IV.G.5 Purdue Hydrogen Technology Program*

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*Congressionally directed project

Objectives

- Investigate and evaluate initial processes for the production of hydrogen from various waste streams using microbial fermentation and investigate possible paths for implementation of the research in an energy source.
- Understand catalytic and thermal mechanisms for hydrolysis/alcoholysis of ammonia borane and to identify viable routes, including recycling, for practical applications.
- Develop a new method for hydrogen generation from water and ammonia borane using self-sustained combustion reactions.
- Develop a subscale recyclable ammonia borane based hydrogen storage system and investigate thermal management issues.

Technical Barriers

This project addresses the following technical barriers from the Production (3.1.4.2) and Storage (3.3.4.2) sections of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan (Revision 1, 2005):

Biological Hydrogen Production

The technical barriers of the present biological hydrogen production using organic wastes are not addressed in the DOE multi-year plan yet. The technical barriers, however, are similar to those addressed in Dark Fermentative Hydrogen Production as follows,

(AI) H_2 Molar Yield
(AK) Feedstock Cost
(AL) Systems Engineering

On-board Hydrogen Storage

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

Technical Targets

On-board Storage	Units	2007	2010	2015
System Gravimetric Capacity	kWh/kg	1.5	2	3

Biological H_2 Production	Units	2007	2010	2015
Hydrogen Yield Percentage	%	20	40	> 45

Approach

We will determine the biological, chemical, and physical parameters that influence hydrogen production levels and develop a scheme to optimize production. We will also develop an energy model that integrates design considerations with the research process.

We will conduct time-resolved temperature-dependence tests of ammonia borane/water/alcohol mixtures with different additives and determine their reactivity and thermal characteristics. Several transition metal salts in different solvents will be tested as catalytic additives; corresponding reaction rates will be measured and compared with characteristics of non-catalyzed mixtures. Combustion methods have also been recently shown to be effective stimulants for hydrogen release

from boron compounds. In this context, addition of metals, such as Al and Mg, which react with water generating heat and additional hydrogen, will also be investigated.

We will design, model and construct a sub-scale ammonia borane-based hydrogen generation apparatus and a sub-scale ammonia borane recycling apparatus. We will conduct systematic tests to obtain comprehensive process data of recyclable chemical hydride-based systems. To develop our understanding in thermal management needs in these apparatuses, we will also, measure thermo-chemical properties that are not available in the literature.

Accomplishments

We have achieved the following:

- Verified the feasibility to use anaerobic digestion of organic waste for the production of hydrogen in preliminary laboratory studies.
- Examined the transition-metal catalyzed dehydrogenation of ammonia borane in solution at lower temperatures.
- Examined the transition-metal catalyzed alcoholysis and hydrolysis of ammonia borane.
- Achieved several new syntheses of ammonia borane (and amine boranes) that should decrease the cost of ammonia borane.
- Developed mixtures of sodium borohydride with water, metal (Al or Mg) and additional minor ingredients (gellant, stabilizer).
- The developed mixtures exhibited stable combustion and 7 wt% H_2 yield, with safe solid byproducts.
- Reviewed heat transfer issues in various on-board hydrogen storage technologies, including compressed H_2, LH_2, chemical hydrides and metal hydrides.
- Measured heat of reaction and kinetics of sodium borohydride hydrolysis.
- Investigated a sub-scale (1-kW_e) sodium borohydride system experimentally and numerically.

FY 2006 Publications/Presentations

1. Zhang, J., Fisher, T. S., Gore, J. P., Hazra, D., and Ramachandran, P. V., "A Review of Heat Transfer Issues in Hydrogen Storage Technologies," International Journal of Hydrogen Energy, 2006, in press.

2. Shafirovich, E., Diakov, V., and Varma, A., "Combustion of Novel Chemical Mixtures for Hydrogen Generation," Combustion and Flame, Vol. 144, 2006, pp. 415-418.

3. Zhang, J. S., Zheng, Y., Fisher, T. S., Ramachandran, P. V. and Gore, J. P., 2006, "Experimental Study of a 1 kWe Sodium Borohydride Hydrogen Storage System," 2006 National Hydrogen Association Annual Conference, Long Beach, CA.

4. Zhang, J., Zheng, Y. Fisher, T. S., and Gore, J. P., "Modeling of Packed-bed Reactor in a Sodium Borohydride-based Hydrogen Storage System," SAE paper 06P-612, 2006.

5. Zhang, J., Fisher, T. S., Ramachandran, P. V., Gore, J. P., and Mudawar, I., "A Review of Heat Transfer Issues in Hydrogen Storage Technologies," Journal of Heat Transfer, Vol. 127, 2005, pp. 1391-1399.

6. Shafirovich, E., Diakov, V., and Varma, A., "Hydrogen Generation via Combustion of Metal Borohydride/Aluminum/Water Mixtures," Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry, Vol. 50(2), 2005, pp. 450-451.

7. Shafirovich, E., Diakov, V., and Varma, A., "Novel Chemical Mixtures for Hydrogen Generation by Combustion," 2005 AIChE Annual Meeting, October 30–November 4, 2005, Cincinnati, OH.