Hydrogen Reactor Development and Design for Photofermentation and Photolytic Processes

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This presentation does not contain any proprietary or confidential information
Overview

Timeline
• Start: October 2003
• End: 2016
• Complete: 1%

Barriers
• Production barriers addressed
  – L. Systems Engineering
  – N. Materials and System Engineering

Budget
• Total project funding
  – DOE share – not determined
  – Contractor share - NA
• Funding received
  FY04 - $129K
• FY05 - $100K

Subcontractor
• Nuclear Filter Technology, Inc.
Project Objectives

Develop advanced renewable photolytic hydrogen generation technologies.

- By 2015, demonstrate engineering-scale biological system to produce \( \text{H}_2 \) at a plant-gate cost of $10/kg projected to commercial scale.
- By 2015, demonstrate direct photoelectrochemical water splitting. Plant-gate \( \text{H}_2 \) production cost of $5/kg projected to commercial scale.
- The long-term objective fuels cost competitive with gasoline.

- Assist DOE with the identification of solar reactor concepts and related materials’ needs in support of photobiological and photoelectrochemical \( \text{H}_2 \) production

- Reactor Concepts
  - Review literature, work with program scientists and engineers, and industry

- Materials Needs:
  - Determine time zero properties of polymers – polycarbonate, acrylic, polyethylene terephthalate, and fluoropolymers (solar transmittance, \( \text{O}_2 \) and \( \text{H}_2 \) permeability, tensile strength, and cost)
  - Conduct accelerated and outdoor weathering tests for polymers and other materials of construction
  - Identify and begin to test strategies for reducing hydrogen permeability, if necessary
Approach

• Develop large area solar reactors for photobiological and photoelectrochemical water splitting systems
  – Assemble data base of existing literature on reactors and materials
  – Identify candidate transparent materials
  – Measure key properties (e.g. transmittance, H₂ and O₂ permeation rates, mechanical properties, and cost)
  – Perform outdoor and accelerated weathering tests on candidate materials of construction
  – Identify reactor concepts with the potential to meet the process requirements
  – Provide data for techno-economic process analyses
Solar Reactor Considerations

• What will very large area reactors look like?
• How do solar reactors differ from conventional reactors?
• What are the key design constraints?
  – 0.05-0.1 sun optimum light intensity for algae
  – Photoelectrochemical systems can use concentrated sunlight
  – Must have low hydrogen loss
• Design for daily and annual solar cycles
• Other – cleaning, heat rejection, gas clean-up, materials lifetime, light-dark cycles
Schematic diagram of a proposed photobioreactor system. The primary and secondary mirrors collect and concentrate the light while the light distribution waveguide conditions and transports the light to the photobioreactor.
Conceptual Design of a Photoelectrochemical Water Splitting System with Light Concentration
Active Solar Photocatalytic Treatment - NREL Flat Plate Reactor at McClelland AFB 1995

Fluorocarbon glazing
Polymer catalyst support
Reactor Concepts May Come from Other Sources

Lengths of polymer panels, with the cross-section shown, containing a fluid to collect solar heat for power generation.

Technical Accomplishments & Results

• Current literature database contains about 200 references
  – Identification of solar reactor concepts is underway
  – Compiled list of important material properties

• Selected candidate transparent material families
  – Polycarbonates, Fluoropolymers, Acrylics, and Polyesters
  – Multiyear weathering tests in progress ("piggy backing" on work in the DOE Solar Programs)

• Obtained $\text{H}_2$ and $\text{O}_2$ permeation parameters for a range of polymers
Outdoor Weathering Data - Polycarbonate

SparTech Plastics Sungard Ultra-weatherable Polycarbonate (coextruded PC & acrylic) with Korad UV protection layer as a function of accelerated Ci5000 WOM and outdoor exposure in Golden, CO, Phoenix, AZ, and Miami, FL after cleaning.
Outdoor Weathering Data - PET

Melinex D387 PET films w/ & w/o Korad UV protection layer as a function of accelerated Ci5000 WOM and outdoor exposure in Golden, CO, Phoenix, AZ, and Miami, FL after cleaning.
Weathering Data - Fluoropolymers

8 Fluoropolymers as a function of accelerated Ci5000 WOM and outdoor exposure in Golden, CO after cleaning

Equivalent NREL Exposure Time (yr)

% Hemispherical Transmittance from 300nm-1200nm

Total UV Dose (100 x MJ/m²)
H₂ and O₂ Permeation Data

Permeability Coefficient (cm³·mm/m²·day·atm)

- Hydrogen
- Oxygen

Materials:
- DuPont Melinex D387 PET (1.2 mils)
- DuPont Melinex ST504 PET (7 mils)
- Saint Gobain FEP (2 mils)
- Saint Gobain FEP (30 mils)
- Arekma Kynar PVDF (1 mils)
- Cyro Acrylic (3 mils)
- Korad Acrylic (2.4 mils)
- GE Lexan HP92WDB PC (7 mils)
- GE Lexan 9034 PC (93 mils)
- GE Lexan HP92WDB112 PC (20 mils)
- GE Lexan 9034 PC (93 mils)
- Polyethylene (HDPE) *PDL Handbook
- Polymethylene (HPE) *PDL Handbook
- Polyeester (PEF) *PDL Handbook
- Polycarbonate (PC) *PDL Handbook
- Silicone *PDL Handbook

*PDL Handbook
Work in Other Technologies Requiring Low Gas Permeability

![Graph showing barrier requirements for different product sectors](image)

**Figure 1.** Barrier requirements for different product sectors (dotted lines, italics) and performance of flexible polymeric structures (shaded areas) [1].

(from H.-C. Langowski, 2004)
General Observations

• Acrylics have good outdoor durability but are brittle and subject to hail damage
• Polycarbonates are tough but “yellow” and crack outdoors over time – protection strategies are being evaluated
• PET formulations have not yet proven durable outdoors but have favorable gas permeation properties
• Kynar has very good outdoor durability and favorable gas permeation properties
• Guidance on gas permeation and other specifications will come from the systems engineering analysis that will be completed in September 2005
Responses to Previous Year Reviewers’ Comments

• **Approach to performing the research and development**
  - *Could probably be assigned to a contract lab and done for less money.*
  Measurements of hydrogen permeation rates are being done on a subcontract. The same may be done with oxygen measurements when routine testing of weathered and modified materials begins. In house work on accelerated and real time weathering is being done in DOE/EERE facilities in conjunction with a group that has been involved with materials performance in solar applications for over 30 years and has a very large database of materials performance and properties.

• **Specific recommendations and additions or deletions to the work scope**
  - *Better define “issues” – target properties of H\textsubscript{2} and O\textsubscript{2} permeability, strength, brittle, transparency (and aging).*
  Target properties related to permeability, e.g. transparency, cost, and service lifetime will be addressed in the systems engineering study being done in FY05.
  - *In the later stages of this work the PI and staff should be strongly encouraged to work very closely with the photobiological and photoelectrochemical experts to ensure reactors are appropriate.*
  This interaction was established from the start. The PI and staff participate in planning and review meetings with the photoelectrochemical and photobiological teams and regularly exchange information.
Future Work

• Remainder of FY 2005
  – Provide input on reactor configurations, materials of construction, and annual solar energy availability to the systems engineering for photobiological hydrogen production

• FY 2006
  – Begin to address reactor issues raised by the technoeconomic analysis completed in FY05
  – Identify strategies for reducing hydrogen permeation rates – If needed
  – Continue materials testing and evaluation
  – Work with material vendors to identify methods to overcome materials issues
  – Identify reactor concepts and begin to identify design issues
What is possible for production of hydrogen using solar bio- or photoelectrochemical reactors?

Photobioreactors produce all the food and oxygen consumed by the entire animal population of the earth. That includes our 6+ billion close relatives, and all of our cousins in the animal kingdom.

It is reasonable to expect that solar water splitting processes will be a significant contributor to hydrogen production in the future.
Questions?

- Contact: Dan Blake, 303-384-7701, dan_blake@nrel.gov
Publications and Presentations

“Overview of Solar Reactors and Design Considerations,” Meeting of the photobiology team, ORNL, November 3-5, 2004

“Project overview,” Hydrogen Tech Team Meeting, NREL, January 13-14, 2005
Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Fire or explosion caused by inadvertent mixing of hydrogen and oxygen in test systems is the most significant hydrogen hazard. It will not be until laboratory and engineering scale testing of photolytic reactors begins (probably after 2010) that there will be potential for this to occur. This could conceivably occur because of material failures or assembly flaws which cause leaks in reactor systems.
Our approach to deal with this hazard is:

Laboratory and engineering scale experimental work and material testing are covered by NREL safety procedures that require extensive review, readiness verification, safe operating procedures, hazard analysis, and training. The Safe Operating Procedures are subject to annual review and renewal. When laboratory and engineering scale testing of reactors begins there will be procedures in place to evaluate materials and leak test equipment in advance of work that will generate hydrogen.
Milestones

1. Progress report documenting the results of the FY05 work on polymer durability and properties - September 2005
2. Set target range for hydrogen and oxygen permeation rates for materials identified for use in solar reactors for photobiological and photoelectrochemical hydrogen production - December 2005
3. Provide input on materials properties, cost, and conceptual design for solar reactors for the photoelectrochemical hydrogen production cost as needed - May 2006
4. Progress report documenting the results of the FY07 work on polymer durability and properties, updating material specifications, and surveying the status of conceptual designs for solar photobiological and photoelectrochemical reactors - September 2007
5. Report documenting the gaps in understanding necessary for the design of solar photobiological and photoelectrochemical reactor systems - June 2008
7. Document design concepts for photobiological and photoelectrochemical reactor systems - September 2009

Go/No-Go Decisions
1. Go/No-Go: Identify cost-effective (based on analysis) transparent hydrogen-impermeable material for use in photoelectrochemical and photobiological hydrogen production systems - 2010