Purdue Hydrogen Technology Program

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May 18, 2006

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Project ID # STP 40

Overview (storage)

Timeline

- Start – June 2006
- End – May 2007

Budget

- $825,000
  - $660,000 (DOE)
  - $165,000 (Purdue)
- Funding for FY06: expected

Barriers

- Barriers addressed
  - Cost of ammonia borane
  - Formation of harmful compounds in combustion-based methods
  - Thermal Management
- Targets – storage system

		2007	2010	2015
Specific Energy	kgH_2/kg (wt%)	(4.5%)	(6%)	(9%)

Partners

- General Motors
- General Atomics

Overview (bio-production)

Timeline

- Start – June 2006
- End – May 2007

Budget

- $415,500
  - $330,000 (DOE)
  - $85,500 (Purdue)
- Funding for FY06: expected

Barriers

- Barriers addressed
  - Hydrogen production levels
  - Gas Separation
  - System Efficiency
- Targets

	2006	2010	2015
Hydrogen Production percentage	20	40	45+

Partners

- Cargill
- Grifffith Labs
- Advanced Power Technologies
- Innovene

Objectives (storage)

- Examine the dehydrogenation of ammonia borane at lower temperatures
- New synthesis of ammonia borane to decrease the cost
- Develop a method for generating hydrogen from boron-hydrogen compounds with hydrogen yield >6 wt%, no catalyst and no harmful byproducts
- Design efficient thermal management sub-systems to facilitate dehydrogenation and fast-filling processes

Objectives (bio-production)

- Provide a renewable energy source to further DOE goals for development of a hydrogen energy economy
- Use biological organisms to produce hydrogen from waste using anaerobic process
- Use solar energy to preprocess the feed material
- Produce electricity in remote locations with the produced hydrogen used in either a fuel cell or reciprocating engine
- Consider ways to produce fertilizer
- Possibly separate/sequester carbon dioxide by use of organometallic nano catalysis

Approach (storage)

- Mixtures of boron-hydrogen compounds with metal (Al or Mg) and gelled water, upon ignition, exhibit parallel reactions :

$NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4\ H_2$	$NaBH_4 + 2\ H_2O \rightarrow NaBO_2 + 4\ H_2$
$Al + 1.5\ H_2O \rightarrow 0.5\ Al_2O_3 + 1.5\ H_2$	$Mg + H_2O \rightarrow MgO + H_2$

- The highly exothermic metal-water reaction assists hydrolysis of B-H compound, eliminating the need for catalyst.
- Water is an additional H_2 source.
- Solid byproducts are environmentally friendly materials.

Approach (storage)

- Reviewed heat transfer issues in on-board hydrogen storage technologies, including compressed_H_2, LH_2, chemical hydrides and metal hydrides
  - Zhang et al., *J. Heat Transfer*, 127, pp1391 (2005).
- Studied SBH systems
  - Heat of reaction measurement
  - Kinetics measurement
  - Sub-scale (1-kW_e) system design, construction and tests
  - Sub-scale (1-kW_e) system modeling
- Investigating high-pressure metal hydride systems
  - Sub-scale (1/50) system design, construction and tests
  - Sub-scale (1/50) system modeling

Approach (bio-production)

- Preliminary laboratory studies have verified the feasibility to use anaerobic digestion of organic waste for the production of hydrogen
- Determine the biological, chemical, and physical parameters that influence hydrogen production levels and develop a scheme to optimize production.
  - Individual organism
  - Consortium of organisms
- Develop an energy model that integrates design considerations with the research process
  - Heat flow modeling
  - Biological processes
  - Preliminary bio reactor concepts
  - Overall energy balance

Technical Accomplishments (storage)

- 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

Technical Accomplishments (storage)

New Synthesis of Borane-Ammonia

$$LiBH_4 + NH_4Cl \xrightarrow[40\,^{o}C,\ 7\ h]{THF} BH_3NH_3 + LiCl + H_2\uparrow$$

$$B(OMe)_3 + LiAlH_4 + NH_4Cl \xrightarrow[3\ hrs]{THF} BH_3NH_3 + Al(OMe)_3 + LiCl + H_2\uparrow$$

$$B(OMe)_3 + 4\ LiH + NH_4Cl \xrightarrow[AlCl_3,\ 8\ hrs]{THF} BH_3NH_3 + Al(OMe)_3 + 4\ LiCl + H_2\uparrow$$

***Unpublished results*, patent applied**

Technical Accomplishments (storage)

Comparison of Procedures for the Synthesis of BH_3NH_3

Existing Methods:

$B(OMe)_3 \rightarrow NaBH_4 \rightarrow LiBH_4 \rightarrow BH_3NH_3$

New Method: One-pot Reaction

$B(OMe)_3 \rightarrow BH_3NH_3$ Yield: 86%, Purity: > 95%

***Unpublished results*, patent applied**

Technical Accomplishments (storage)

Dehydrogenation of Borane-Ammonia

$$3\ NH_3\text{-}BH_3 \xrightarrow[\text{THF, reflux}]{PdCl_2} B_3N_3H_6 + 6\ H_2$$

Other transition metal salts used: $NiCl_2$, $CoCl_2$, etc.
Similar results were obtained with all other TM salts.

***Unpublished results*, patent applied**

Technical Accomplishments (storage)

One-pot Synthesis and Dehydrogenation of Borane-Ammonia

$$3\ LiBH_4 + 3NH_4Cl \xrightarrow[\text{THF, reflux}\ \ 6\ \text{h}]{PdCl_2} B_3N_3H_6 + 3\ LiCl + 9\ H_2$$

Other transition metal salts used: $NiCl_2$, $CoCl_2$, etc.
Similar results were obtained with all other TM salts.
Various other ammonium salts gave similar results.

***Unpublished results*, patent applied**

Technical Accomplishments, (storage)

- Mixtures of $NaBH_4$ with water, metal (Al or Mg) and additional minor ingredients (gellant, stabilizer) were developed.
- The developed mixtures exhibit stable combustion and 7 wt% H_2 yield, with safe solid byproducts.

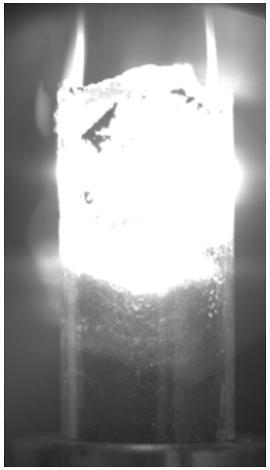
Technical Accomplishments, (storage)

Combustion of mixture

Example: $NaBH_4$: nanoAl : H_2O=1:2:3 (mass ratio). Sample diameter: 10 mm

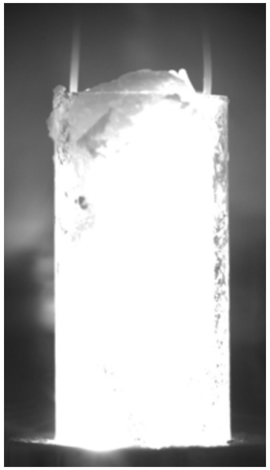
t = 1 s

t = 4 s



t = 7 s

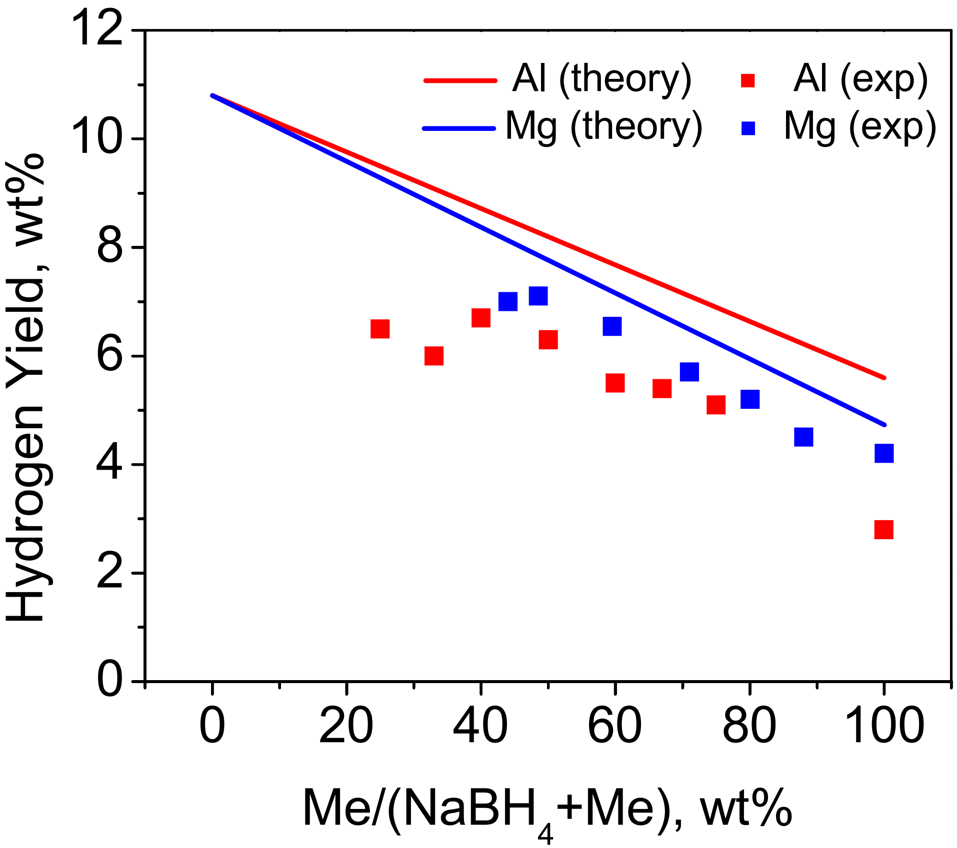
t = 10 s



- The reaction wave propagates uniformly along the sample.
- The gaseous products flow in the reverse direction through the combustion products towards the open top end of the sample.

Technical Accomplishments (storage)

Hydrogen generation



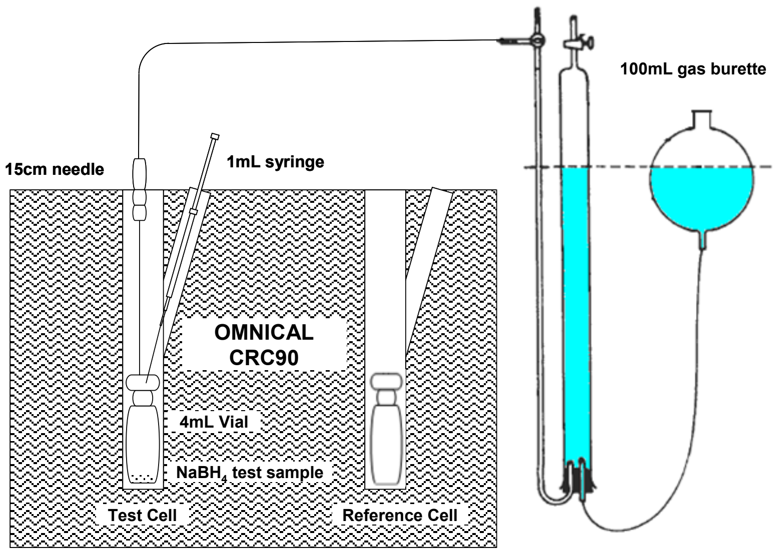
- Evolved gas: H_2 (>99%).
- Efficiency of H_2 generation:

Al	74-77%
Mg	88-92%

The maximum observed H_2 yield is ~7 wt%.

Technical Accomplishments (storage)

- Heat of reaction (SBH)

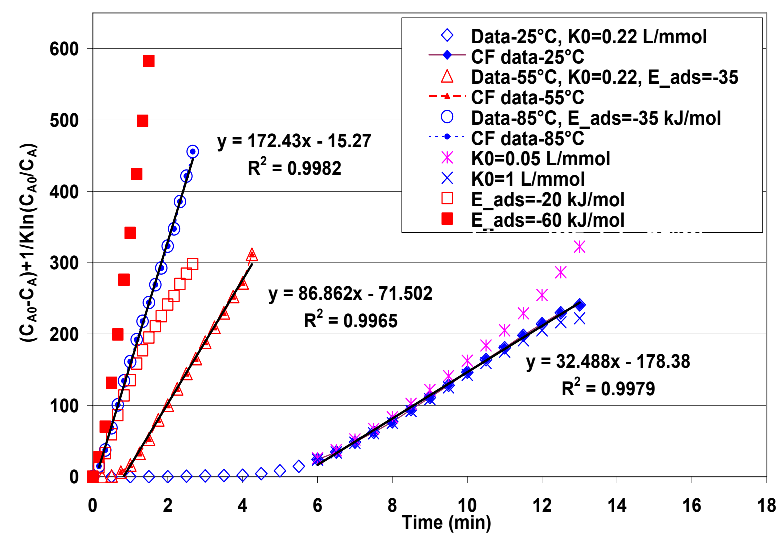


  - Widely cited: 75 kJ/molH_2
  - This study: 52.5 kJ/molH_2

- Kinetics (SBH)

  commercially available 3% Ru on 2mm carbon extrude

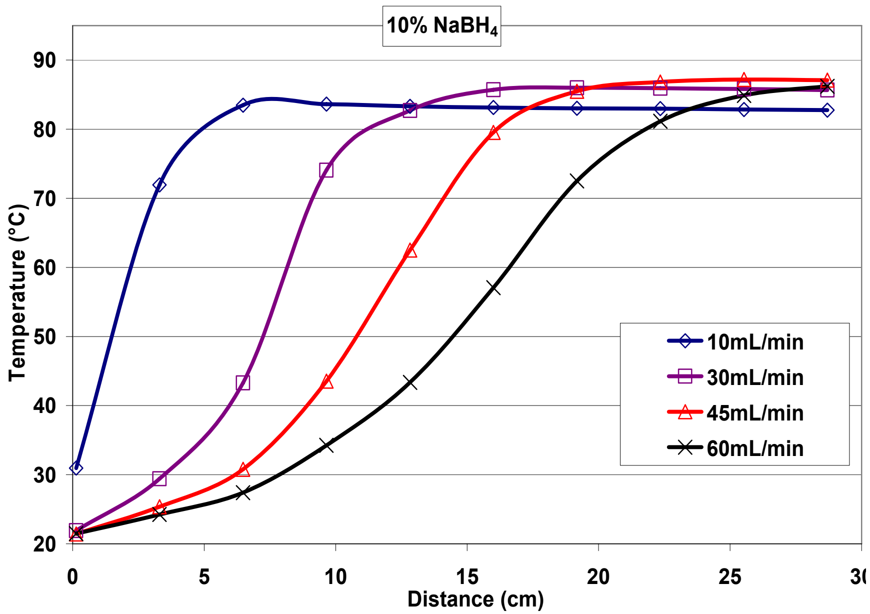
$$r_{SBH} = -A\exp\left(\frac{-E_a}{R_u T}\right)\frac{KC_{SBH}}{1+KC_{SBH}}$$



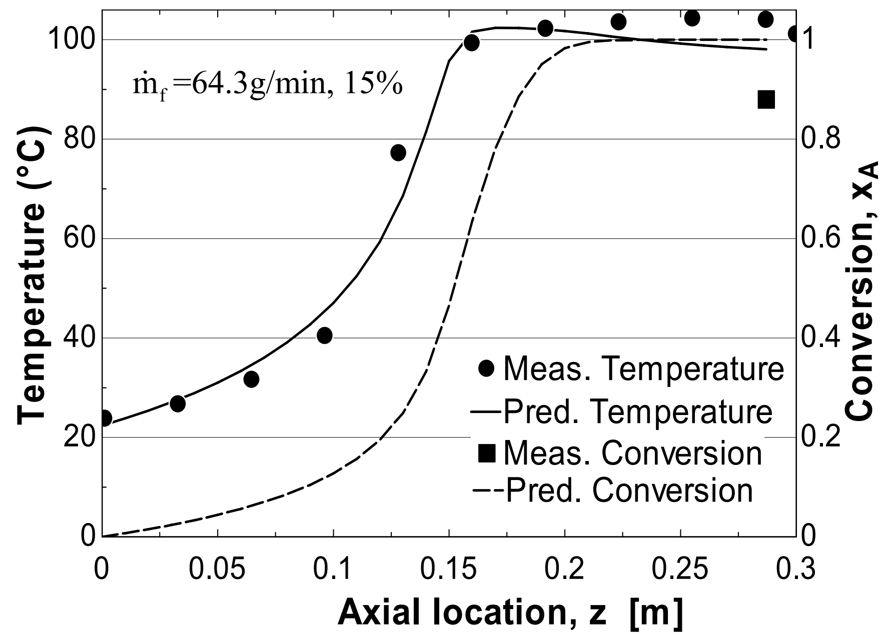
Zhang et al., *Int. J.Hydrogen Energy*, in press, (2006)

Technical Accomplishments (storage)

- 1-kW$_e$ SBH reactor measurements



- 1-kW$_e$ SBH reactor modeling



$$\rho u C_{p,eff}\frac{dT}{dx} = k_{eff}\frac{d^2T}{dx^2} - h_r^o \dot{\omega}_f MW_f - h_{fg}\dot{m}_v$$

Technical Accomplishments (storage)

- High-pressure metal hydride sub-scale system modeling

$$\rho C_p \frac{\partial T}{\partial t} = -\frac{[\mathrm{H}]_m}{2} \Delta H_r \frac{\partial F}{\partial t} + \lambda_{eff} \nabla^2 T$$

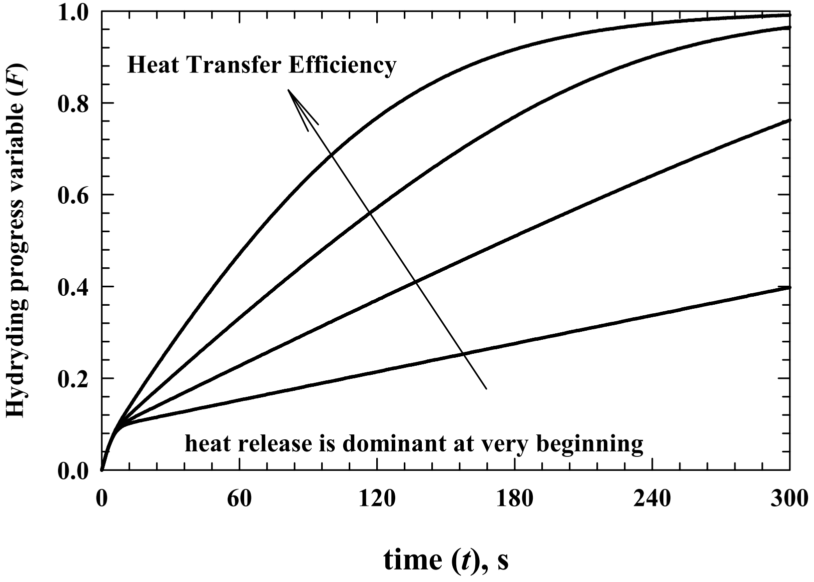
$$F = \frac{x}{x_m}$$

$$x = \frac{[\mathrm{H}]}{[M]}$$

$$\frac{\partial F}{\partial t} = k(1 - F)$$

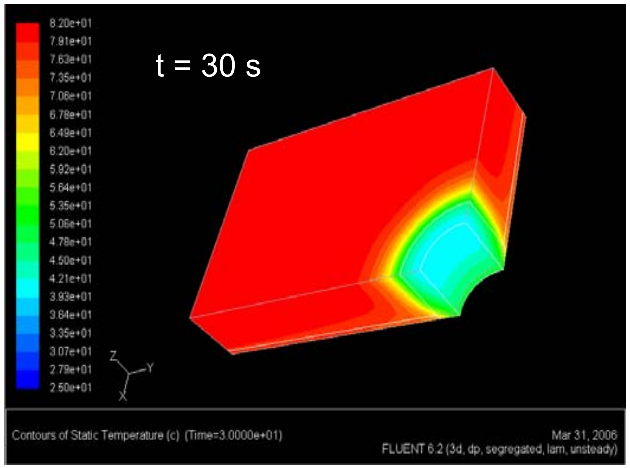
$$k = C_a \exp\left(-\frac{E_a}{R_u T}\right) \ln \frac{P}{P_{eq}}$$

$$P_{eq} = P_o \exp\left[\frac{\Delta H_r}{R_u}\left(\frac{1}{T} - \frac{1}{T_o}\right)\right]$$



Technical Accomplishments (storage)

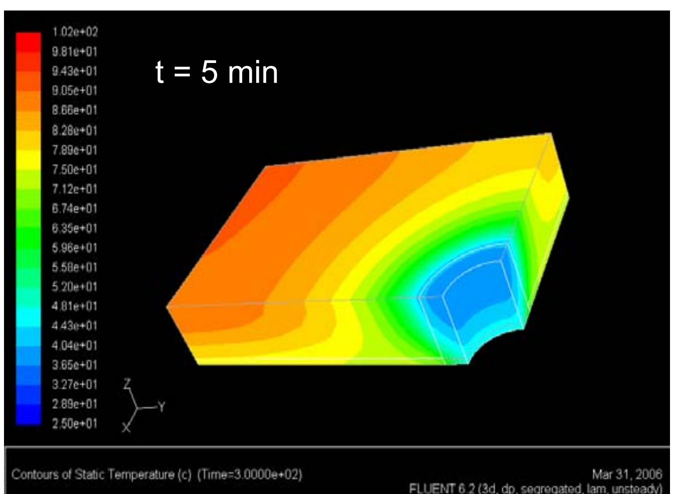
- High pressure metal hydride sub-scale system modeling (3D)

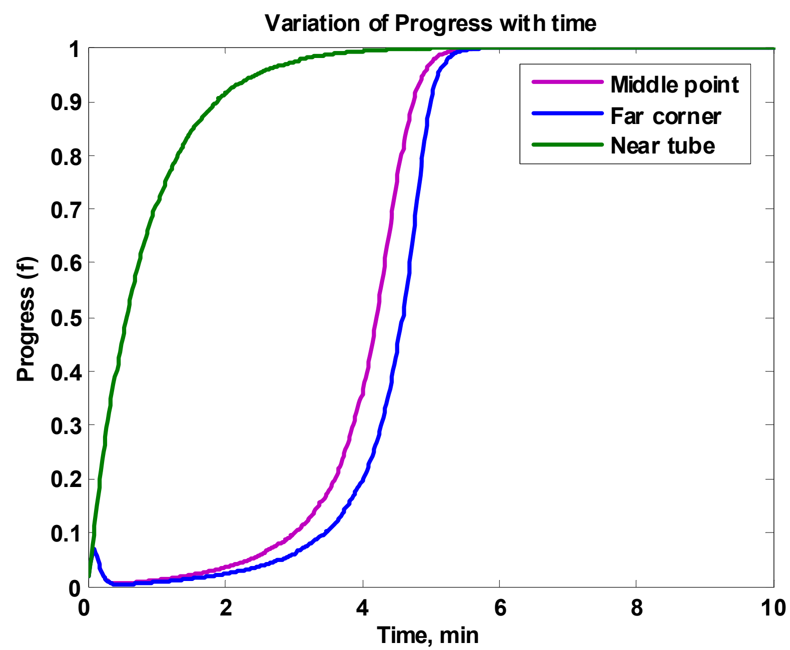


$P_{charging}$ = 400 bar,

T_{max}= 82 ^{o}C, t_{ss}= 6 min,

κ_{eff} = 1 W/mK





Technical Accomplishments (bio-production)

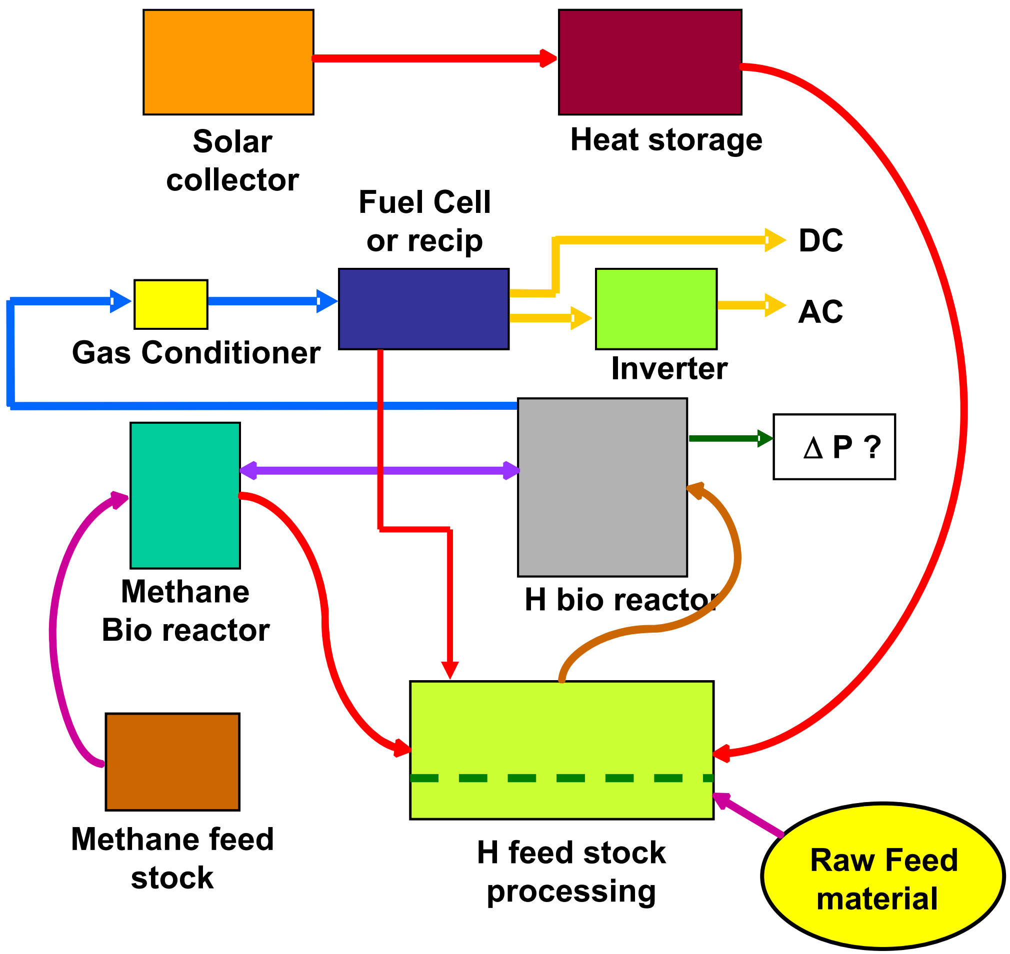
- Preliminary laboratory studies have verified the feasibility to use anaerobic digestion of organic waste for the production of hydrogen

Vial #	Treatment	Initial pH	Final pH	H_2 (μmol)	Digestion fraction
25	Inoc	6.8	6.17	933.63	.529
26	Inoc	6.8	6.17	1989.67	.512
27	Inoc	6.8	6.15	0	.479
28	Inoc	6.8	6.07	0	.444
37	Inoc, Boil	6.8	6.18	7323.00	.624
38	Inoc, Boil	6.8	6.19	5435.99	.466
40	Inoc, Boil	6.8	6.19	9144.62	.469
43	Inoc, Boil	6.8	6.16	6706.92	.372
21	Uninoc	6.8	6.5	0	.250
41	Uninoc	5.8	5.74	0	.245

Note: Inoc = inoculated with anaerobic waste water treatment effluent
Boil = boiled for 10 minutes before start
Uninoc = not inoculated

Technical Accomplishments (bio-production)

- An initial computer simulation model of the proposed system has been developed
- Model will be used to consider possible design and process alternatives as well as means to optimize the process



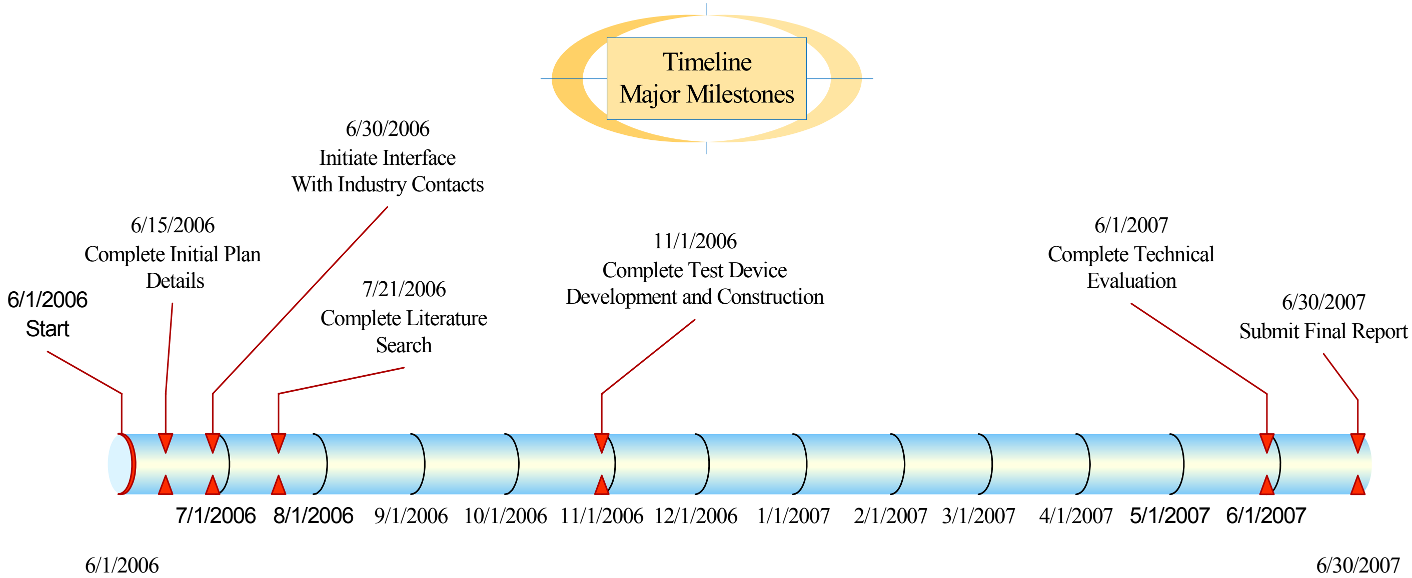
Future Work (storage)

- New formulation of ammonia-borane (AB) doped with transition metal salts
- Thermolysis of AB in the presence of water vapor
- Thermal management for AB systems
  - Thermo-chemical property measurements
  - Hydrogen generator and AB regenerator modeling
  - Sub-scale hydrogen generator and AB regenerator tests

Future Work (storage)

- Insight into combustion mechanisms of B-H compounds mixed with metals and water.
- Optimization of mixture compositions and process conditions
- Focus on ammonia borane, with the goal to further increase hydrogen yield
- Design and construction of power system demonstration unit

Future Work (bio-production)



Task Schedule

ID	Task Name	Start	Finish	Duration
1	Develop Initial Plan Details	6/1/2006	6/15/2006	11d
2	Conduct Literature Search	6/8/2006	7/21/2006	32d
3	Establish Interface With Industry Contacts	6/30/2006	9/29/2006	66d
4	Construct Test Device	7/3/2006	11/1/2006	88d
5	Conduct Evaluation of Innoculum and Conditions to Maximize H Production	6/15/2006	6/1/2007	252d
6	Conduct Energy Evaluation	11/1/2006	6/1/2007	153d
7	Prepare Final Report	4/17/2007	6/29/2007	54d

Summary (storage)

- All on-board hydrogen storage technologies involves heat transfer challenges
- Unknown thermo-physical properties need to be measured or modeled
- Designs of reactors and other components need to be tested and modeled at appropriate sub-scales
- Mixtures of boron-hydrogen compounds with metal and water can be used for hydrogen generation by combustion
  - high specific energy
  - no catalyst for H_2 generation
  - safe reaction byproducts, which can be recycled

Summary (bio-production)

- Anaerobic production of hydrogen holds promise as a viable source of energy
- Waste streams provide a low cost source of feed for the energy production process
- Initially this approach holds promise to provide an environmentally friendly means to produce electricity in remote or third world applications
- As the technology is developed there is the opportunity to scale up the size of the energy production

Publications and Presentations

Patents

1. Shafirovich, E., Diakov, V., and Varma, A., “System and Method for Generating Hydrogen,” U.S. Patent application 60/663,238 (March 18, 2005).

Archival Journal Articles

1. Shafirovich, E., Diakov, V., and Varma, A., “Combustion of Novel Chemical Mixtures for Hydrogen Generation,” *Combustion and Flame*, Vol. 144, 2006, pp. 415-418.
2. Shafirovich, E., Diakov, V., and Varma, A., “Combustion-Assisted Hydrolysis of Sodium Borohydride for Hydrogen Generation,” *International Journal of Hydrogen Energy*, in review.
3. 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
4. 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.

Conference Presentations

1. “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.
2. “Novel Chemical Mixtures for Hydrogen Generation by Combustion,” 2005 AIChE Annual Meeting, October 30-November 4, 2005, Cincinnati, OH.
3. “Novel Chemical Mixtures for Hydrogen Generation by Combustion,” 44th AIAA Aerospace Sciences Meeting and Exhibit, January 9-12, 2006, Reno, NV, AIAA Paper 2006-1445.
4. “Combustion-Based Methods to Generate Hydrogen for Fuel Cells,” NSF Workshop on Research Frontiers for Combustion in the Hydrogen Economy, March 10, 2006, NSF Headquarters, Arlington, VA.
5. 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.