National Renewable Energy Laboratory

Hydrogen from Algae

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ASES – Renewable Hydrogen Forum
April 10 - 11, 2003
World Resources Institute Washington, D.C.

Background

Resource

Algae are ubiquitous in the environment

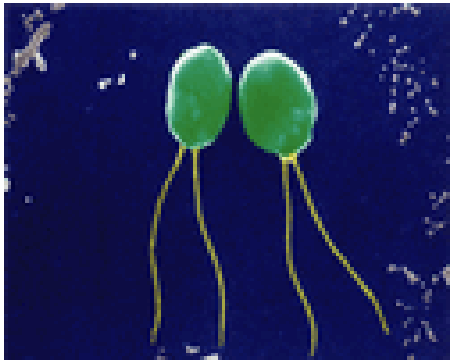
- Performance advantage over Terrestrial Plants
  - > 40,000 species adapted to many different aqueous environments
  - No roots, leaves, No active transport of H_2O and CO_2
  - Growth rates exceed terrestrial biomass by factors of 10 - 100
    - Soy bean productivity about 3 t/ha/y or 2 g/m2/d
    - Algal protein synthesis 96 g/m2/d
- All are capable of photosynthesis
  - Class *Phycophyta*
    - Oligocellular and monocellular eucaryotes
    - Procaryotic cyanobacteria
    - Photoactive bacteria
  - Ocean – Macro, microplankton and nanoplankton is about half of the global photosynthesis
  - Brown algae up to 100 m long, most < 60 micro metre in size

Algal Utilization

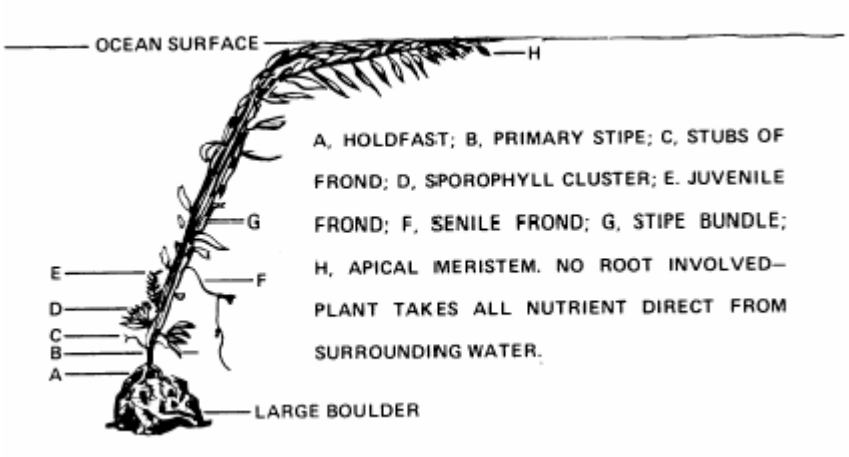
- Production as feed for aquaculture
- Human and Animal feed supplements
  - Vitamins, pigments, anti-oxidants, natural colors, food additives
  - Macro-algae
    - Alginates, Agar etc from red or brown seaweeds
  - Commercial microalgae
    - Chlorophyl, Carotenoids from *Spirulina*, *Chlorella*, and *Dunaliella* species
- Energy and Environment
  - Heavy metal accumulators
  - CO_2 elimination
  - Agriculture and ecosystems e.g. *Azolla* spp associated cyanobacteria fix N_2 for rice cultivation

Algae

Monterey Aquarium



Photosystem I Deficient microalgal mutants
Credit ORNL



1970s Macro Algae to Methane

- High yields required
- Successful bioconversion t CH_4
- Open Ocean
  - Storm Damage
- Costs very high
  - 2 – 8 x Natural Gas
- Concept Abandoned by 1990
  - Current interest in GHG discussions – either as fossil fuel offset or capture-sequestration option with deep sea burial of organic matter.

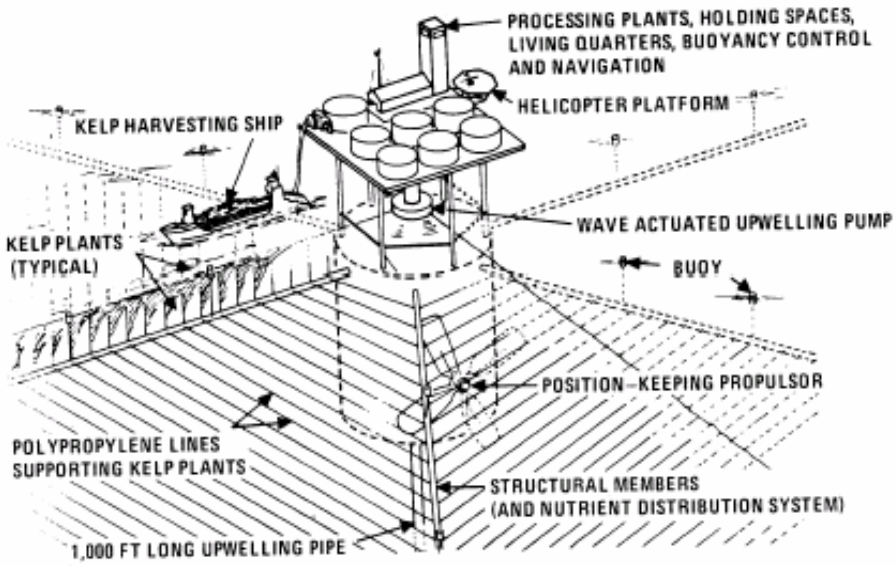
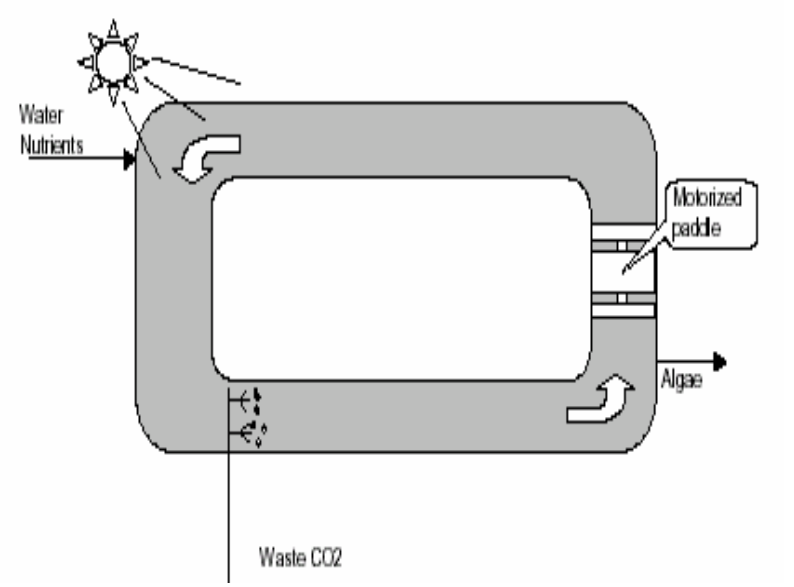
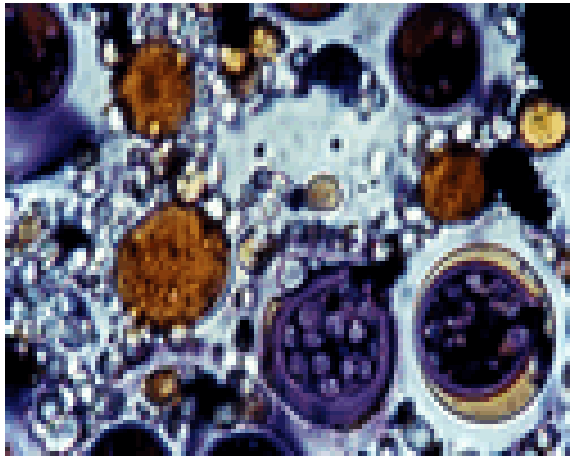


Figure 3. Conceptual design of 405 ha (1,000 acre) ocean food and energy farm unit. (Leese 1976)

1980s - 90s Micro algae to oil with CO_2 capture

- Successful Breeding Program *Dunaliella spp*
- Large scale testing of CO_2 capture
  - 90% achieved
- Fuel product
  - Triacylglycerols (Lipids)
  - Aka biodiesel
- Use of saline water in high solar insolation environments (deserts)
- Barriers
  - Open ponds always taken over by wild species!
  - Program terminated due to high cost of biodiesel



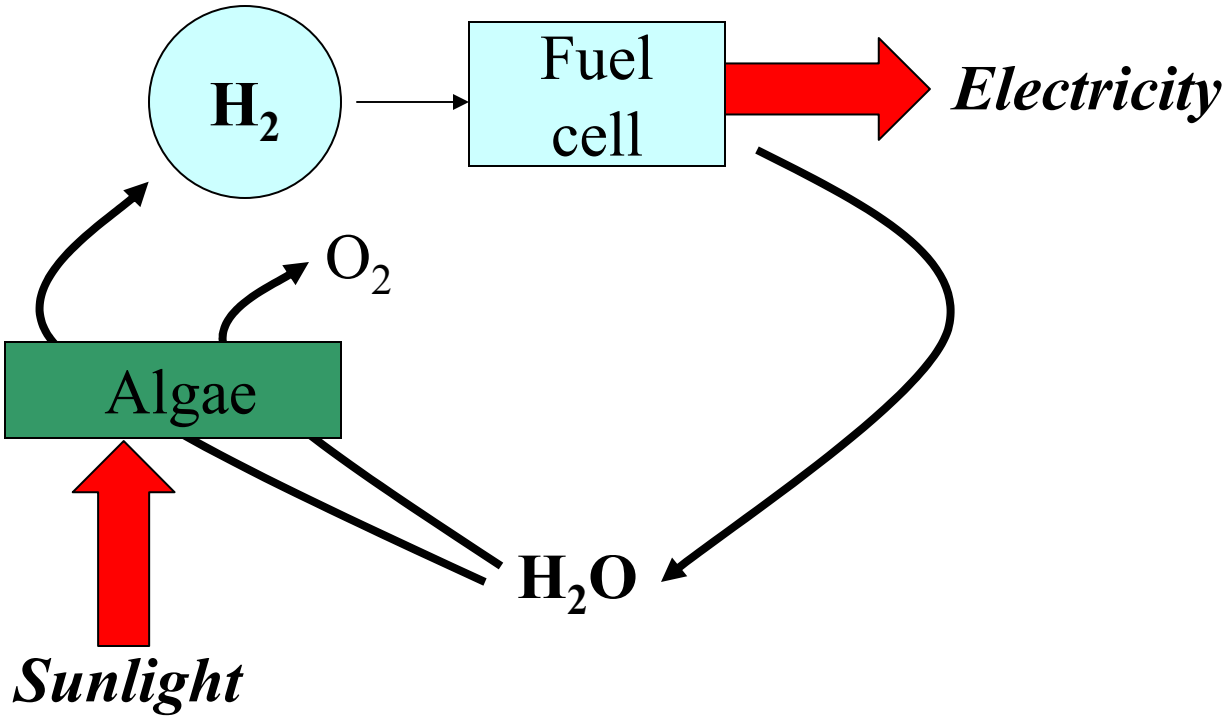


Biological H_2-Production Systems

		Advantages	Disadvantages
• CO → H_2	*Rubrivavax gelatinosum*	many feedstocks dark phase	large reactor
• sugars → H_2	anaerobic bacteria	process similar to anaerobic digestion	large reactor
• H_2O → H_2	green algae (*Chlamydomonas Reinhardtii*)		
•		no feedstock	light- phase reaction

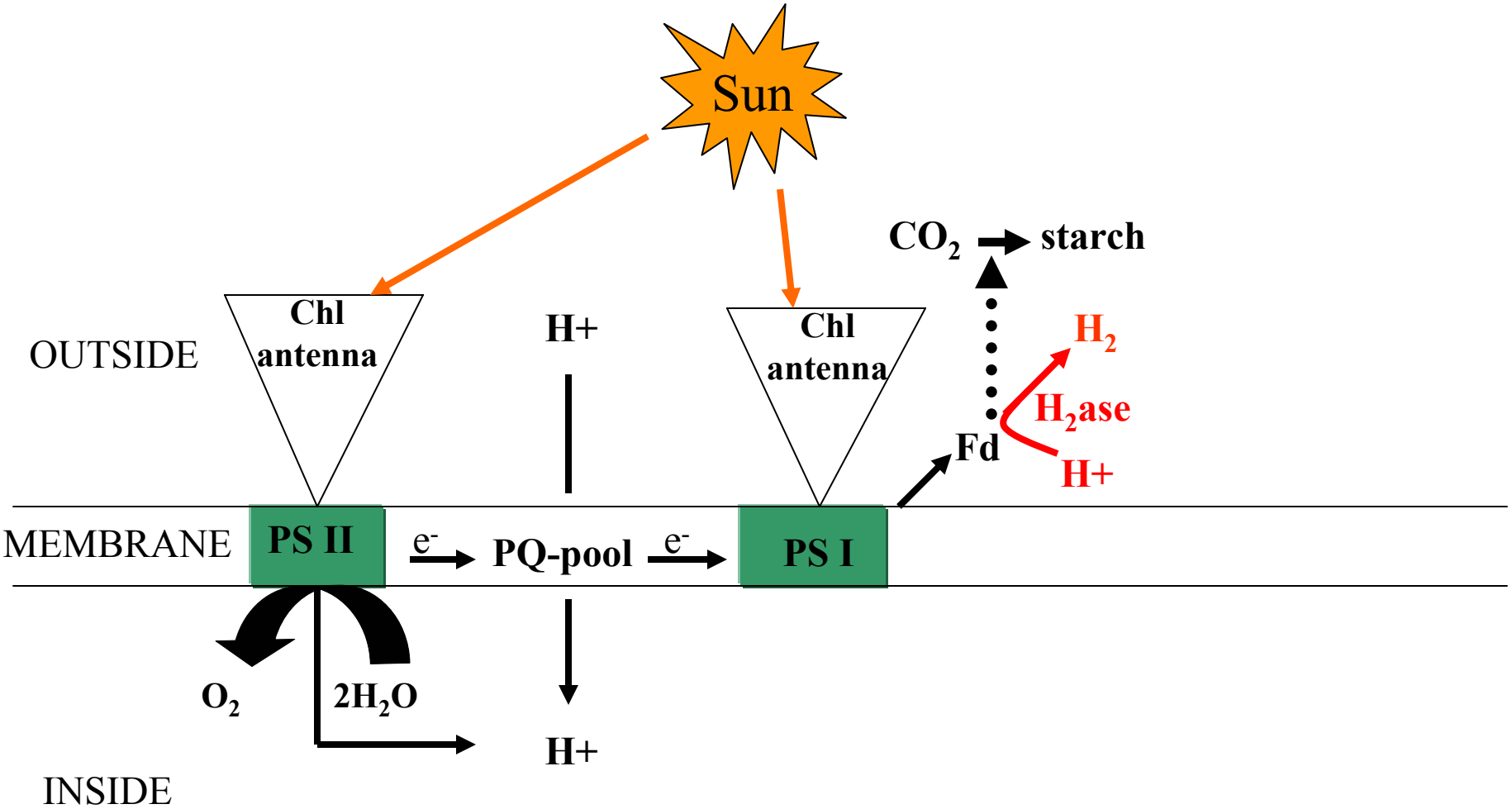
Hydrogen Production by Algae

Goal is to develop a cost-effective system for algal H_2 photoproduction that is (a) renewable (uses water as the substrate and light as the source of energy), (b) stable and self-sustaining, (c) efficient and (d) clean.



How do Algae Photoproduce H_2?

Biochemistry of the Process



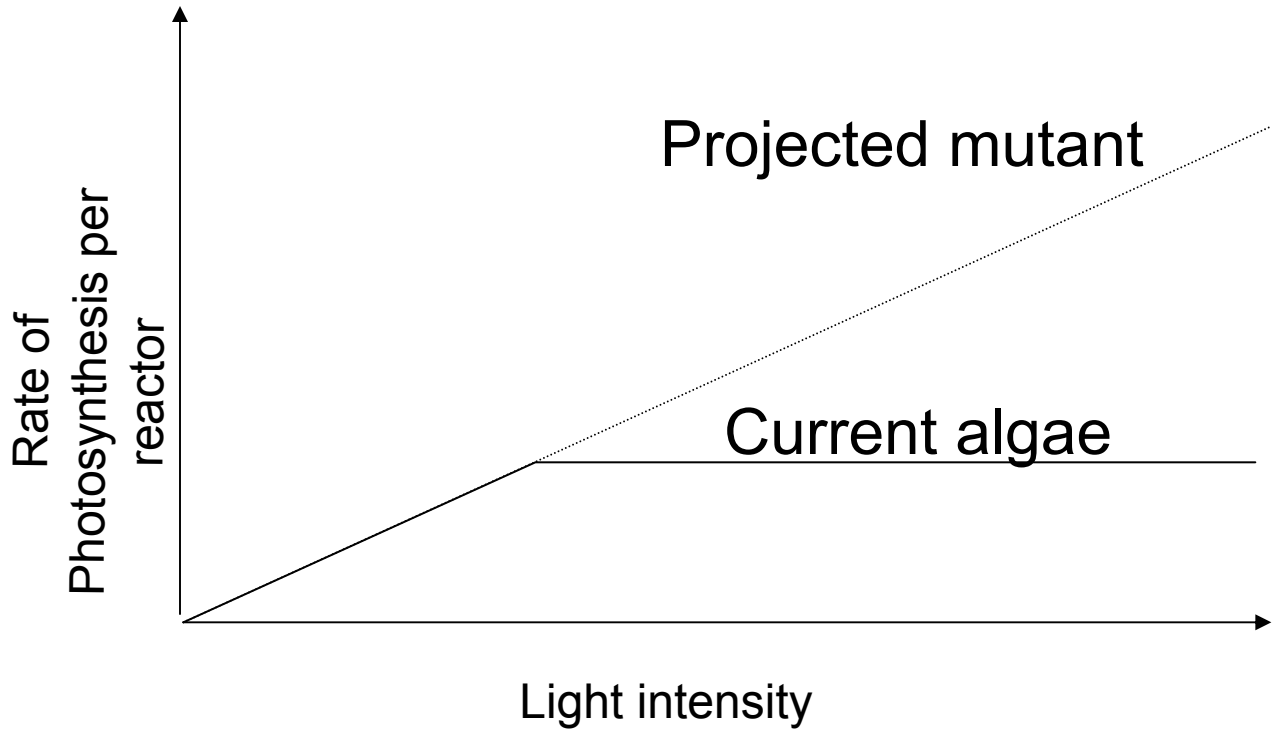
Technical Challenges and Approaches

- Light saturation of H_2 production occurs at low light intensities due to the large light-harvesting antenna of the algae. (Light can't penetrate into liquid.) – molecular engineer the antenna size (UC Berkeley).
- The algal hydrogenase enzyme is sensitive to O_2 and is neither synthesized nor active in the presence of even small amounts of O_2 (O_2 shuts down reaction.) –confer O_2-tolerance by molecular engineering or separate O_2 from H_2 production (NREL).
- The rates of electron transport are ultimately limited by a proton gradient. (H^+ builds up in cell and shuts down reaction.) – engineer a proton pore through the membrane (ORNL).

Research at UC Berkeley

Prof. Anastasios Melis

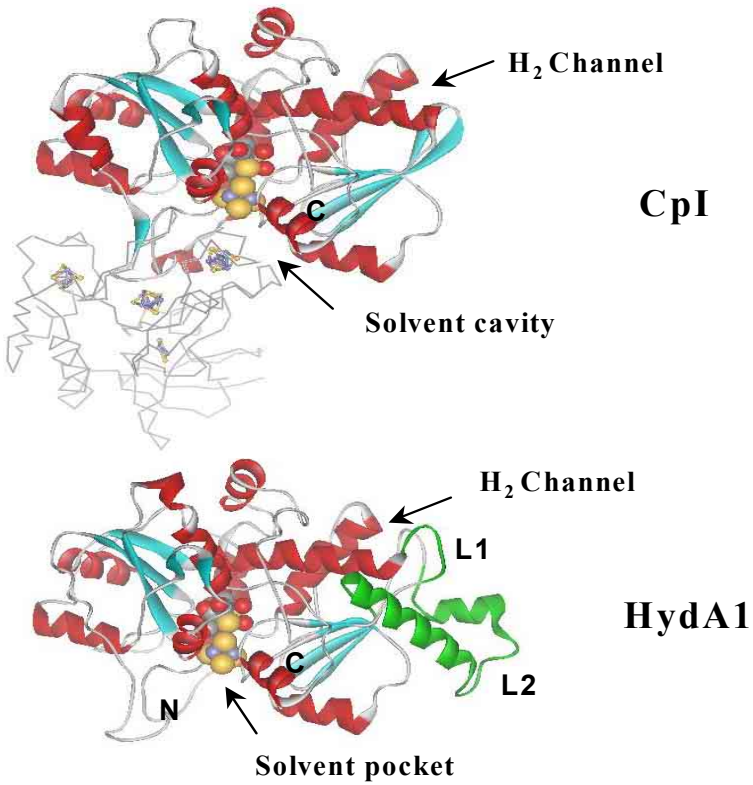
- Reduce the antenna size of the photosystems to increase the light saturation level of photosynthetic H_2 production

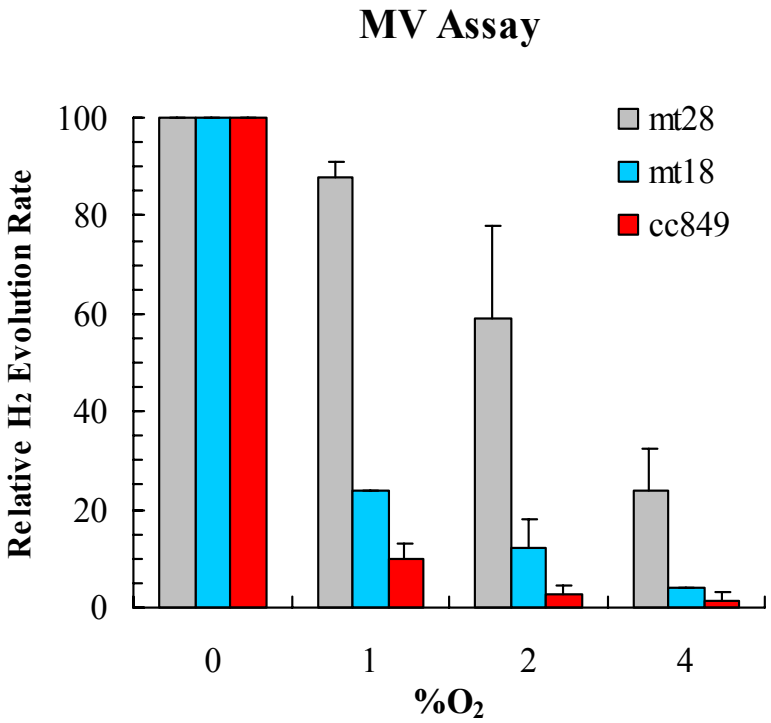


Research at NREL (I)

Dr. Michael Seibert

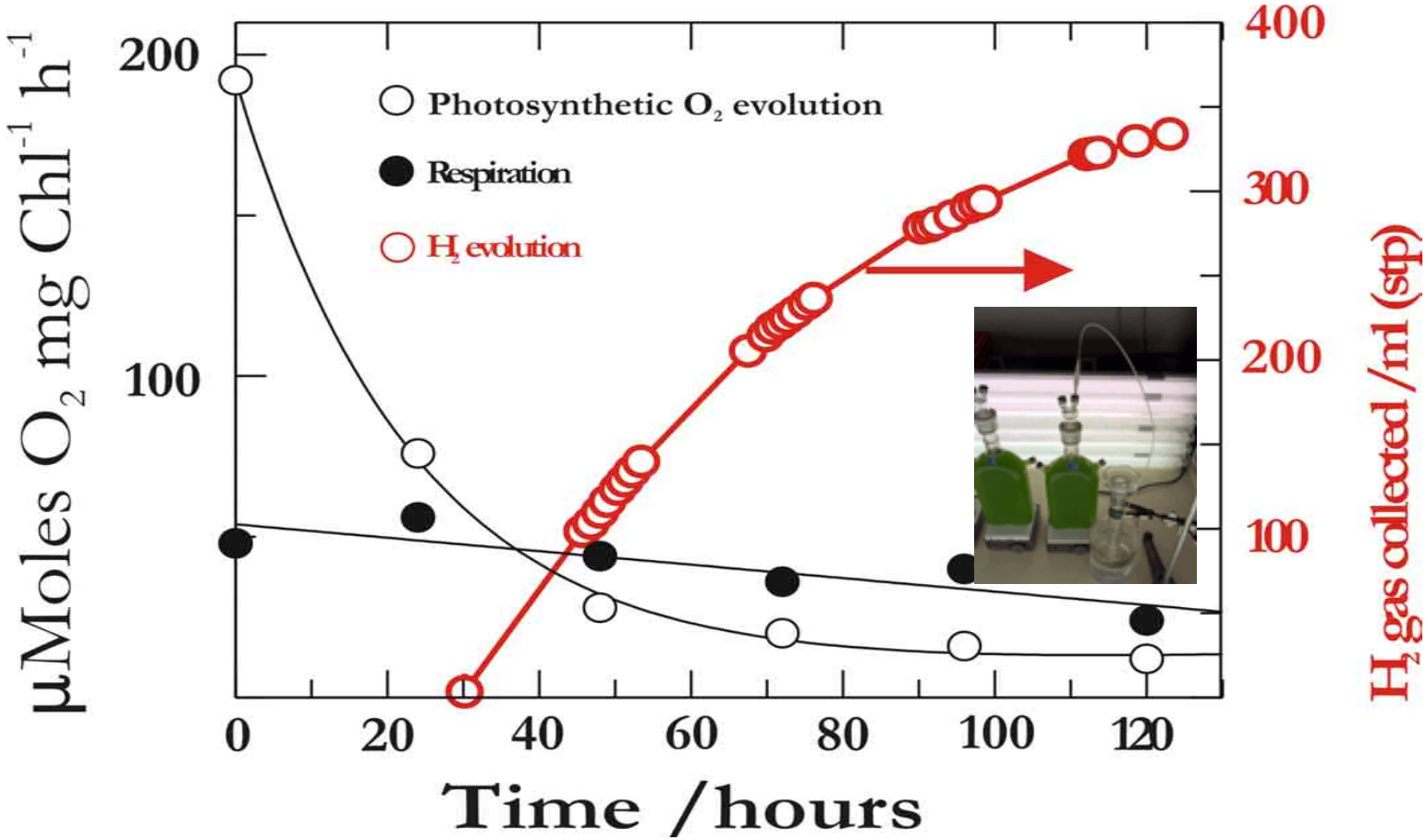
• Molecular engineer the hydrogenase gene to improve tolerance of the enzyme to O_2.



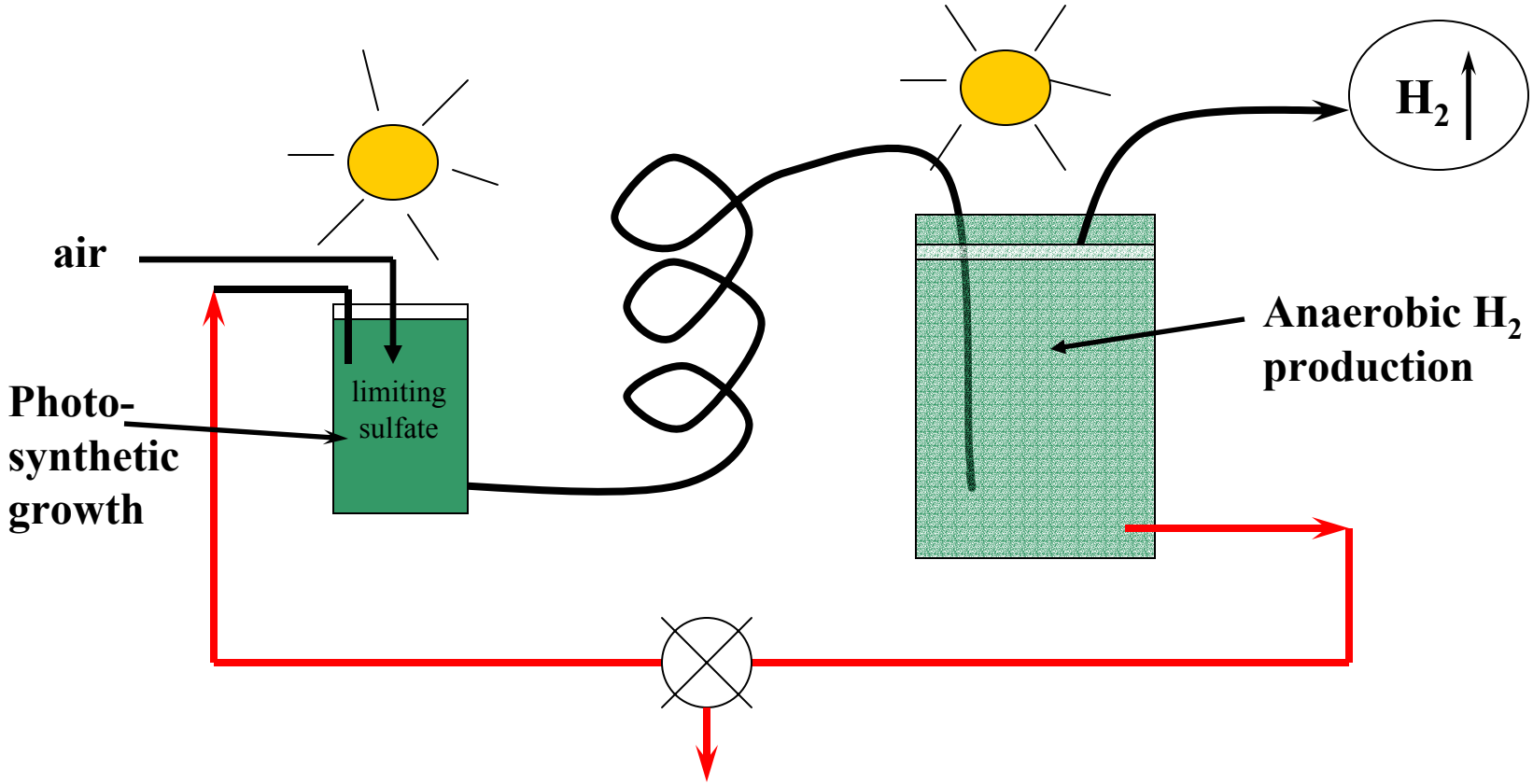


Research at NREL (II) Dr. Maria Ghirardi

•Separate the O_2 from the H_2 evolution reaction either temporally (batch system) or physically (continuous system)

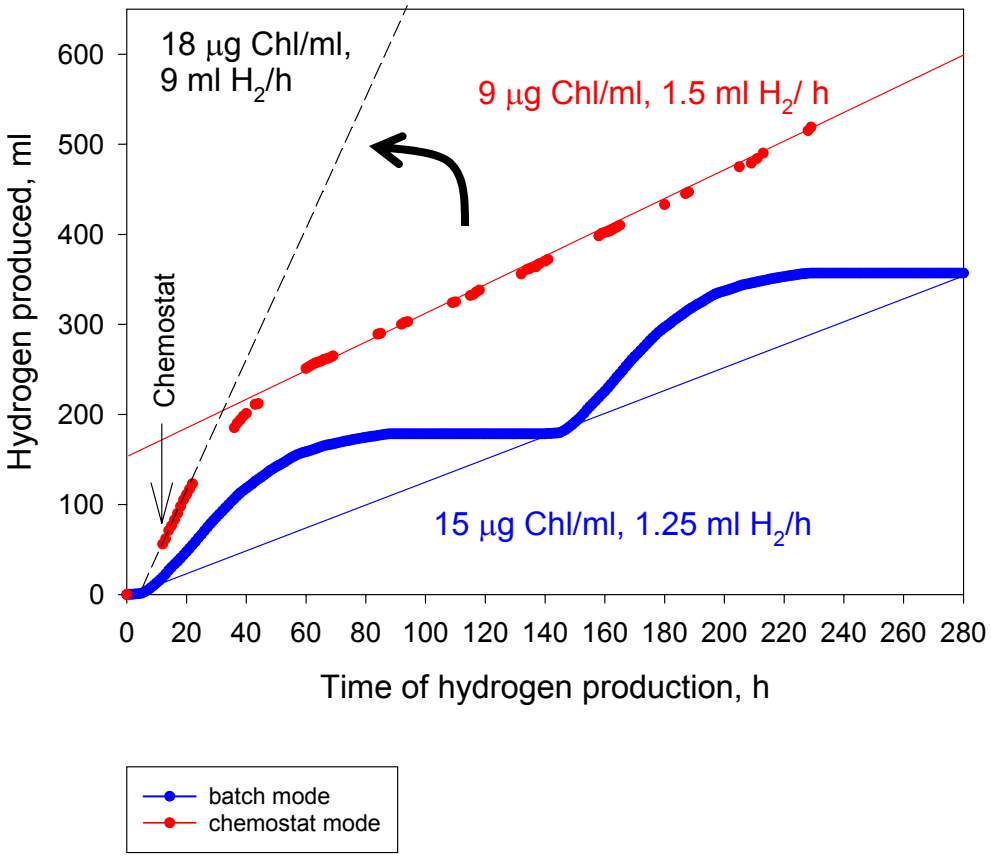


Chemostat System



- biomass (substrate for other processses)
- co-products (dyes, protein, antioxidants, nutritional supplements, pharmaceuticals, etc.)
- fermentation products (acetate, formate)

Current Status (I)



Current Status (II)

	Batch mode	Chemostat mode
Average rate of H_2 production/ reactor	1.25 ml/h	1.5 ml/h
Average specific rate of H_2 production/ reactor	3 μmoles H_2/(mg Chl x h)	5 μmoles H_2/(mg Chl x h)
Duration of H_2 production	3-4 days	10 days
Estimated cost of H_2	$760/kg	$200/kg
Recovery time	2 days	None

Advantages of the chemostat system: higher average specific activity, longer operating time, less energy consumption by elimination of centrifugation steps, lower costs.

A work in progress

- Current production costs: $100-200/kg H_2
- Projected costs: $10/kg <u>or lower</u>
- Cost drivers:
  - Light penetration/pond depth
  - Reactor cost
  - Productivity
  - Co product values
    - Proteins
    - Colorants
    - Carbohydrates
- Acknowledgments
  - Maria Ghirardi
  - Mike Seibert
  - Wade Amos
  - J.S. Craigie – Institute for Marine Biosciences, Halifax, Canada for getting me interested in marine algae a long time ago