CALIFORNIA
ENERGY
COMMISSION

ENERGY INNOVATIONS SMALL GRANT PROGRAM
Renewable Energy Technologies

RENEWABLE HYDROGEN FUEL PRODUCTION BY MICROALGAS PHOTOSENTHESIS

FEASIBILITY ANALYSIS

March 2002
P500-02-008F

Gray Davis, *Governor*

CALIFORNIA ENERGY COMMISSION

Prepared By:
Hal Clark
Grant Program Administrator

Prepared For:
California Energy Commission
Energy Innovations Small Grant Program (EISG)

Researcher:
Anastasios Melis

EISG Grant Number:
99-06

Philip Misemer
Grant Program Manager

Terry Surles
Deputy Director
Technology Systems Division

Steve Larson
Executive Director

LEGAL NOTICE

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace.

The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which $2 million/year is allocated to the Energy Innovation Small Grant (EISG) Program for grants. The EISG Program is administered by the San Diego State University Foundation under contract to the California State University, which is under contract to the Commission.

The EISG Program conducts four solicitations a year and awards grants up to $75,000 for promising proof-of-concept energy research.

PIER funding efforts are focused on the following six RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies
- Environmentally-Preferred Advanced Generation
- Energy-Related Environmental Research
- Strategic Energy Research

The EISG Program Administrator is required by contract to generate and deliver to the Commission a Feasibility Analysis Report (FAR) on all completed grant projects. The purpose of the FAR is to provide a concise summary and independent assessment of the grant project using the Stages and Gates methodology in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions (as presented in the Independent Assessment section).

The FAR is organized into the following sections:

- Executive Summary
- Stages and Gates Methodology
- Independent Assessment
- Appendices
    - Appendix A: Final Report (under separate cover)
    - Appendix B: Awardee Rebuttal to Independent Assessment (Awardee option)

For more information on the EISG Program or to download a copy of the FAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049 or email eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Executive Summary

Introduction

The ability of unicellular green algae to produce hydrogen (H_2) gas in the presence of sunlight has been recognized by the scientific community as being a possible way to generate hydrogen gas for energy production. Below is a list of important known factors specific to green algal H_2-production.

1. Photosynthesis can operate with a photon conversion efficiency of >80%,
2. Microalgae can produce H_2 photosynthetically with a photon conversion efficiency of >80%,
3. Molecular Oxygen (O_2) acts as a switch by which H_2 production is turned off,
4. Sixty years of research has failed to overcome the incompatibility of simultaneous O_2 and H_2 production by photosynthesis.

Recent work has shown that the absence of Sulfur (S) from the growth medium of the green algae Chlamydomonas reinhardtii (*C reinhardtii*) causes a specific but reversible decline in the rate of oxygenic photosynthesis but does not affect the rate of mitochondrial respiration. The absence of sulfur from the growth medium triggers a metabolic switch, one that selectively and reversibly turns-off photosynthetic O_2 production. In the presence of S, green algae photosynthesize normally (H_2O oxidation, O_2 evolution and biomass accumulation), however, in the absence of S and absence of O_2, photosynthesis in *C. reinhardtii* produces H_2 rather than O_2. Further refinement of this method may lead to full understanding of the green algae hydrogen-related metabolism and ultimately the generation of H_2 gas for the fuel and chemical industries.

Objectives

The goal of this project was to determine the feasibility doubling the hydrogen production efficiency of *C. reinhardtii* from the level of ~10% of the theoretical maximum to the level of ~20% of the theoretical maximum. The following project objectives were established:

1. Improve the H_2 production by shifting forward the equilibrium of the reversible hydrogenase catalyzed reaction.
2. Design and test cell growth media that accentuate the metabolism of H_2 production.
3. Test the effect of diurnal cycles on starch mobilization and H_2 production.
4. Identify the rate-limiting step in the H_2 production process.

Outcomes

1. Two approaches were investigated attempting to shift forward the equilibrium of the reversible hydrogenase catalyzed reaction:

   a. The atmospheric air within the photobioreactor was purged with argon to remove dissolved O_2 prior to initiation of H_2 production. Independent measurements have shown that such degassing is sufficient to reduce the O_2 content of the culture to less than 2% of saturation. This purge resulted in almost immediate initiation of H_2 production, while H_2 production by the control culture was delayed for another 10 to 15 hours, hence this approach shifted the reaction forward, reducing the wait time by roughly 10-15% of the hydrogen production cycle length.
   b. The pH balance of the water in the gas collection device was modified with the thesis that the water was saturated with H_2 gas and perhaps contained a significant amount. No detectable increase in the collected amount of H_2 gas was observed.

2. Multiple designs of cell growth media were tested to accentuate the metabolism of H_2 production.

   a. Determined the effects of salinity:
      i. On chlorophyll content and cell viability. Cell density increased then remained constant with moderate levels of salinity.
      ii. On cellular photosynthesis and respiration. Neither photosynthesis nor respiration appeared to be effected by reasonable amounts of salinity.
      iii. On H_2 production. A moderate level of salinity, 10 mM NaCl enhanced the rate and yield of H_2 gas by 30% and 40% respectively over the control.

   b. Determined the effects of ATP biosynthesis uncouplers as follows:
      i. Methylamine-hydrochloride. Over a very narrow range centered on 5 mM Methylamine, H2 production increased as much as 20-25% over the control.
      ii. Gramicidin. This chemical was not sufficiently soluble to allow investigation of concentrations greater than about 5 micromoles. However, at that level the effect was similar to that of Methylamine, above.
      iii. FCCP. This chemical significantly reduced the production of H_2.

   c. Determined the effect of trace amounts of S; Used 10, 50 and 100 micromoles S samples. The addition of S was observed to delay the onset of H_2 production. However the total production increased with increase of S until the delay of onset became the dominant factor. Culture with 50 micromoles S added produced about 35% greater H_2 yield than produced by the cultures with no S added.

3. The *C reinhardtii* were cyclically deprived of S and supplied with S, for three complete cycles, and the rate of production of H_2 was recorded. The result was that the single culture of *C reinhardtii* produced about three times as much H_2 in three cycles as the control cultures did in a single cycle. This illustrated the capacity of the *C. reinhardtii* to recover from the catabolic effects of H_2 production when S is provided between H_2 production cycles.

4. The rate limiting step in the H_2 production process was identified by Western Blot analysis of the total cell protein extracts from *C reinhardtii*. This showed that the hydrogenase gene is expressed sparingly under S deprivation conditions.

5. In all cases the gas produced by the *C reinhardtii* algae was collected in a tube (upside down burette) filled with water. The gas collected in this manner was reported as hydrogen. Gas chromatographic analysis of the gas collected showed ~90% H_2, ~10% nitrogen with traces of CO_2 and O_2.

Conclusions

This research indicates that H_2 production rates approaching 20% of theoretical maximum could be achieved by proper combination of the techniques explored in this project.

1. The equilibrium of the reversible hydrogenase catalyzed reaction can be shifted forward.
   a. There is significant benefit, 8 - 12% production improvement to be gained by rapid transition from aerobic to anaerobic environment in the photobioreactor medium, compared to a "natural" transition.
   b. The question of H_2 solubility in water was not definitively answered.
2. H_2 production can be increased by improving the design of the cell growth media.
   a. Moderate levels of salinity of the culture do not adversely affect cell viability and do increase H_2 production by ~40%. However, there may still be room for improvement with further study.
   b. Due to the modest effect and the high cost of ATP biosynthesis inhibitors, their use is not the method of choice for manipulation of H_2 production.
   c. Sulfur titration holds the promise of improving the yield of H_2 production by as much as 35% in this two-stage photosynthesis and H_2 production method. Its utility in a production environment is a concern.
3. It may be possible to extend the production of H_2 by a single culture ad infinitum by alternately supplementing and depriving the culture of its organic sulfur. Three cycles were demonstrated.
4. The sparse expression of the hydrogenase gene within the *C reinhardtii* is responsible for the limited H_2 production. Genetic engineering should be applied to increase the expression of this gene.
5. The technique for removal of nitrogen from the product gas must be identified.
6. It is evident that incremental improvements in the yield of hydrogen production can be accrued upon R&D of the method. However, further improvements need to be achieved to make "hydrogen production by sulfur-deprivation of green algae" a commercial reality.

Benefits to California

Both small-scale (industrial and commercial) and larger (utility) solar energy conversion plants (photobioreactors) can be envisioned utilizing the Two-Stage Photosynthesis and H_2-Production process. Remote photobioreactors could be installed as modules in arid areas where sunlight is plentiful and alternative uses of land are minimal. Such a process of H_2 gas production would be sustainable, environmentally friendly and economically attractive compared to most other hydrogen production alternatives.

In addition to H_2, a valuable and clean fuel, the Two-Stage Photosynthesis and H_2-Production process will generate green algal biomass as a significant "Value-Added Bioproduct" that will enhance the economics and competitiveness of the process.

Recommendations

Further Research and development should address the specific biological and engineering challenges facing commercialization of this technology.

- Further basic research should be done to improve understanding of the cellular metabolism and basic biochemistry that support this process.
- This project demonstrated that hydrogen production of 20% of theoretical is achievable, however, further research should be done to improve the hydrogen production further.
- Preliminary designs for the scale-up of the process should be created, and a preliminary life cycle cost analysis performed. This analysis should compare the cost of producing electricity by this method to the cost of PV. Further, this analysis should compare the cost of producing hydrogen by this method compared to the electrolysis method.

The technology developed in this project will take 8 to 12 years to advance to the state of market readiness.

Stages and Gates Methodology

The California Energy Commission utilizes a stages and gates methodology for assessing a project's level of development and for making project management decisions. For research and development projects to be successful they need to address several key activities in a coordinated fashion as they progress through the various stages of development. The activities of the stages and gates process are typically tailored to fit a specific industry and in the case of PIER the activities were tailored to be appropriate for a publicly funded energy research and development program. In total there are seven types of activities that are tracked across eight stages of development as represented in the matrix below.

Development Stage/Activity Matrix

	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7	Stage 8
Activity 1								
Activity 2								
Activity 3								
Activity 4								
Activity 5								
Activity 6								
Activity 7								

A description the PIER Stages and Gates approach may be found under "Active Award Document Resources" at: http://www.energy.ca.gov/research/innovations and are summarized here.

As the matrix implies, as a project progresses through the stages of development, the work activities associated with each stage needs to be advanced in a coordinated fashion. The EISG program primarily targets projects that seek to complete Stage 3 activities with the highest priority given to establishing technical feasibility. Shaded cells in the matrix above require no activity, assuming prior stage activity has been completed. The development stages and development activities are identified below.

Development Stages:	Development Activities:
Stage 1: Idea Generation & Work Statement Development	Activity 1: Marketing / Connection to Market
Stage 2: Technical and Market Analysis	Activity 2: Engineering / Technical
Stage 3: Research & Bench Scale Testing	Activity 3: Legal / Contractual
Stage 4: Technology Development and Field Experiments	Activity 4: Environmental, Safety, and Other Risk Assessments / Quality Plans
Stage 5: Product Development and Field Testing	Activity 5: Strategic Planning / PIER Fit - Critical Path Analysis
Stage 6: Demonstration and Full-Scale Testing	Activity 6: Production Readiness / Commercialization
Stage 7: Market Transformation	Activity 7: Public Benefits / Cost
Stage 8: Commercialization	

Independent Assessment

For the research under evaluation, the Program Administrator assessed the level of development for each activity tracked by the Stages and Gates methodology. This assessment is summarized in the Development Assessment Matrix below. Shaded bars are used to represent the assessed level of development for each activity as related to the development stages. Our assessment is based entirely on the information provided in the course of this project, and the final report. Hence it is only accurate to the extent that all current and past work related to the development activities are reported.

Development Assessment Matrix

Stages / Activity	1 Idea Generation	2 Technical & Market Analysis	3 Research	4 Technolog y Develop-ment	5 Product Develop-ment	6 Demon-stration	7 Market Transfor-mation	8 Commer-cialization
Marketing								
Engineering / Technical								
Legal/ Contractual								
Risk Assess/ Quality Plans								
Strategic								
Production. Readiness/								
Public Benefits/ Cost								

The Program Administrator's assessment was based on the following supporting details:

Marketing/Connection to the Market

Melis Energy, a California Corporation was formed in January, 2001 in order to advance the commercialization of the process of hydrogen production by microalgal photosynthesis. A detailed and fully documented business plan does not yet exist.

Engineering/Technical

This project successfully demonstrated that Two-Stage Photosynthesis and H_2-Production process can be operated at efficiencies approaching 20% of theoretical with current techniques. That is, through the simultaneous use of sulfur titration, moderate levels of salinity in the culture and through rapid transition from aerobic to anaerobic environment in the photobioreactor medium, though not demonstrated explicitly, the outcomes indicated that the H_2 production rate should approach 20% of theoretical.

Legal/Contractual

There is no indication of patent or invention disclosure filing, nor is there any certainty that such filings are appropriate in this case.

Environmental, Safety, Risk Assessments/ Quality Plans

This aspect of hydrogen gas production was not addressed by this project although it may be reasonably assumed that this technology will have unique and potentially serious risks associated with it. Initial drafts of the following Quality Plans are needed prior to initiation of Stage 4 development activity; Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety**.**

Strategic

This product has no known critical dependencies on other projects under development by PIER or elsewhere.

Production Readiness/Commercialization

There was no activity reported in this area beyond that to which technical feasibility relates. However, Melis Energy was formed in January, 2001 in order to advance the commercialization of this process.

Public Benefits

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system.
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the rate payer from this research will be reduced environmental impacts of the California electricity supply or transmission or distribution system. In order to supply this benefit, hydrogen for electrical generation must directly compete with photovoltaic technology. Projected costs of PV range below $50 per square meter at 10% to 15% efficiency. This project did not provide sufficient information to formulate comparative cost estimates.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)