

IV.F.2 Purdue Hydrogen Systems Laboratory*

Jay Gore (Primary Contact), P. Ramachandran, A. Varma, Y. Zheng, R. Kramer (Purdue Calumet), J. Patterson, P. Maness (NREL), E. Shafirovich, P. Gagare, M. Diwan, S. Basu, A. Brockman, E. Ting (Purdue Calumet), L. Pelter (Purdue Calumet)

Purdue University
500 Central Drive
West Lafayette, IN 47907
Phone: (765) 496-2829; Fax: (765) 494-9321
E-mail: gore@purdue.edu

DOE Technology Development Manager:
Grace Ordaz

Phone: (202) 586-8350; Fax: (202)586-9811
E-mail: Grace.Ordaz@ee.doe.gov

DOE Project Officer: Jim Alkire

Phone: (303) 275-4795; Fax: (303)275-4753
E-mail: James.Alkire@go.doe.gov

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*Congressionally directed project

Objectives

- Understand catalytic ammonia borane (AB) dehydrogenation and discover novel procedures for recycling the spent borates.
- Develop AB slurry-based subscale onboard hydrogen storage systems.
- Develop new non-catalytic methods for hydrogen generation from AB and water.
- Investigate production of hydrogen from various waste streams using microbial fermentation.
- Study implementation of the hydrogen production and storage methods into an energy system.

Technical Barriers

This project addresses the following technical barriers from the 3.1.4 and 3.3.4 sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 2007).

The relevant subsections are listed below with labels and designators from the above document.

On-board Hydrogen Storage Technical Barriers

- (A) System Weight and Volume
- (B) System Cost
- (J) Thermal Management
- (R) Regeneration Process
- (S) By-product/Spent Material Removal

Biological Hydrogen Production Technical Barriers

- (AR) H₂ Molar Yield
- (AT) Feedstock Cost
- (AU) Systems Engineering

Technical Targets

Off Board Regeneration	Units	2010/2015	Purdue 2007
Regeneration Energy Efficiency	%	60%	TBD
Regeneration Mass Efficiency	Mass %	90%	64%

On-board Storage	Units	2010/2015	Purdue 2007
System Gravimetric Capacity	H ₂ wt%	6/9	7.5 (material)

Biological H ₂ Production	Units	2013/2018	Purdue 2007
Hydrogen Yield Percentage	mol H ₂ /mol glucose	4/6	1* *utilizing organic wastes with ~25% weight percent of glucose

TBD - to be determined

Accomplishments

- Achieved 64% overall yield of AB regeneration from borate.
- Demonstrated the use of AB slurry hydrolysis with measured hydrogen capacity of 7.5 wt% and measured dehydrogenation rate of 0.032 g H₂/s/kg-slurry at room temperature.
- Demonstrated that heating aqueous AB solutions to temperatures 117-150°C under modest pressure (~10 atm), and without use of catalyst, releases three equivalent hydrogen per mole AB.

- Isotopic (D_2O) tests clarified the mechanism of non-catalytic hydro-thermolysis, showing that in the released three equivalent of hydrogen per mole AB, 2-2.1 equivalent originate from AB and 0.9-1 equivalent from water.
- The experimental matrix-assembly is operational with pressure and pH measurement instrumentation.
- A process to increase the homogeneity of feed material is operational.
- The solar thermal apparatus for providing heat for pre- and post-processing of biomaterial is operational.



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 U.S. DOE Hydrogen, Fuel Cells, and Infrastructure Technologies Program.

The hydrogen storage work has been focused on improving the engineering performance of AB-based onboard hydrogen storage and finding energy efficient ways to recycle the byproducts. The AB slurry dehydrogenation work has been focused on measuring engineering properties, which are critical to system gravimetric and volumetric capacities, onboard hydrogen discharge, fresh/spent fuel transfer and segregation, and long term storage. Slurries are easier to be transported onboard than solids. Slurries can provide higher energy capacity than solutions and may be highly desired when the byproduct solubility is significantly lower than that of the reactant. We will develop a subscale AB slurry reactor module to provide a platform for the studies of AB and other potential off-board recyclable hydrogen storage materials. In addition, an innovative method utilizing aqueous AB solutions with no catalyst is also being investigated. In this approach, the solution is heated to temperature $\sim 120^\circ\text{C}$ under modest pressure (<10 atm).

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.

Approach

We are developing methods for AB dehydrogenation and regeneration that will enable its use for onboard hydrogen storage. We screened various transition metal catalysts for AB hydrolysis and found that ruthenium (Ru) resulted in the best performance. Using a bench-scale experimental apparatus (approximately 350 mg H_2), we measured dehydrogenation conversions, dehydrogenation kinetics, and ammonia generation of fresh and aged (60 days) aqueous AB solutions and AB slurries up to the AB to water molar ratio of 1:2. We also tested and simulated a subscale (~ 1 kW_e) AB solution reactor with consideration of coupled heat/mass transfer and chemical reaction. We will improve the Ru catalyzed AB slurry hydrolysis approach by using advanced ultrasonic slurry/solution mixing techniques to achieve higher than 8.5 wt% hydrogen storage capacity. We will also design, test, model and analyze a benchmark continuous flow AB slurry reactor module to address various common engineering issues in onboard chemical hydrogen storage systems, such as slurry handling and thermal management.

We also characterized the AB hydrolysis byproducts and initiated a regeneration scheme involving the use of $NaAlH_4$. We will develop novel regeneration procedures to convert the spent borates to triacylborates followed by their reduction to AB in high yield and purity without using $NaAlH_4$.

Since significant decomposition of AB occurs at temperatures 100 - 170°C , it is expected that heating aqueous AB solution up to such temperatures may stimulate hydrolysis. To suppress water boiling, we are conducting AB hydrothermolysis under inert gas pressure (5-10 atm) without the use of catalyst. To clarify the reaction mechanisms, isotopic labeling (D) is used, where measurements of H_2 and HD concentrations in gaseous products allow us to differentiate between the sources of the released hydrogen, i.e. AB vs. water.

We are also considering methods to optimize hydrogen production and will form the foundation for the subsequent development of a modular device that will use various waste streams, including garbage and possibly animal or human waste, 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 to sequester carbon dioxide as part of the process are also being considered. Energy

170°C. Note that the constancy is even more striking for the sum of H₂ and HD, i.e., some redistribution between H₂ and HD occurs but the total amount of released hydrogen remains the same (3 equivalent). There is no significant effect of pressure or heating rate on either amount over the tested ranges of initial pressures and heating rates (11.2-18 atm and 1-10°C/min, respectively). A ¹¹B nuclear magnetic resonance (NMR) spectrum of the obtained condensed products shows the formation of boric acid, B(OH)₃, in good agreement with the NMR results for catalyzed AB hydrolysis. The presented results indicate that heating AB/D₂O solution to temperatures 117-170°C releases 3 equivalent (H₂ + HD), where the H₂/HD mole ratio varies in the range from 1:2 to 1.25:1.75. Note that total hydrogen originating from AB is expressed as H₂ + 0.5HD, where H₂ varies from 1 to 1.25 and HD from 2 to 1.75. Thus, independent of the specific reaction pathway, in the produced 3 equivalent of hydrogen, 2-2.1 equivalent comes from AB. For comparison, dry thermolysis of AB at temperatures less than 135°C yields 1.1±0.1 equivalent hydrogen, while ionic liquids based methods provide only up to 1.6 equivalent.

Various inoculua have been tested and the concentration of hydrogen in the produced gas has been correlated with the experimental variables: pH, temperature, and substrate concentration. A micro gas chromatograph is used to determine the composition of the produced gas. The testing program is based upon a central composite experimental design. A preliminary numeric optimization of the hydrogen production level was conducted to identify combinations of variable that produce maximum amounts of hydrogen. Figure 3 depicts the optimization using the Simplex methodology with an optimum point at 37°C, starting pH 6.5 and 0.93

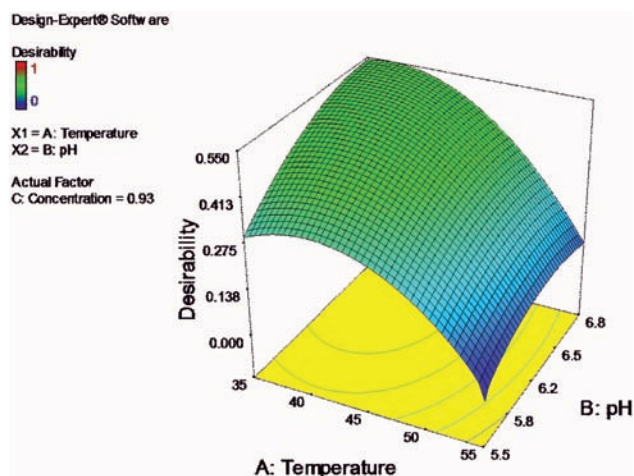


FIGURE 3. Bio-Hydrogen Production Optimization

g/25ml concentration. Construction of a multiple testing device is completed. This device provides the capability to conduct multiple simultaneous tests with automated data processing and monitoring. Continuous production testing capability is currently under development at Purdue Lafayette and the National Renewable Energy Laboratory. Preliminary approaches to a dry substrate design are being investigated at Purdue University Lafayette. The model for the modular energy system was updated. New experimental values were used for production and sizing calculations. Efforts using a catalyst process for capture of carbon dioxide have been initiated. The production of potable water from the modular system is also being considered as a future enhancement to the process.

Conclusions and Future Directions

We investigated fundamental chemistry of AB recycling and achieved 64% overall yield. Using catalytic AB slurry hydrolysis, we have demonstrated a slurry-based hydrogen storage capacity of 7.5 wt% at room temperature with excellent reaction kinetics (0.038 gH₂/s/kg). In addition, we have discovered a non-catalytic hydrogen generation approach using AB hydrothermolysis. The obtained results on AB hydrothermolysis suggest that heating aqueous AB solutions to temperatures >120°C under modest pressure (~10 atm) is a promising noncatalytic method for releasing hydrogen from AB. Finally, the biological hydrogen production component of the project has been conducted with a focus on optimizing the microbial fermentation process for hydrogen generation.

We will work towards maximum AB recycling yield *via* a novel recycling pathway. We will improve the AB slurry hydrolysis approach by using advanced ultrasonic slurry/solution mixing techniques. We will also develop a subscale AB aqueous and/or non-aqueous slurry reactor module to address various common engineering issues in on-board chemical hydrogen storage systems. Further, investigations to determine the actual reaction route in AB hydrothermolysis, and reaction kinetics, using methods that allow one to distinguish H and D in the molecular structure, are planned. 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 developed will be used to further consider optimal hydrogen production conditions using statistical testing procedures. We will also explore existing catalytic methods including nano catalysts for capture of CO₂ from the fermentation process.

FY 2008 Publications/Presentations

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11. Shafirovich, E., Varma, A., and Diwan, M., "Method for Releasing Hydrogen from Ammonia Borane," *Provisional Patent Application* No. 60/957, 11 (2007).
12. Ting, E., Susoreny, S., Krajnak, K., Pelter, L., and Kramer, R., "Production of Hydrogen by Dark Fermentation of Food Waste", *American Society for Microbiology Meeting*, Boston, June 1-5, 2008.