

# Purdue Hydrogen Systems Laboratory

## Part I: Modular Energy System Employing Anaerobic Biological Production of Hydrogen

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June 2010

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# Overview

## Timeline

**Start – September 2006**  
**End – September 2010**  
**80% complete**

## Budget

- \$3,659,403\*
  - \$2,875,500 (DOE)
  - \$50,000 (FFRDC)
  - \$733,903 (Cost Share)
- Funding received in FY09  
 \$951,500

\* This is the overall budget for both hydrogen production and storage research. This presentation only covers the production part.

## Barriers

### Barriers addressed

- AL. H<sub>2</sub> molar yield
- AK. Feedstock cost
- AL. Systems engineering

### Targets

	2007	2010	2015
Hydrogen Concentration (volume %)	10	15	> 25
Achieved to Date	9	14	

## Partners

- Cargill
- INEOS Technologies
- Advanced Power Technologies
- BP
- NREL
- Ajinomoto Food Ingredients, LLC

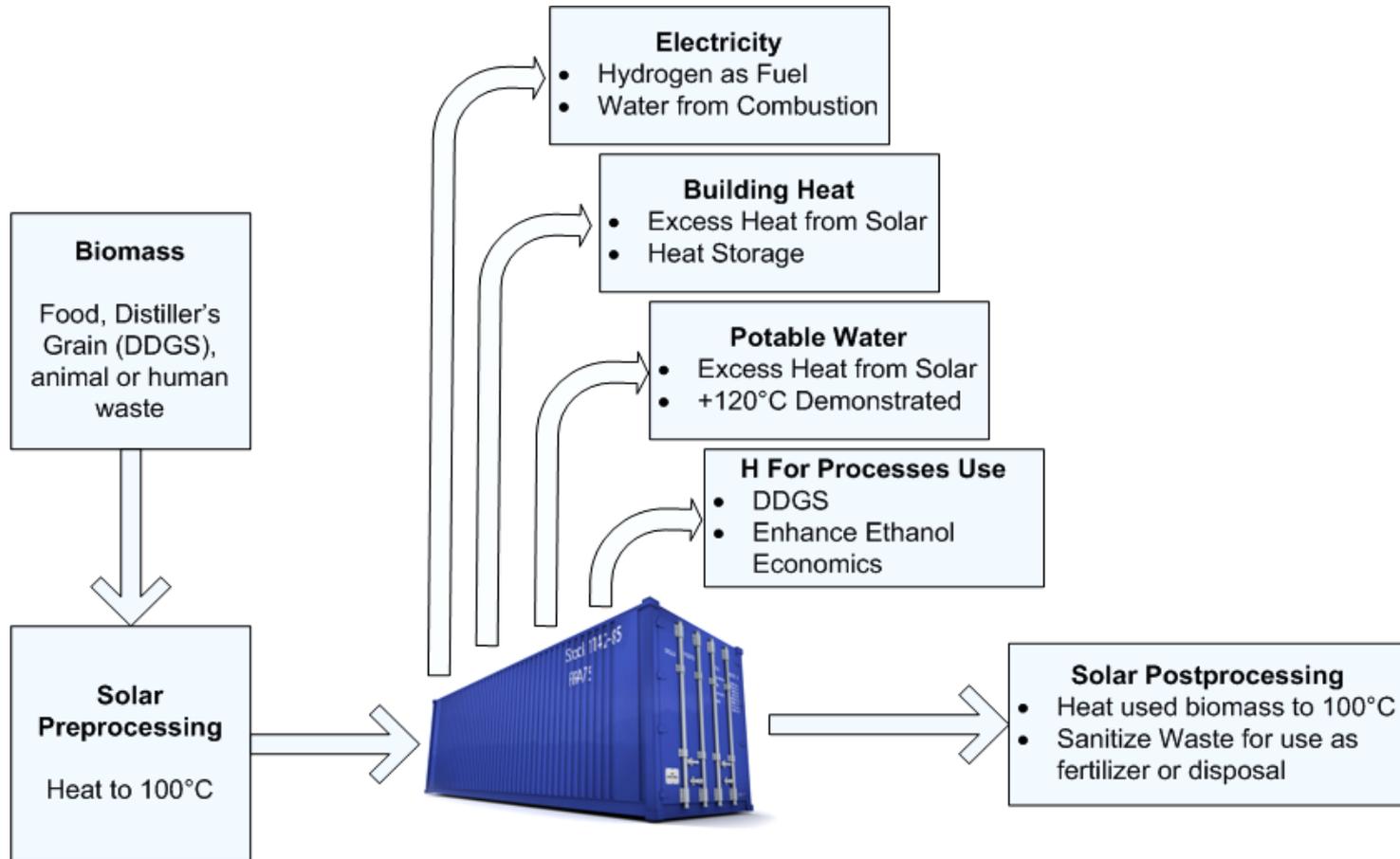
## Project Objectives - Relevance

- Increase the biological production of hydrogen by optimizing the anaerobic fermentation of organic wastes for applications, such as local energy production, that produce value in the short term and leverage the technology for expanded future applications.
- When the value of ancillary energy and waste disposal are considered, the developed technology is comparable or lower in cost than current alternatives for remote applications. Due to scale, the electric generation efficiency will be 25-50% smaller than that of large power plants, but since the feed material for the system has minimal (or possibly negative) value, the technology will be comparable or less expensive than current alternatives for these applications, when all costs and benefits are considered.
- Leverage all related energy processes to optimize value, increase commercial applications, and decrease technological, timing, and business risk. Reduces CO<sub>2</sub> emissions and environmental and health issues associated with various organic wastes.
- Investigate new methods to use Distiller's Grain to produce hydrogen for process or commercial purposes thereby increasing the energy efficiency of ethanol production.
- Develop a solar thermal energy system to locally pre and post process associated waste streams and thereby reduce ancillary energy requirements, reduce environmental contamination, and provide limited ancillary heat and potable water.
- Identify methods to separate hydrogen from bio gas and investigate feasibility of using catalysis to produce a marketable chemical product from the produced carbon dioxide.

## Approach

- Investigate methods to increase hydrogen production from organic waste streams using microbial fermentation through the use of an automated statistical experimental design that employs variations in organism type, waste, pH, temperature, buffer, and waste concentration to determine the optimal operating condition.
- Develop and utilize automated testing device to speed the determination of parameters that maximize hydrogen production.
- Investigate various microbial consortia.
- Investigate various waste materials that maximize value. Utilize a continuous feed fermentor to determine key operating parameters for hydrogen production and initiate efforts to scale up the process.
- Utilize a vacuum tube solar collector system for the pre and post treatment of organic waste material and investigate suitability of sanitized waste by product as fertilizer.
- Minimize ancillary energy requirements and investigate alternatives for CO<sub>2</sub> use.
- Develop initial designs for operating parameter and process control for the modular energy system.
- Develop designs for implementation of the technology as a local electric and thermal energy source.
- Use the vacuum tube solar collector system to produce potable water.

# Approach



## Milestones

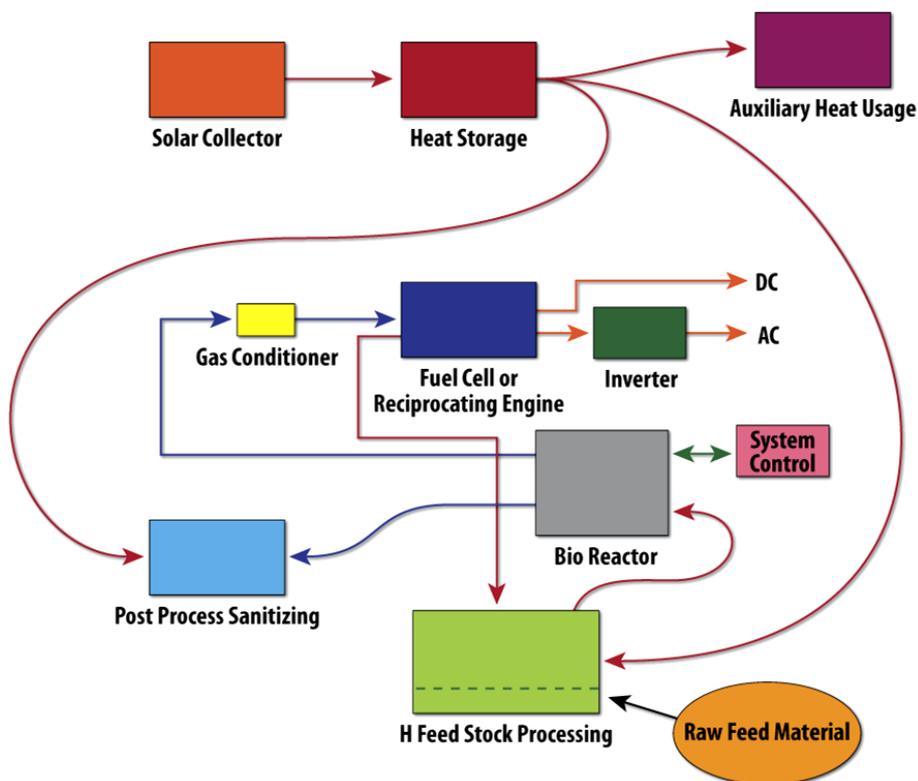
Month/Year	Milestone or Go/No-Go Decision
Nov-08 Apr-09 Sep-09	Make contacts with industrial advisors and hold industry advisor meetings. 100% complete
Aug-09	Milestone: Complete development and initial testing of automated testing device to determine optimal conditions for anaerobic hydrogen production. This device accelerates the determination of optimal hydrogen production conditions. Consider design for batch vs continuous methods. 100% complete
Jun-10	Milestone: Construct solar system, including a processing test vessel. Evaluate effectiveness for processing waste. 99% complete
Sep-10	Milestone: Consider hydrogen production from low water content substrates. 90% complete
Sep-10	Milestone: Initial evaluation of inocula and operating conditions that maximize hydrogen production. 90% complete

## Previous Technical Accomplishments

- Testing of various combinations of microbial consortia was conducted with organic waste materials to determine parameters that maximize production. It was determined that pH, temperature and waste material concentration had the greatest influence on hydrogen production for the test conditions considered.
- An automated testing system was designed and constructed as a tool to assist in determining optimal operating parameters for the process.
- An energy balance model was developed to assess the value of the technology as a local energy source.
- Tests of continuous production system conducted at NREL for Purdue food waste and inoculum samples.
- Added a steam generator to the vacuum tube solar collector system and used this to investigate feasibility of distilling water.

# Technical Accomplishments and Progress

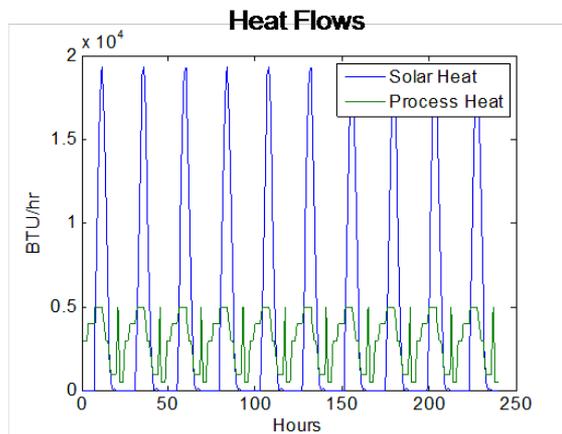
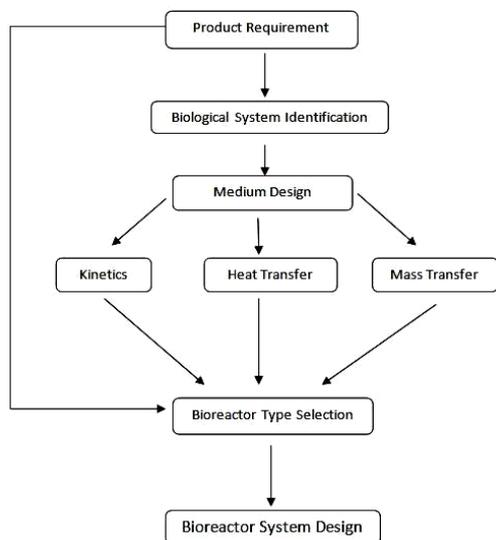
## Development of a Modular System for Local Energy Production



- The initial design of a modular energy system for local energy production and waste treatment has been completed and is being used to optimize value.
- Organic waste material is used in an anaerobic process to produce hydrogen. A new procedure has approximately doubled hydrogen production from Distiller's Grain.
- Research to maximize hydrogen production with a statistical experimental design is ongoing. A 3 L batch/continuous fermentor is being implemented to enhance testing and consider scale up issues.
- Solar thermal system is used for pre and post waste processing and other ancillary uses such as building heating and production of potable water.
- Initial designs are being investigated for development of a prototype system with reduced substrate water concentration.

# Technical Accomplishments and Progress

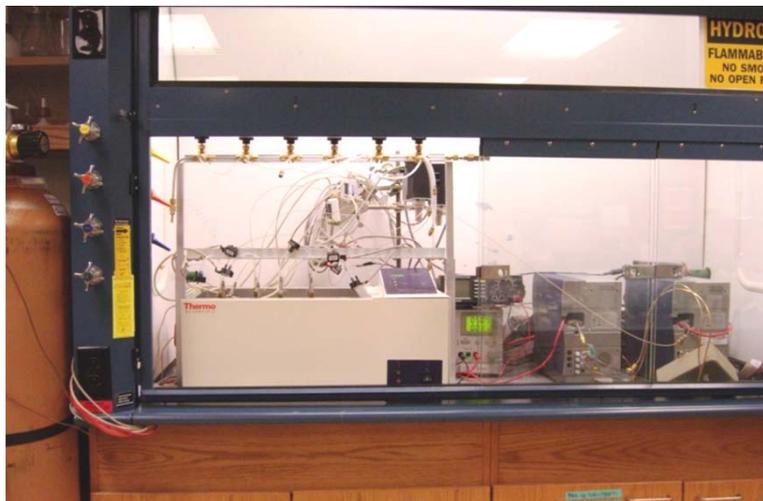
## Development of a Modular System for Local Energy Production



- Initial designs of the material, process, and energy flows for the modular energy system were developed and used to evaluate design and operating alternatives.
- Initial experimental hydrogen production rates were used to determine the size and timing for a prototype design. Next step is to develop bench top test unit with reduced water concentration and material handling.
- Electric output from energy model based on measured hydrogen production levels (10 mL H<sub>2</sub>/ g substrate in 36 hours) was used as a modeling parameter for the basic energy balance.
- The solar system was sized to provide heating for pre and post processing and limited ancillary purposes.
- Heat storage is used to store excess heat for purposes such as building heating.
- Use of excess heat to produce potable water was tested.

# Technical Accomplishments and Progress

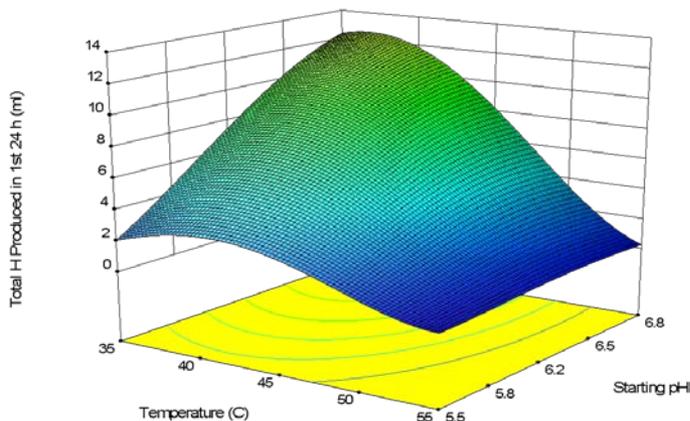
## Determination of Initial Optimal Hydrogen Production Parameters



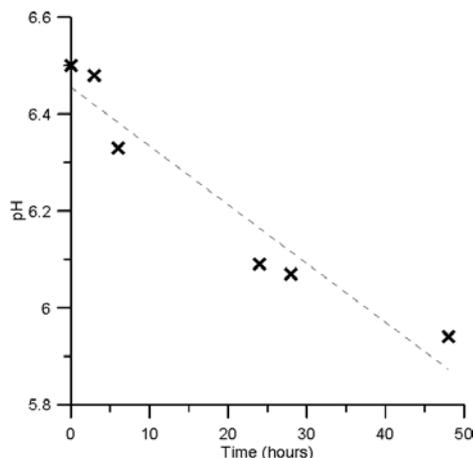
- Waste material is statistically sampled from entire stock of processed food waste and Distiller's Grain.
- Homogeneous waste is placed in 120 mL bottles, buffer is added, bottles are purged with nitrogen, bottles are sealed and autoclaved.
- Bottles are placed in constant temperature bath.
- Gas collection, pressure measuring, and purging needles are inserted into bottles.
- Bottles are purged with nitrogen until  $< 0.05\% \text{ O}_2$  is detected by Gas Chromatography (GC).
- Bottles are initially pressurized slightly with nitrogen.
- During fermentation, pressure is continuously monitored by transducers attached to each bottle.
- The head space gas is sampled automatically for each bottle over time. The composition of the gas is determined by GC analysis (Varian Micro GC equipped with molecular sieve and PoraPLOT columns).

# Technical Accomplishments and Progress

## Determination of Initial Optimal Parameters



Hydrogen produced (mL/g substrate) in 1st 24 hrs from Food Waste – Third Generation

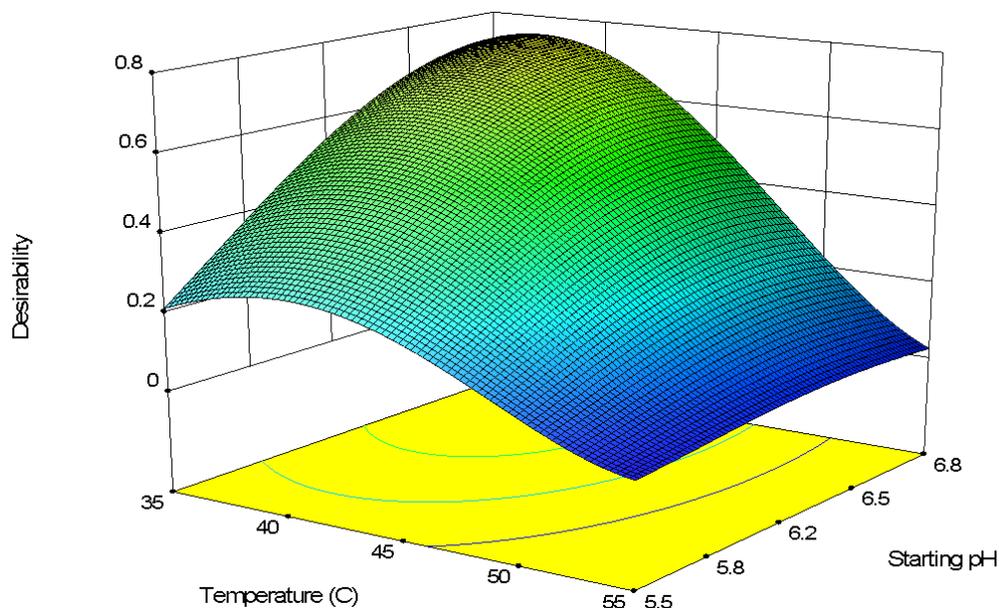


pH vs Time for Distiller's Grain Test

- Fourth generation tests are now being conducted using the developed automated testing device.
- The iterative testing approach has increased hydrogen production for both food waste and Distiller's Grain.
- A Central Composite Design was used to determine operating values that maximize hydrogen production.
- For each type of waste and inoculum, operating parameters were varied to maximize hydrogen production.
- Sensitivities to differences in substrate, pH, buffer, temperature, time, and organism were considered.
- pH values were measured at start of and selectively during the fermentation process.
- Comprehensive tests are ongoing using automated testing device.

# Technical Accomplishments and Progress

## Determination of Initial Optimal Parameters



Desirability for Hydrogen produced  
 in 1st 24 hrs from Food Waste – Third Generation

- Volume and hydrogen concentration are maximized for the Central Composite design using the Simplex Method to determine the most desirable operating conditions.
- Sensitivity tests for the predicted operating values are done to determine the validity of the prediction.
- Influence of water concentration is being considered as another optimization parameter.
- Decreasing water concentration significantly increases value for the modular energy system design.
- Water concentration has been decreased from 95% to 75% with little loss in hydrogen production rates.

# Technical Accomplishments and Progress

## Initial Food Waste Nutrient Analysis, Ford Hall Food Waste 1

Component	As Sent	Dry Wt.
Moisture (%)	06.30	////
Dry Matter (%)	93.70	////
Crude Protein (%)	17.40	18.60
Crude Fat (%)	12.60	13.40
Acid Detergent Fiber (%)	33.20	35.40
Ash (%)	03.35	03.58
Total Digestible Nutrients (%)	81.50	87.00
Net Energy-lactation (Mcal/lb)	00.85	00.91
Net Energy-maint. (Mcal/lb)	00.90	00.96
Net Energy-gain (Mcal/lb)	00.59	00.63
Digestible Energy (Mcal/lb)	01.63	01.74
Metabolizable Energy (Mcal/lb)	01.51	01.61
Sulfur (%)	00.26	00.28
Phosphorus (%)	00.25	00.27
Potassium (%)	00.37	00.40
Magnesium (%)	00.06	00.07
Calcium (%)	00.90	00.96
Sodium (%)	00.50	00.53
Iron (ppm)	66.00	70.00
Manganese (ppm)	09.00	10.00
Copper (ppm)	06.00	06.00
Zinc (ppm)	28.00	30.00

# Technical Accomplishments and Progress

## Use of Distiller's Grain From Ethanol Production

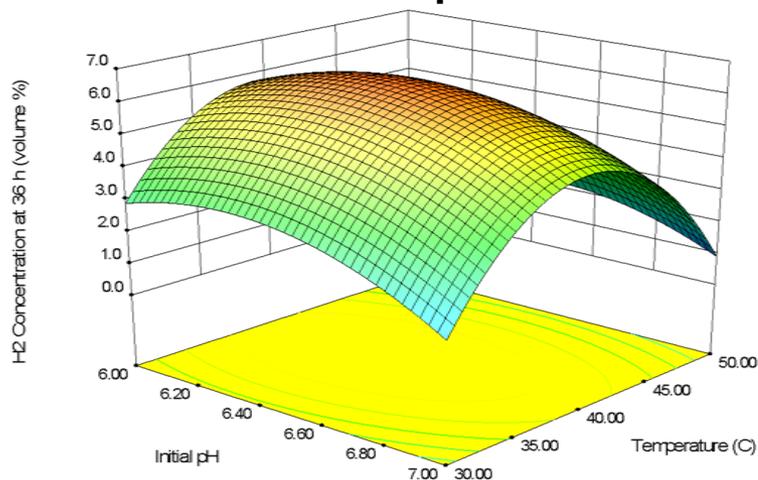


Adkins Energy, LLC

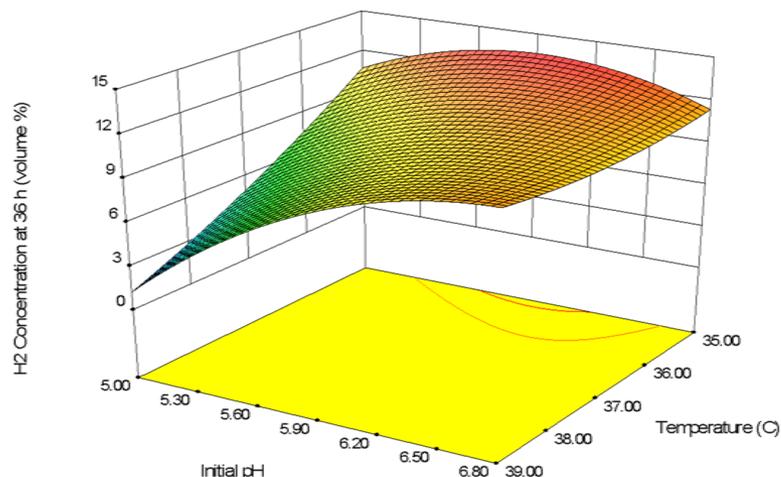
- Use of Distiller's Grain for hydrogen production is being investigated.
- With increased levels of ethanol production from corn there is an increasing amount of Distiller's Grain (residue remaining after ethanol production).
- Cattle will tolerate < 40% concentration of Distiller's Grain mixed with feed.
- Significant hydrogen production was demonstrated using DDGS as substrate. New method has doubled production levels.
- Currently considering effect of inoculum type and concentration, pH, and substrate concentration.
- 120 ml serum bottles used for gas production.
- Initiating efforts to use fermentor to maximize hydrogen production for larger batch sizes and continuous feed of DDGS.

# Technical Accomplishments and Progress

## Determination of Optimal Parameters For Distiller's Grain From Ethanol Production



Previous H Production From Distiller's Grain

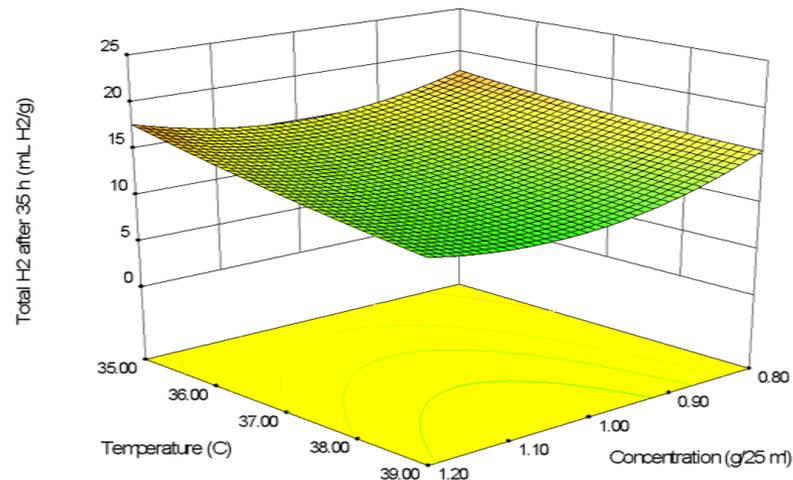
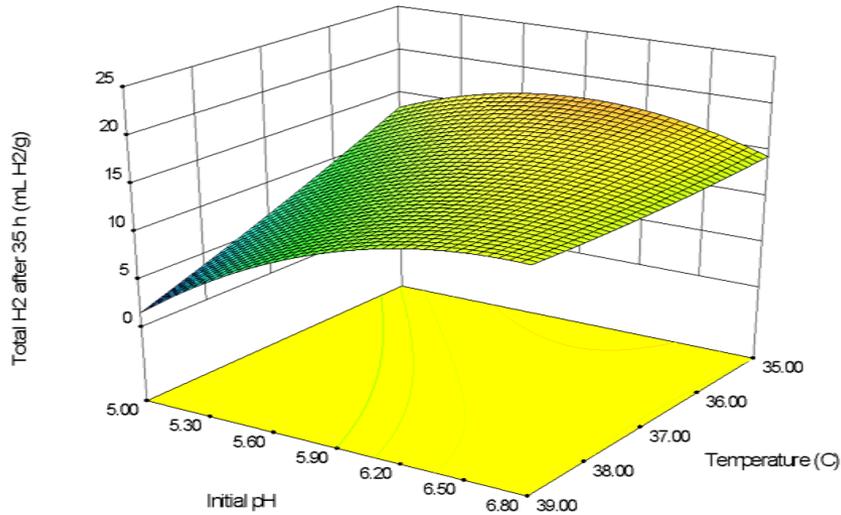


Current H Production From Distiller's Grain  
 Using Optimized Method

- Central Composite Design is used to determine operating values that maximize hydrogen production. anaerobic
- DDGS type, inoculum, and operating parameters are varied to determine what combination of conditions maximizes hydrogen production.
- Sensitivities to operating parameters are being considered.
- pH values are recorded at the start of the fermentation process.
- Comprehensive tests are ongoing using automated testing device.

# Technical Accomplishments and Progress

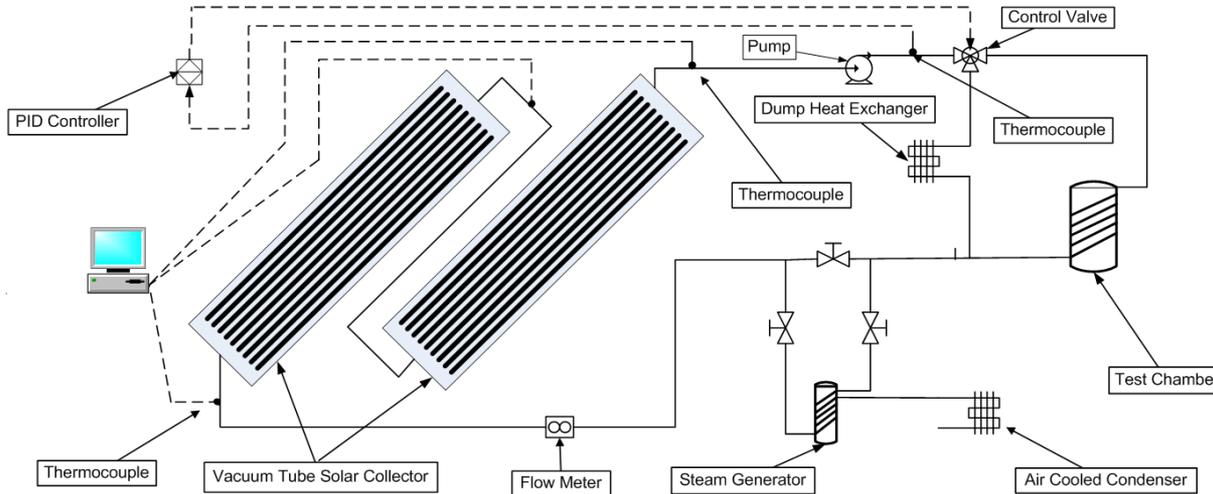
## Determination of Optimal Parameters For Distiller's Grain From Ethanol Production



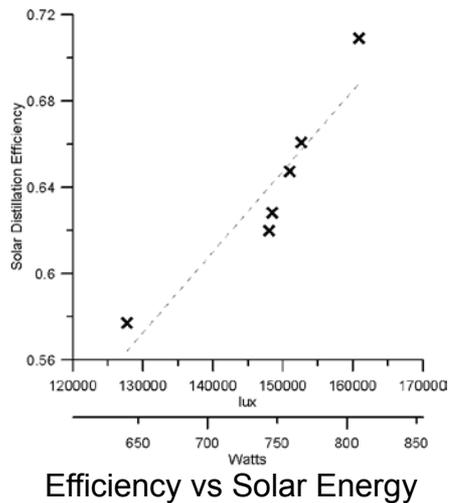
- Volume and hydrogen concentration are maximized for the Central Composite design using the Simplex Method to determine the most desirable operating conditions.
- Maximized operating conditions has shown significant increase in hydrogen production levels for second generation tests of Distiller's Grain.
- Sensitivity to different substrates and inoculum are being considered.
- Influence of water concentration is being considered as another optimization parameter. Production levels at higher substrate concentrations (up to 1.2 g/25 mL from previous value of .7 g/25 mL) has increased for optimized method.

# Technical Accomplishments and Progress

## Solar Thermal System Designed, Constructed and Tested

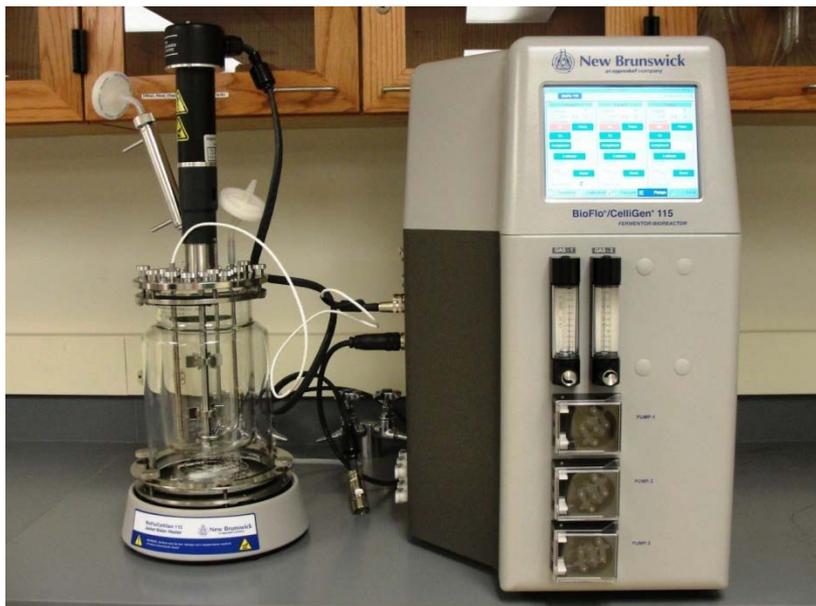


- Vacuum tube solar collector used to produce heat for pre and post processing.
- Control system developed to produce high temperatures.
- Routinely obtain temperatures + 120 °C.
- Waste material is routinely batch processed.
- Steam generator tests demonstrated ability to distill water with maximum solar energy conversion efficiency of ~70%.



# Technical Accomplishments and Progress

## Larger Scale Batch and Continuous Testing Being Implemented

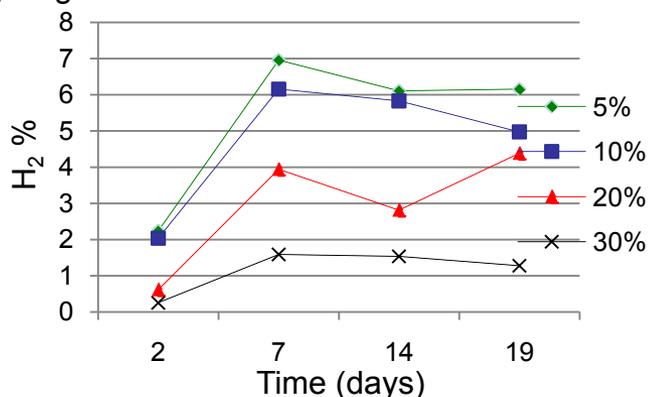


- Batch sizes up to 3 L and continuous sample flow aspects are starting using a fermentor.
- Allows for continuous pH and temperature measurement - control, gas mass flow measurement, and gas sampling.
- Consideration of process scale up issues is being expanded.
- Expanded testing of influence of water concentration on hydrogen production.
- Initial testing involves batch and continuous feed cases for Distiller's Grain

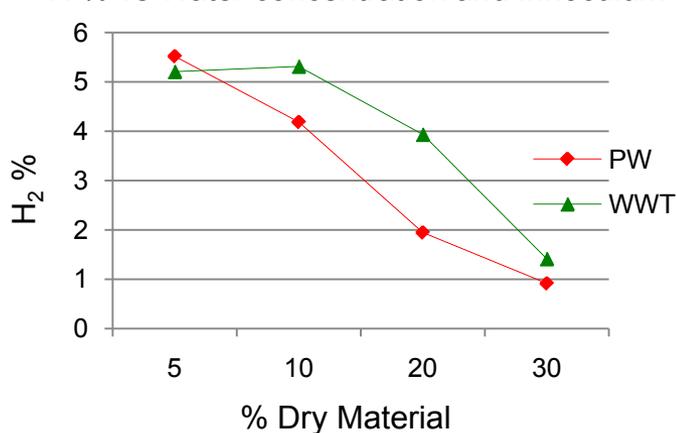
# Technical Accomplishments and Progress

## Reduce Water Concentration

Hydrogen % for Various Substrate Concentrations



H<sub>2</sub> % vs Water concentration and Inoculum

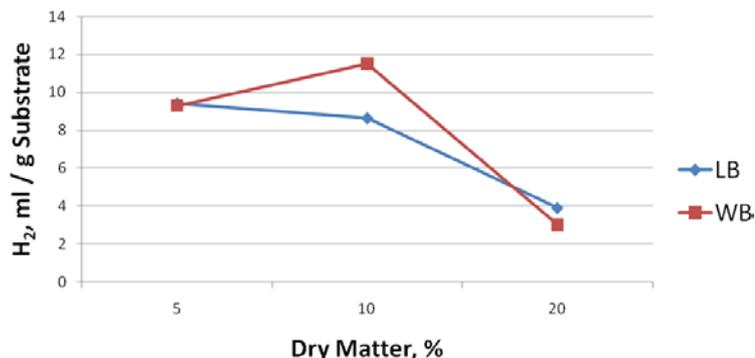


- Reducing water content allows for a decrease in size and weight of modular hydrogen energy system and thereby improves economics and viability.
- Food waste was dried at 50 °C and then passed through 1 mm screen in a hammer mill with dry ice.
- Dried food waste (1.0 g ± 0.05 g) was added to vials and appropriate amounts of anaerobic buffer was added to give final concentrations of 5%, 10%, 20% and 30%.
- The vials were autoclaved and cooled.
- Vials were inoculated with 1.0 ml of diluted pig waste (PW) or waste water anaerobic sludge (WWT) and incubated at 37 °C.
- Production occurs in tubes that are rotated along their axis with and without glass beads to study influence of reduced water concentration.
- Currently investigating use of support structures to further reduce water concentration.

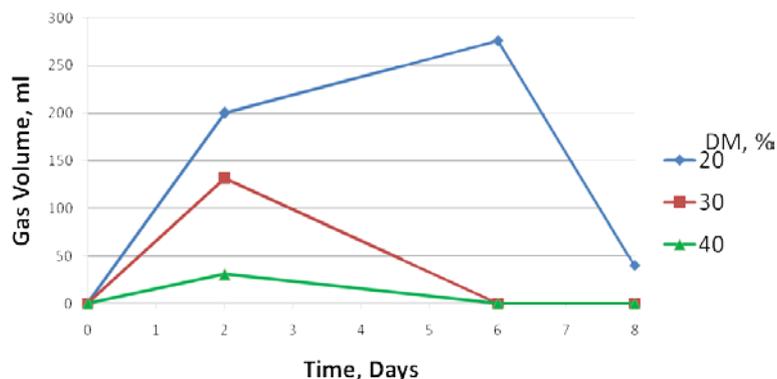
# Technical Accomplishments and Progress

## Reduce Water Concentration

H<sub>2</sub> Production from Food Waste, Influence of Inoculum and DM%



Gas Production from Food Waste, Influence of Dry Matter % and Incubation Time



- Hydrogen production was similar for inoculums from the Lafayette and West Lafayette Waste Water Anaerobic Digesters
- Reducing water content allows for a decrease in size and weight of modular hydrogen energy system.
- Major challenge involves maintaining hydrogen production levels as concentration increases.
- Methods to physically move the substrate through the modular system are being investigated that involve minimal use of energy.
  - Horizontal and vertical configurations under consideration.
- Methods to support drier substrate and facilitate gas transfer are being investigated
  - Coating on tubular structure
  - Coating on plate structure
  - Addition of glass beads to enhance support
- Methods to maintain temperature and pH with reduced water content are under development.

## Collaborations

- Communications and collaboration with National Renewable Energy Laboratory have continued.
- Periodic advisory board meetings are held to gain input from industry.
- Advisory board members include: Cargill, INEOS Technologies, BP, Advanced Power Technologies, and Ajinomoto Food Ingredients, LLC.
- Collaborative efforts with researchers at the Purdue Calumet and Lafayette campuses continue.

## Future Work

- Continue efforts to increase hydrogen production by optimizing operating parameters.
- Continue efforts to reduce the water concentration of waste material during processing.
- Commence larger sample testing and continuous parameter control with fermentor.
- Consider influence and optimize hydrogen production for larger batches and continuous substrate feed using fermentor and continuous mass flow measurement of produced hydrogen.
- Obtain and test new waste materials including additional testing of Distiller's Grain.
- Continue initial design of bench top test reactor.
- Continue modular energy system design and optimization of energy production and cost/benefit.
- Start conceptual design for commercial prototype system to be housed in a shipping container.

## Project Summary

- Currently developing engineering designs for a continuous process with greatly reduced water content. The next step is to construct a bench top reactor based on these 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.
- Operating parameters that maximize hydrogen production for initial inoculum and waste material samples have been identified.
- The solar thermal system has been effective in pre and post processing of waste material and expanding the value to include production of a sanitized fertilizer product.
- Initial results indicate this approach can viably be used for local energy production.
- Other uses for excess solar heat including building heating and potable water production are under investigation.
- Possibility of conversion of carbon dioxide into a marketable chemical product is being investigated.

## Questions?

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