

## II.H.5 Purdue Hydrogen Systems Laboratory: Hydrogen Production\*

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Contract Number: DE-FC36-06GO86050

### Subcontractors:

- National Renewable Energy Laboratory, Golden, CO
- University of Wyoming, Laramie, WY

Project Start Date: September 16, 2006

Project End Date: September 30, 2011

\*Congressionally directed project

### Technical Targets

Biological H <sub>2</sub> Production	Units	2013/2018	Purdue 2010
Hydrogen Yield Percentage	%	20/30	utilizing organic wastes

### FY 2011 Accomplishments

- Currently completing the fourth generation of the experimental test matrix and continue to test various combinations of waste material and inocula under various operating conditions. The developed optimized process has significantly increased hydrogen production. For the test matrix, gas volume is being measure by a calculation employing head space pressure. These values are correlated with gas molecular composition values from the gas chromatograph to give hydrogen production levels. The optimized values are used in the energy model and initial design the modular energy system. Measurements of pH are recorded during a portion of data runs.
- Homogeneity of feed stock is assured through the use of statistical sampling techniques. The water content of the substrate was preliminarily reduced from 98% to 60% with minimal decrease in hydrogen production. Methods to further decrease water content and ways to support substrate were tested. Distiller's dried grains (DDGS) are being tested as a substrate for hydrogen production. A new process has been developed that has greatly increased hydrogen yields for DDGS. This could significantly increase the efficiency of ethanol production from corn. A continuous fermentor (New Brunswick, BioFlo<sup>®</sup>/CelliGen<sup>®</sup> 115, 3 L) is being used to consider larger batch sizes and the influence of continuous feed of substrate on the values of optimal operating parameters. Currently DDGS is being tested in the fermentor. We are also exploring existing catalytic methods including nano catalysts for capture of CO<sub>2</sub> from the fermentation process. The vacuum tube solar pre and post process apparatus is fully operational and being used for pre and post processing of waste material.



### Fiscal Year (FY) 2011 Objectives

- Investigate and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation.
- Investigate paths for implementation of the research as a modular energy source initially for application in remote locations.

### Technical Barriers

This project addresses the following technical barriers from the Biological Hydrogen Production section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(AR) H<sub>2</sub> Molar Yield

(AT) Feedstock Processing Cost

(AU) Systems Engineering

### Introduction

This project allows the creation of a Hydrogen Research Laboratory in a unique partnership between Purdue University's main campus in West Lafayette and the Calumet campus. This laboratory is engaged in basic research in hydrogen production and storage and has initiated

engineering systems research with goals established as per the DOE Fuel Cell Technologies Program.

Bio-production of hydrogen is potentially an important renewable source of energy. Using organic wastes for bio-production of hydrogen not only has the potential to generate cost-effective and renewable energy but also can reduce pollution in the environment and provide a source of fertilizer for growing crops. The purpose of the current research effort is to investigate, obtain data, and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the technology as a local electric and thermal energy source. This effort is targeted to assure that the developed technology will be applicable for integration into various current and future energy supply options including the Department of Energy Road Map. This effort is investigating ways to develop a modular anaerobic biological hydrogen production and energy system for applications initially in remote locations. It is realized that hydrogen production levels from conventional anaerobic processes are not as great as is desired in the long-term perspective for bulk production systems. This research is focusing on a process that has multiple products and associated values. Value streams include hydrogen, waste disposal function, heat for buildings, drinking water, and possibly a marketable chemical product produced from process carbon dioxide. After it is proven, it is anticipated that the technology will be leveraged to larger applications in continuing research

efforts. We have performed preliminary cost analysis studies, but factors such as the water content greatly influence the design and consequently the cost. It is also necessary to consider aspects such as the value of waste disposal, sanitized fertilizer, and ancillary energy. These aspects depend on the details of the process currently being developed. Preliminary estimates indicate that when all costs and benefits are considered, the technology has advantages over other alternatives for this application. The carbon dioxide capture portion of the process is intended principally for gas conditioning. Carbon dioxide is a co-product and H<sub>2</sub> purification is usually necessary. The potential for utilization of the captured CO<sub>2</sub> in the production of chemical products is under investigation as a part of maximizing the utility of the proposed self-contained system. Figure 1 shows an overview of major process inputs and products.

### Approach

We have developed methods to optimize hydrogen production from waste through the use of a fermentation process. The optimization procedure forms the foundation for the subsequent development of a modular device that will use various waste streams, including garbage, animal or human waste, and DDGS for the production of hydrogen. This hydrogen will be separated from the bio-gas stream by use of nano catalyst or a membrane for use in a fuel cell or reciprocating engine to produce electricity locally. Methods

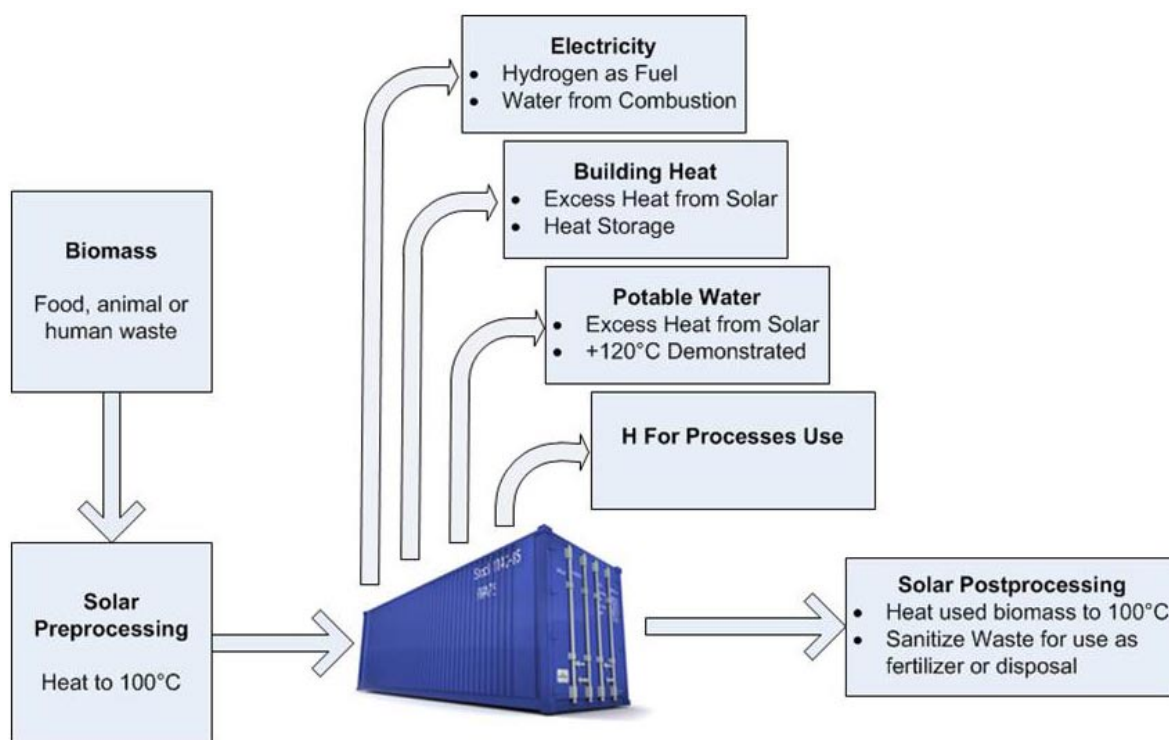


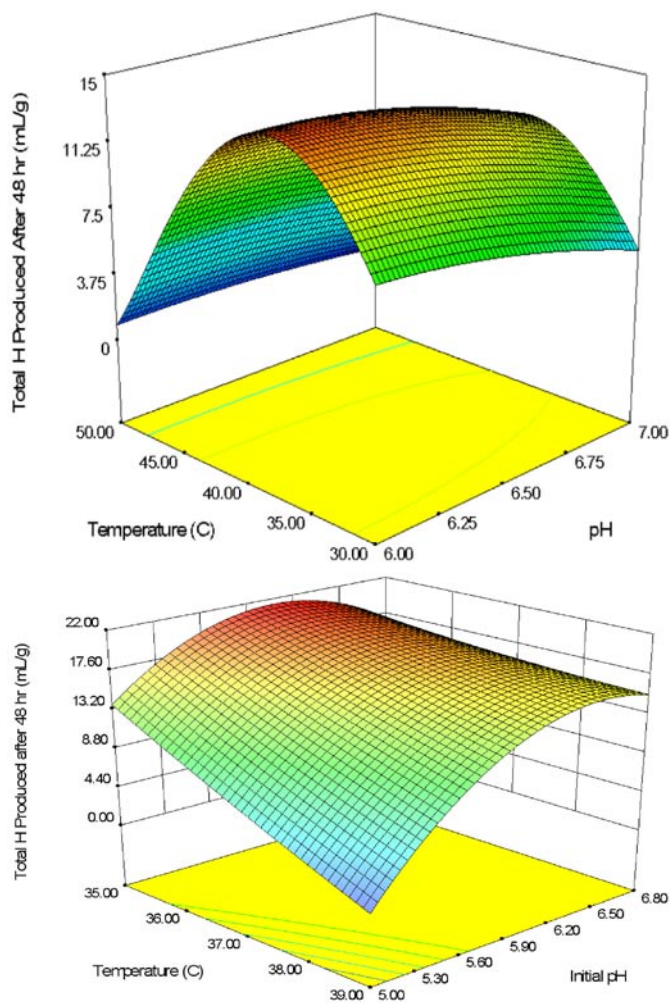
FIGURE 1. Modular System Major Inputs and Products

to sequester  $\text{CO}_2$  as part of the process are also being considered. Energy for the pre- and post-processing of feed streams is being obtained from a solar collector system. A steam generator is attached to the solar system and is used to test production of potable water. Computer simulations of the process indicate that the system can be installed in a shipping container and used to provide local electric and thermal energy. Initial efforts have reduced the amount of water in the processed waste material from 98% to 75% with minimal decrease in hydrogen production. By reducing the fraction of water it will be possible to reduce the volume and weight of the bio reactor and increase the system efficiency and viability.

## Results

Additional inocula have been tested and the concentration of hydrogen in the produced gas has been correlated with the experimental variables: pH, temperature, and substrate concentration. We have developed a new procedure for producing hydrogen with DDGS that shows considerably higher hydrogen production levels than any observed to date. We continue to investigate this approach. If verified, this may provide a new alternative for increasing hydrogen production levels with DDGS and provide a potential enhancement to the energy balance for ethanol production. Considerable interest in these results has been shown by the Industrial Advisory Board for the project since it could be of value for multiple industrial processes.

Test samples and data are being exchanged between Purdue Calumet and Lafayette and trials to test repeatability continue. A micro gas chromatograph (GC, CP-4900 Dual Channel Micro-GC; Varian Inc., equipped with a thermal conductivity detector and a 10 M-5A molecular sieve column with argon as the carrier gas for hydrogen and a 10 M Poraplot® [Varian, Inc.] column with helium as the carrier gas for  $\text{CO}_2$ ). The testing program is based upon a central composite experimental design. We are currently completing the fourth iteration for the optimization of the hydrogen production levels. This process identifies combinations of operating variables that maximizes hydrogen production. Figure 2 shows a comparison of hydrogen production from the initial and optimized procedure for hydrogen production from DDGS for the multiple testing device. The multiple testing device that was developed as part of this research effort is fully operational and is being used to generate data. This device provides the capability to conduct multiple simultaneous tests with automated data processing and monitoring. Continuous production testing is currently being conducted at Purdue Lafayette. Testing of dry substrate designs are being investigated at Purdue Calumet and Lafayette. The model for the modular energy system was updated based upon new experimental values. Efforts using a catalyst process for capture of carbon dioxide have been initiated. The solar system testing for sanitizing waste material and production of potable water is ongoing.



**FIGURE 2.** Comparison of  $\text{H}_2$  Concentration for Previous (Top) and Optimized (Bottom) Method for DDGS

## Conclusions and Future Directions

The biological hydrogen production work will include investigating optimal hydrogen production cultures for different substrates, reducing the water content in the substrate, and integrating results from the vacuum tube solar collector pre and post processing tests into an enhanced energy system model. The automated testing device will continue to be used to consider optimal hydrogen production conditions using statistical testing procedures. Testing with the continuous fermentor will be expanded to consider issues associated with continuous feed of substrate and scale up of the process. Gas flow from the fermentor is being measured with a mass flow meter. These flow values, combined with GC analysis data, are used to determine the concentration and volume of gas produced as a function of time. Values of pH are recorded continuously and are used to compare hydrogen, dissolved oxygen, and pH values as a function of time. We will also explore existing catalytic methods including nano catalysts for capture of  $\text{CO}_2$  from

the fermentation process. The next phase of the research will involve the construction a bench top reactor based on the current test results and designs that will operate with dryer waste material and use solid material handling techniques. Funding is currently not available for the actual construction of the dry bench top test unit. This research considers hydrogen production, but also considers the leveraging of other value streams to overcome design issues that have arisen in the past. We consider this process to have significant value for waste processing and heat production as well as hydrogen production. The use of catalysis to condition the bio-gas stream also adds value to the process that has not been considered in the past for this application.

### **FY 2011 Publications/Presentations**

1. Kramer, R., Pelter, L., Patterson, J., Kmietek, K., “Modular Energy Production From Waste”, accepted for publication World Energy Engineering Congress, 2011.
2. Kramer, R., Pelter, L., Patterson, J., Kmietek, K., Ting, E., “Modular Waste/Renewable Energy System for Production of Electricity, Heat, and Potable Water in Remote Locations”, submitted for publication, IEEE Global Humanitarian Technology Conference, 2011.
3. Kramer, R., Pelter, L., Liu, W., Branch, R., Martin, R., Kmietek, K., “Utilization of Solar Heat for Processing Organic Wastes for Biological Hydrogen Production”, Energy Engineering, 108, 3, 2011.
4. Kramer, R., Patterson, J., Pelter, L., Ting, E., “Modular Solar/Biological Waste Processing System for Local Production of Energy and Hydrogen,” manuscript in preparation.