy Center, presented at the US DOE Hydrogen Program Annual Review, May, 1996

ii. Solar Photochemical Production of Hydrogen, John Wright, TDA Research, Inc., Report No. TDA-90-SERI-002, 1990, costs taken from the flat plate system