Purdue Hydrogen Systems Laboratory

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STP22

Overview (storage)

Timeline

- Start – September 2006
- End – September 2007
- 40% complete

Budget

- $825,000
  - $660,000 (DOE)
  - $165,000 (Purdue)
- Funding received in FY06: $660,000

Barriers

- Barriers addressed
  - A. System weight and volume
  - J. Thermal management
  - R. Regeneration process
- Targets

		2007	2010	2015
Gravimetric capacity	kgH_2/kg (wt%)	0.045 (4.5%)	0.06 (6%)	0.09 (9%)
Volumetric capacity	kgH_2/L	0.036	0.045	0.081

Partners

- General Motors (lab infrastructure)
- General Atomics (AB synthesis)

Overview (bio-hydrogen)

Timeline

- Start – September 2006
- End – September 2007
- 40% complete

Budget

- $415,500
  - $330,000 (DOE)
  - $84,500 (Purdue)
- Funding received in FY06: $330,000

Barriers

- Barriers addressed
  - AI. H_2 molar yield
  - AK. Feedstock cost
  - AL. Systems engineering
- Targets

	2007	2010	2015
Hydrogen yield percentage (%)	20	40	> 45

Partners

- Cargill
- Grifffith Labs
- Advanced Power Technologies
- Innovene
- NREL
- BP

Outline

- **Ammonia Borane-based Hydrogen Storage Methods**
- **Thermal Management of Recyclable Chemical Hydride Systems**
- **Bio-hydrogen Production from Organic Wastes**

Objectives

(Ammonia Borane-based Hydrogen Storage Methods)

- Improve the extent, rate and control of hydrogen release from ammonia borane (AB) by hydrolysis reactions
- Characterize the dehydrogenation products and develop new methods for AB regeneration
- Investigate a new method for hydrogen generation from water and ammonia borane using self-sustained combustion reactions

Approach

- **Screening transition metal catalyst for the hydrolysis of ammonia borane**

- **Characterization and regeneration reactivity of BN products**

- **Combustion-stimulated dehydrogenation of AB in triple AB/metal/water mixtures; occurring reactions are:**

  $NH_3BH_3 \rightarrow BN + 3\ H_2$; Thermolysis, 19.5 wt% H_2

  $NH_3BH_3 + 2\ H_2O \rightarrow NH_4BO_2 + 3\ H_2$; Hydrolysis, 9 wt%

  $Mg + H_2O \rightarrow MgO + H_2$; Combustion, 5 wt%

  - H_2 yield is the highest if AB thermolysis prevails and AB hydrolysis is negligible, thus it is necessary to find conditions favoring thermolysis

Accomplishments/Progress/Results

Hydrolysis of AB

1. Mineral acid catalyzed

$$NH_3BH_3 + 4\,H_2O \xrightarrow[\text{Instant}]{\text{Mineral acids}} NH_4B(OH)_4 + 3H_2$$

2. Transition metal catalyzed

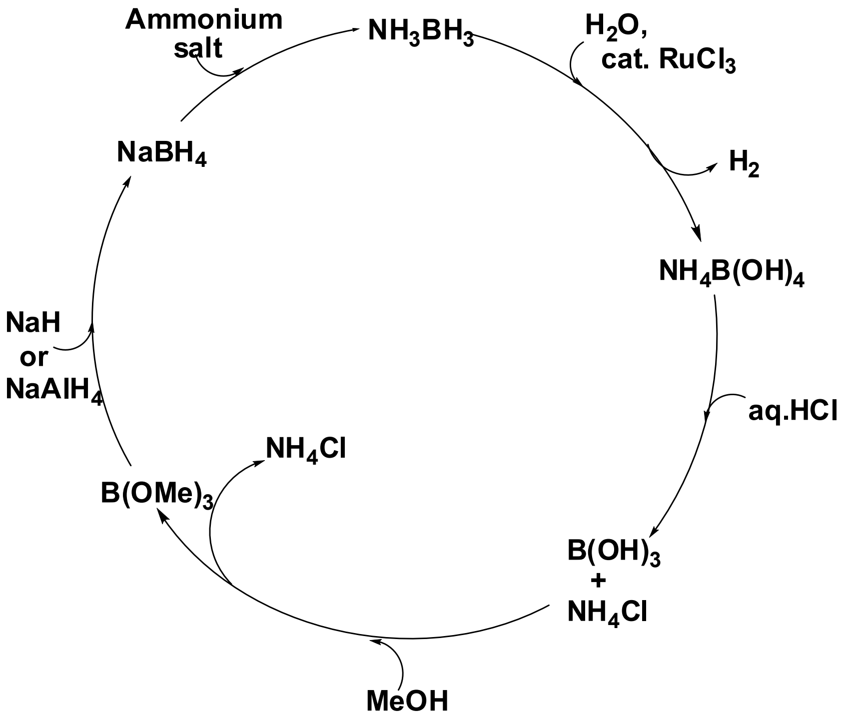
$$NH_3BH_3 + 4\,H_2O \xrightarrow[\text{RT}]{\text{TM cat.}} NH_4B(OH)_4 + 3H_2$$

Accomplishments/Progress/Results

Entry	Catalyst	Catalyst (mol%)	React. Time, min
1	$RuCl_3$	0.2	3
2	$RuCl_3$	0.1	6
3	$RuCl_3$	0.05	20
4	$CoCl_2$	3	5
5	$CoCl_2$	5	3
6	Pd/C	1	25
7	$PdCl_2$	5	25

Transition Metal Catalyzed Hydrolysis of AB

Accomplishments/Progress/Results



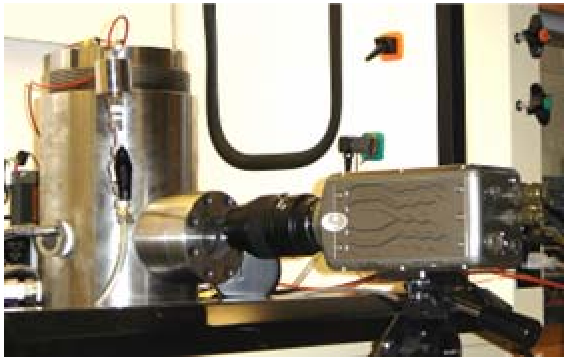
Ammonia borane hydrogen cycle

- Transition metal catalyzed hydrolysis of ammonia borane generates 3 eq. of hydrogen and ammonium tetrahydroxyborate
- Ammonium tetrahydroxyborate was converted to boric acid using aq. HCl
- Boric acid was treated with methanol to form trimethyl borate

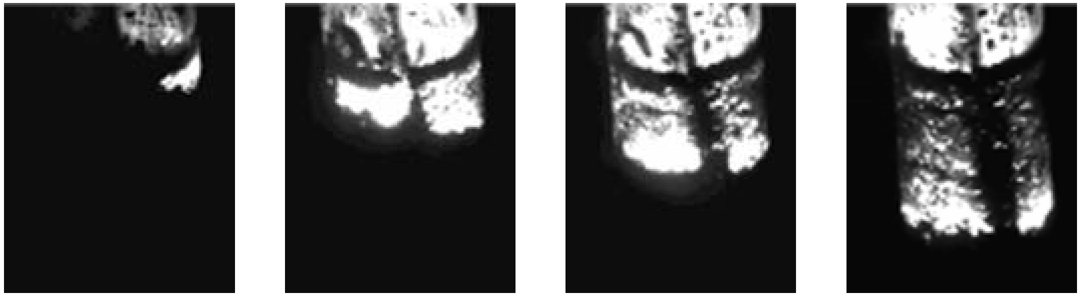
Accomplishments/Progress/Results

Combustion wave propagation

Reaction chamber and high-speed video camera



NH_3BH_3:Al:H_2O (2:3:3 mass ratio)
Sample diameter 1 cm, height 2.5 cm
Images taken at 0.20, 0.33, 0.40 and 0.85 s after ignition



Composition	**H_2 yield (wt%), experimental**	**H_2 yield (wt%), theoretical**
AB:Mg:H_2O (4:4:3)	9.1	10.1
AB:Al:H_2O (2:3:3)	7.7	8.7

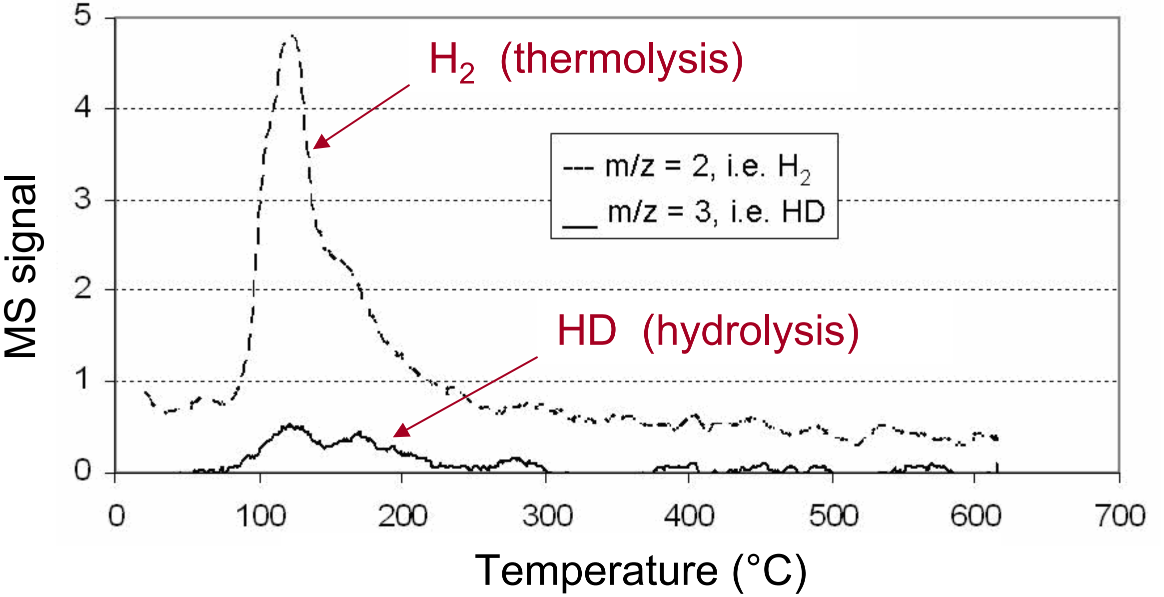
Temperature in the combustion wave exceeds 500 °C, providing conditions for full dehydrogenation of AB. The possibility of some hydrolysis, however, still exists.

Accomplishments/Progress/Results

Isotopic tests of AB under Ar/D_2O flow in TGA (pressure 1 atm)

TGA instrument

MS measurements of generated H_2 and HD



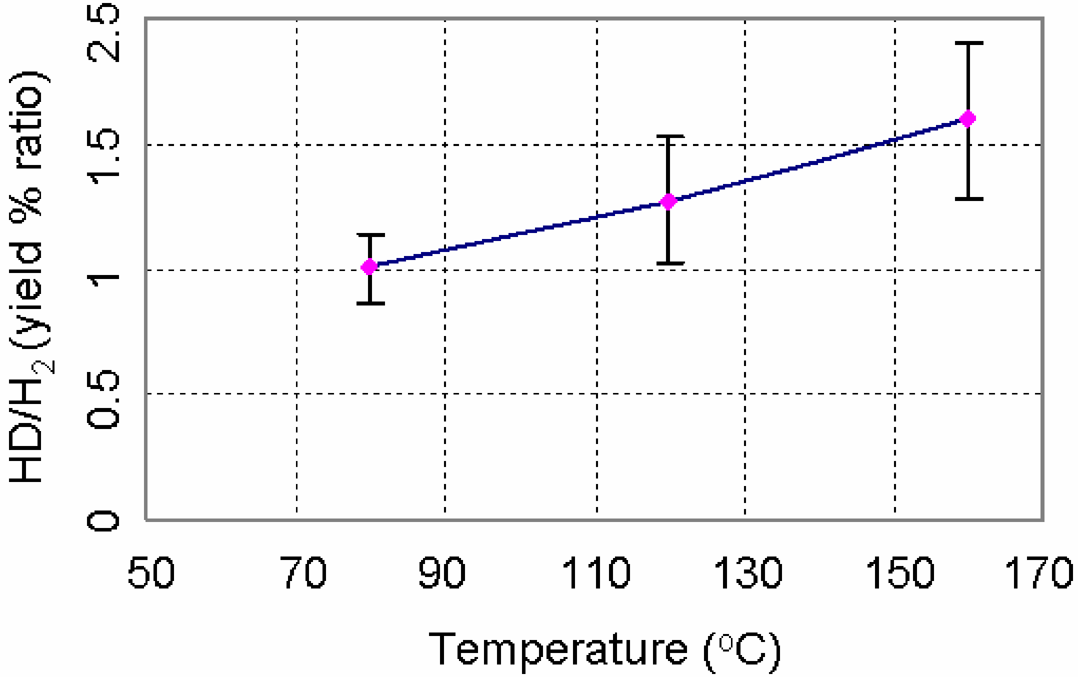
TGA/MS experiments with AB under Ar/D_2O flow at atmospheric pressure indicate the prevalence of *thermolysis*, as the amount of released H_2 well exceeds that of HD.

Accomplishments/Progress/Results

Isotopic tests of AB with D_2O in Parr reactor (initial Ar pressure ~14 atm)

Parr reactor

MS measurements of generated H_2 and HD



Experiments in Parr reactor result in higher amounts of HD as compared to H_2, indicating that higher pressure promotes *hydrolysis.*

Future Work

- **To achieve the conversion of methyl borate to sodium borohydride in high yield**
- **To accomplish ammonia borane regeneration in overall near quantitative yield and in cost effective manner**
  - Go/no go: ammonia borane overall yield of ≥ 60%
- **TGA/MS experiments**
  - higher D_2O vapor pressure
- **Parr reactor**
  - detailed elevated pressure data for the reaction with D_2O
  - analyze product solutions (NMR)
  - measure concentrations of impurities in generated H_2 (FTIR)
- **Combustion stimulated hydrolysis**
  - analyze both gaseous and solid byproducts (FTIR and XRD)
  - test the effect of D_2O on gaseous products (MS)

Summary

- Studied different transition metal catalysts for hydrolysis and observed that $RuCl_3$ gives the best results
- Isolated boric acid from the ammonium tetrahydroxyborate by aq. HCl treatment
- Boric acid was converted to trimethyl borate in the presence of methanol
- Self-sustained combustion was observed in mixtures of AB with water and Mg or nano-Al powder; the maximum hydrogen yield was 9 wt%
- Isotopic tests of AB using D_2O show that thermal decomposition competes with hydrolysis; higher pressure promotes hydrolysis

Objectives

(Thermal Management of Recyclable Chemical Hydride Systems)

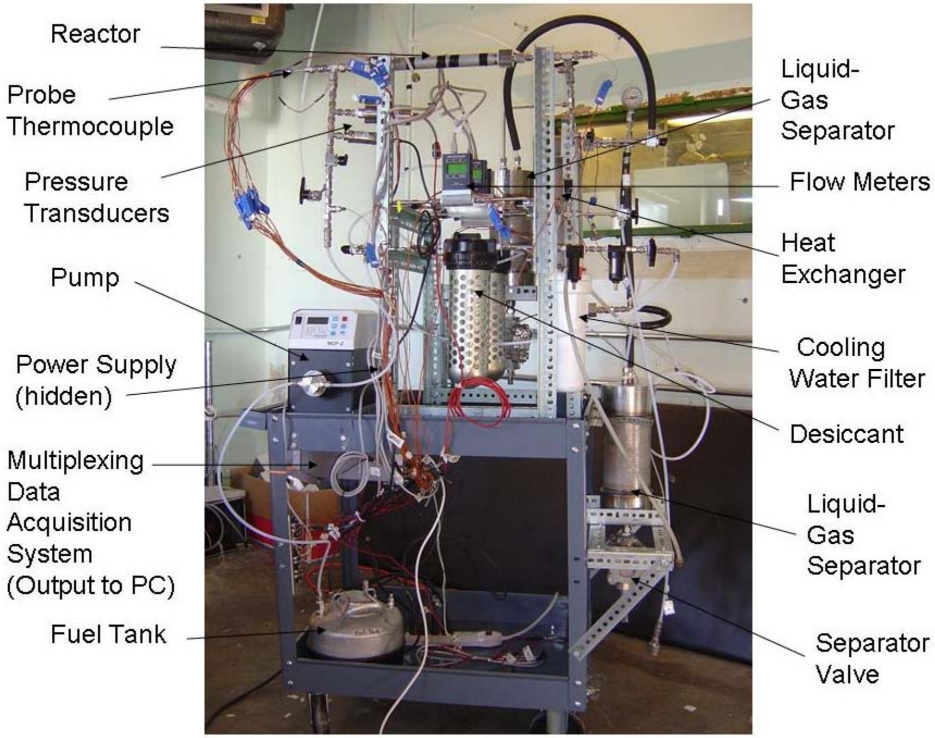
- To demonstrate a recyclable chemical hydride hydrogen storage system
  - Construct and test an AB hydrogen generation system up to 1-kW_{el}
  - Construct and test a 0.2 kg AB/day regeneration system
- To increase system-based volumetric and gravimetric hydrogen densities
  - Investigate thermo-chemical properties and processes experimentally and/or numerically to guide system design and optimization

Approach

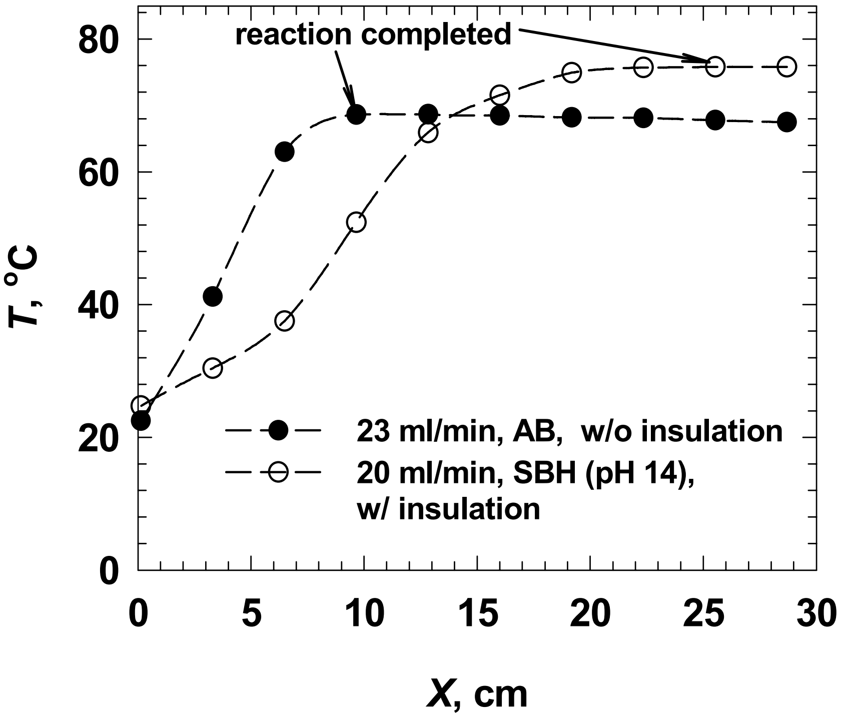
- Investigate reaction kinetics and other key thermo-chemical properties
- Utilize numerical simulations to guide system level (subscale) test apparatus design
- Study key issues in the application of AB hydrolysis onboard hydrogen storage systems, using pre-system-level test apparatus
- Construct or renovate system level apparatus
- Conduct system level tests

Accomplishments/Progress/Results

- **Mobile AB or SBH hydrolysis apparatus**
  - **Packed reactor: 3 wt% Ru on carbon extrudate**



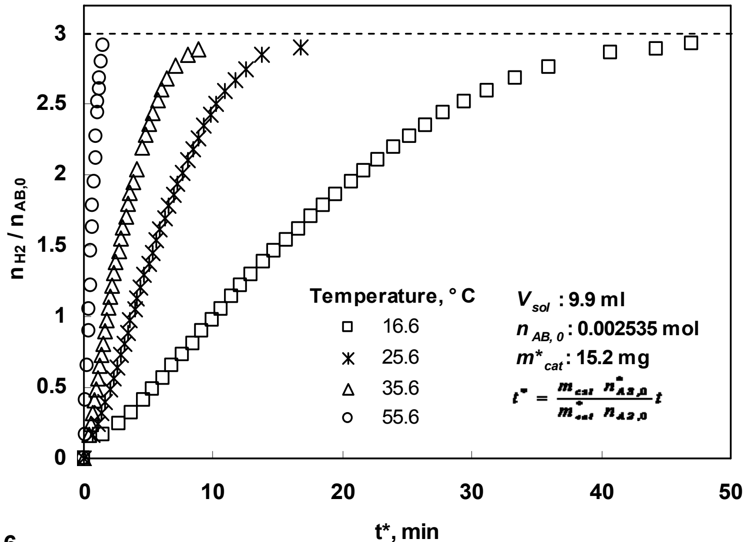
- **First system-level AB hydrolysis test**
  - **5 wt% fuel aqueous solution**
  - **Hydrogen flow rate: ~ 2.9 SLPM**

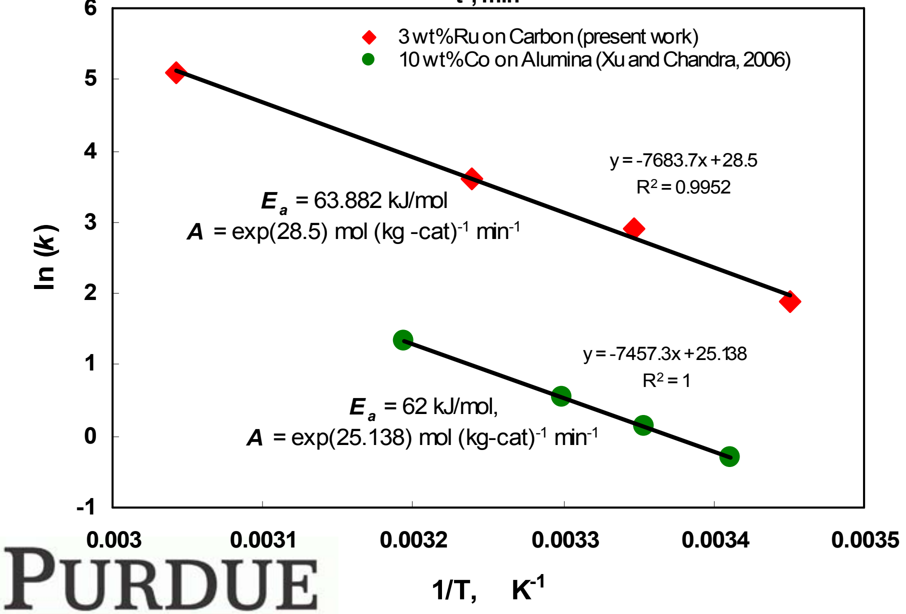


Shorter reactor can be used for AB (w/o NaOH) hydrolysis

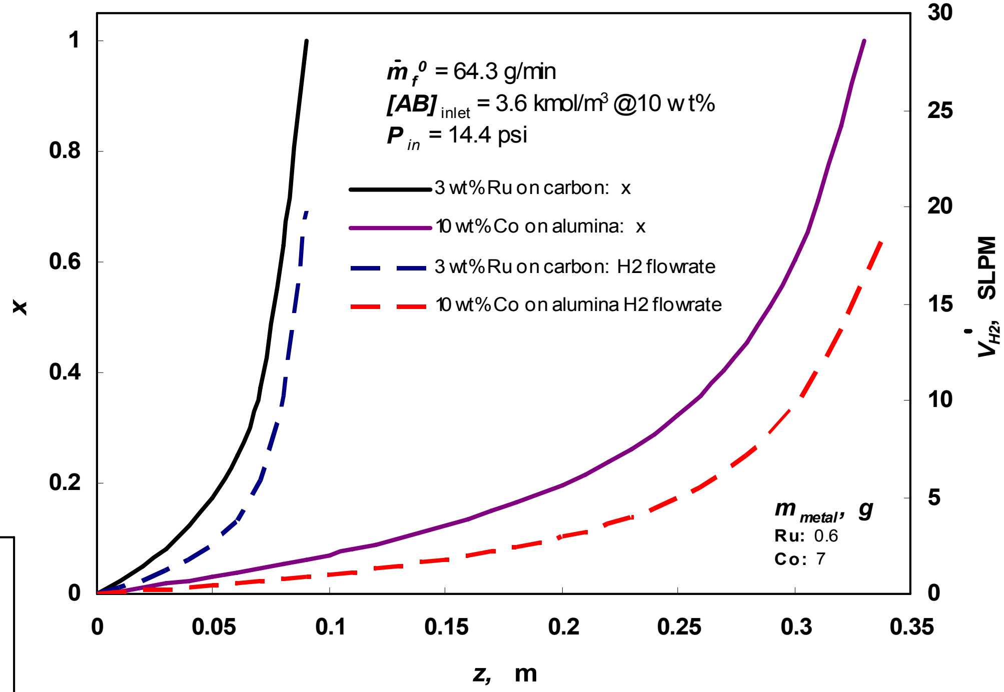
Accomplishments/Progress/Results

- **AB hydrolysis kinetics**





- **AB hydrolysis reactor simulations**

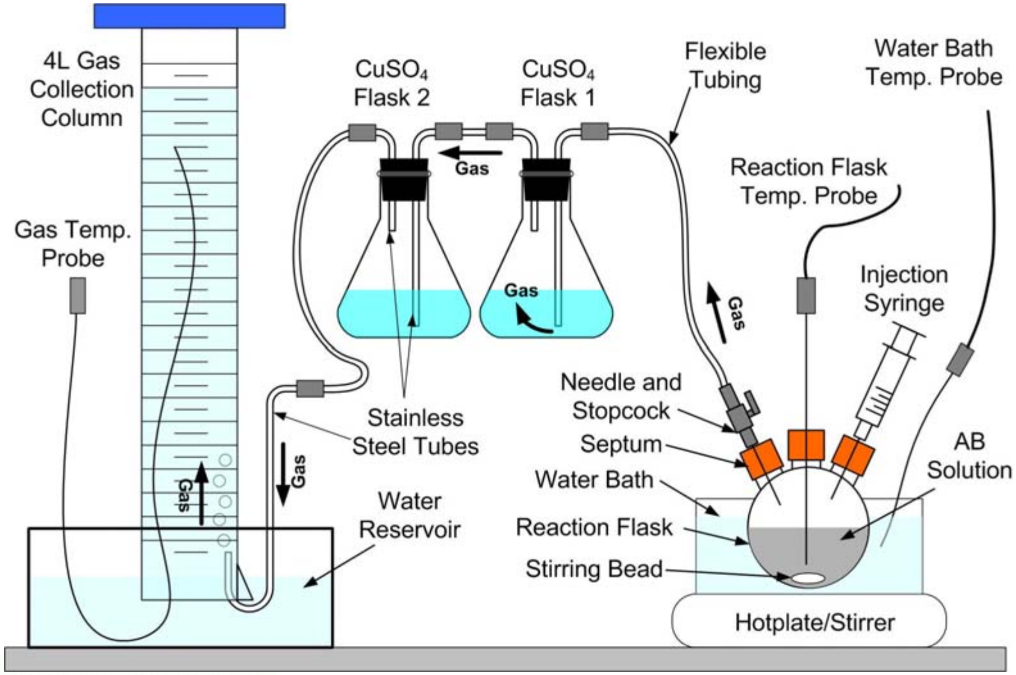


Reactors using cobalt will need much more volume and weight than those using ruthenium

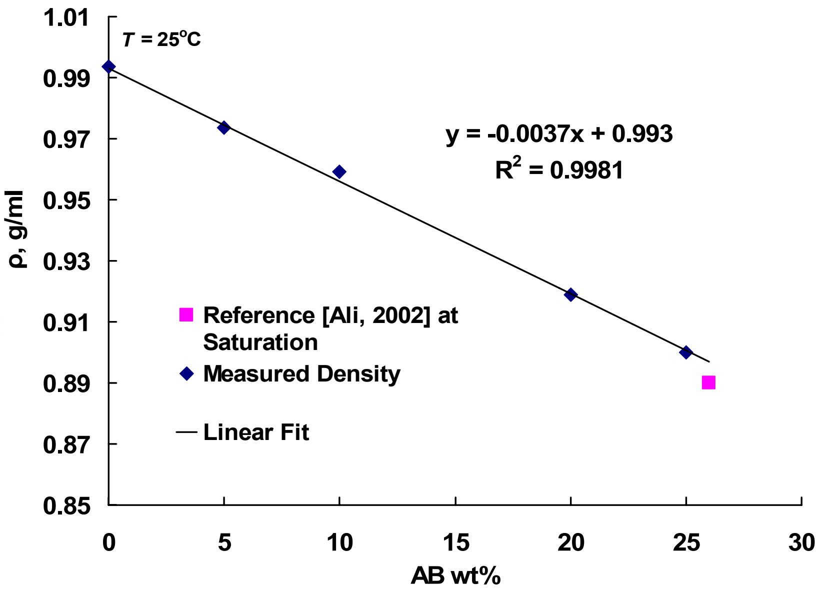
$$\frac{d\left(\frac{n_{H_2}}{n_{AB,o}}\right)}{dt} = \frac{3m_{cat}}{n_{AB,o}} A \exp\left(\frac{-E_a}{R_u T}\right) \frac{K[AB]}{1+K[AB]}$$

Accomplishments/Progress/Results

- **Pre-system-level test apparatus**
  - **To study AB hydrolysis up to saturation condition**
  - **To validate AB hydrolysis kinetics at high concentrations**
  - **To quantify possible ammonia generation**
  - **To study byproduct solubility**

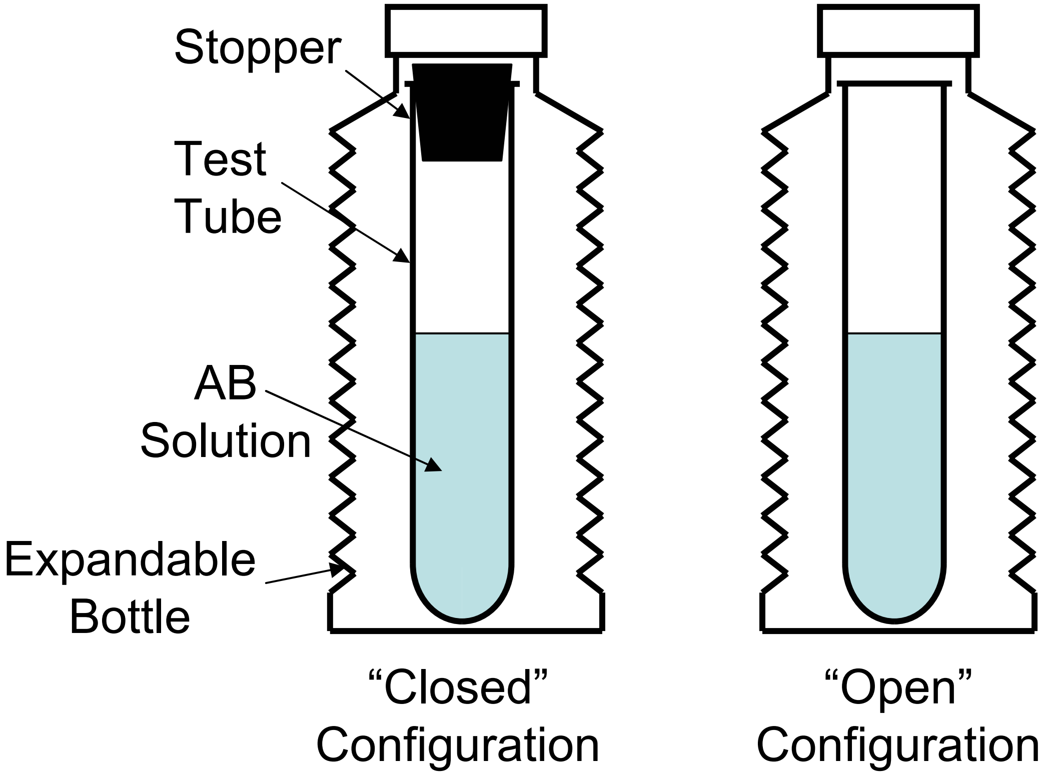


- **AB aqueous solution densities**



Accomplishments/Progress/Results

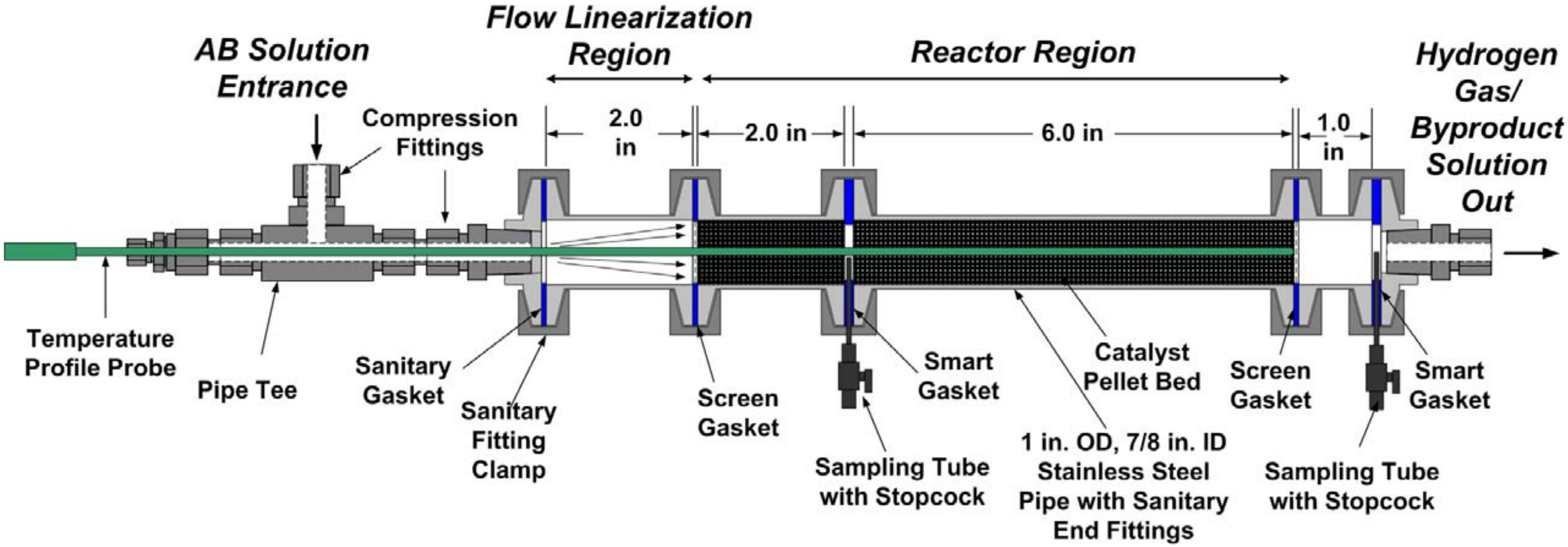
- **30-Day long term storage stability test**



- **Samples of 10% and 25% AB aqueous solution are being studied**
- **Expandable bottle allows outgassing without significant pressurization**
- **Bottle also minimizes evaporation**

Accomplishments/Progress/Results

- **New AB hydrolysis reactor design**
  - To keep multiple point temperature profile probe
  - To prevent leakage when operating at high pressures
  - To facilitate reactants/products sampling



Future Work

- **Construction & testing of AB hydrolysis apparatus**
  - Key issue: possible operation difficulties at high fuel concentrations caused by dissoluble byproduct and/or appreciable ammonia generation
  - Go: no such difficulty occurs or problem can be solved without significant cost increase
  - No-go: problem can't be solved or can be solved but with significant cost increase

- **Design, construction and testing of AB regeneration apparatus**
  - Key issue: yield of AB recycling at system level
  - Go: yield > 50%
  - No-go: yield < 50%

Summary

- AB hydrolysis (w/o NaOH) is faster than SBH hydrolysis (w/ NaOH, pH 14); therefore smaller/lighter system may be used for same hydrogen output
- AB hydrolysis systems using cobalt will need much more volume and weight than those using ruthenium
- Other key issues in the application of AB hydrolysis onboard hydrogen storage systems, such as ammonia generation, byproduct solubility and long term storage stability, are being investigated

Objectives

(Bio-hydrogen Production from Organic Wastes)

- Acquiring data for the volume of hydrogen produced from food waste by fermentation
- Conduct statistical testing to determine parameters that influence hydrogen production rate and optimal configuration
- Optimize the energy balance for a modular device for supply of thermal and electric energy
- Provide data and design information consistent with the DOE objective to utilize anaerobic biological processes as a source of the Hydrogen

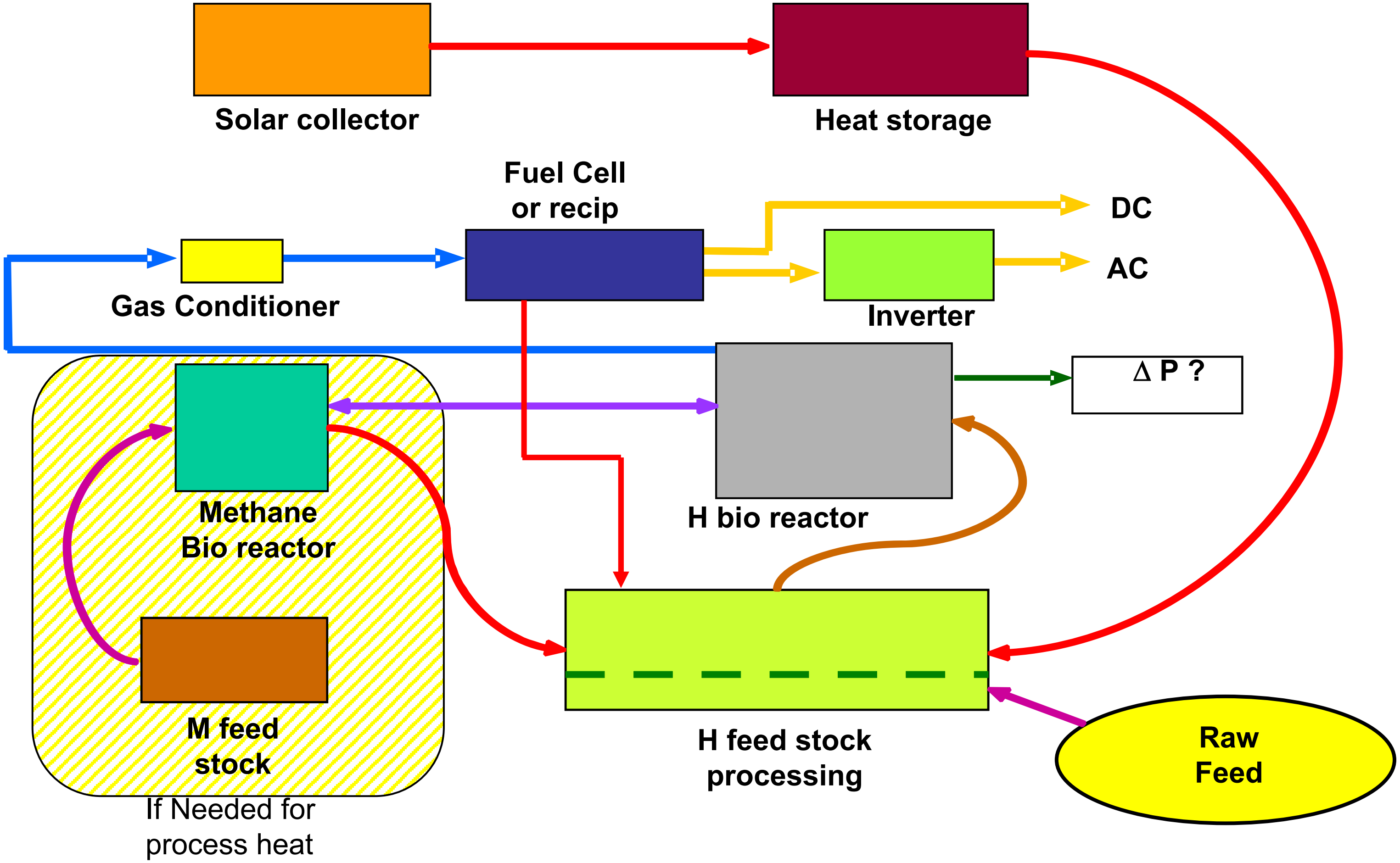
Approach

- **Investigate methods to produce hydrogen from various organic waste streams through the use of a fermentation process.**
  - **The long term goal is to develop a portable unit that can process food or other waste streams locally and produce hydrogen that will subsequently be used to generate electricity in remote locations initially.**
  - **Current efforts are concentrating on isolating biological consortia, characterizing their hydrogen producing capabilities, and determining optimal operating parameters as well as evaluating the interrelation with potential local energy system designs.**
- **We have recently expanded the energy model to also consider the possibility of producing potable water as part of the process.**

Approach

- Samples of food waste were collected, ground, and freeze dried to provide a homogenous substrate for testing.
- Substrate was placed in a bottles, water was added, heated to 100 C for 10 minutes, purged with nitrogen, sealed, inoculated, and placed in an incubator. Gas samples were taken over time and were analyzed in a Gas Chromatograph.
- A statistical testing approach is being developed to determine parameters that optimize hydrogen production.
- A semi continuous production test is under development.
- Energy balance for the remote energy source is being considered based upon design and hydrogen production values.
- Provide training for undergraduate and graduate students in biological hydrogen production by participating in research efforts.

Accomplishments/Progress/Results

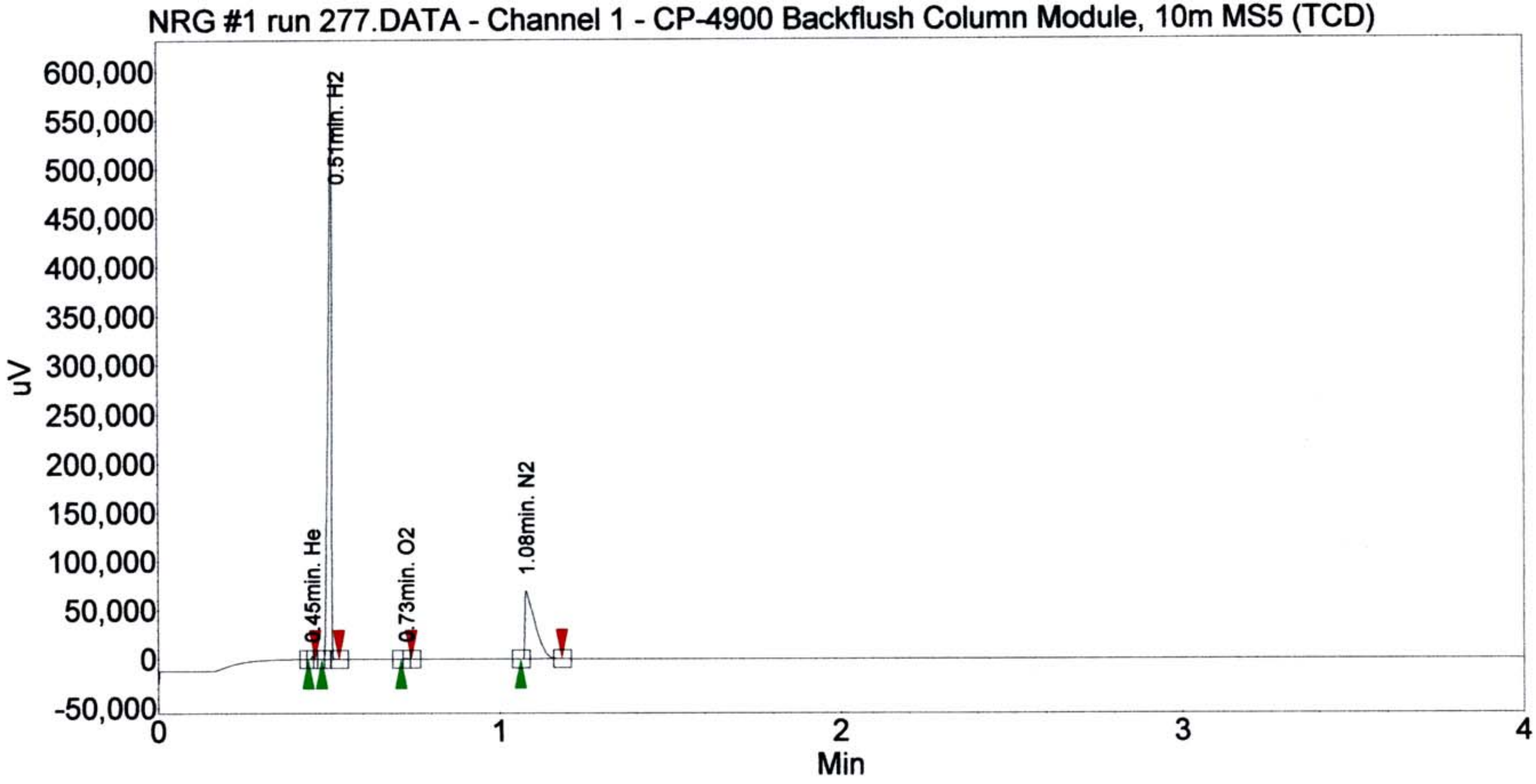


System Overview

Accomplishments/Progress/Results

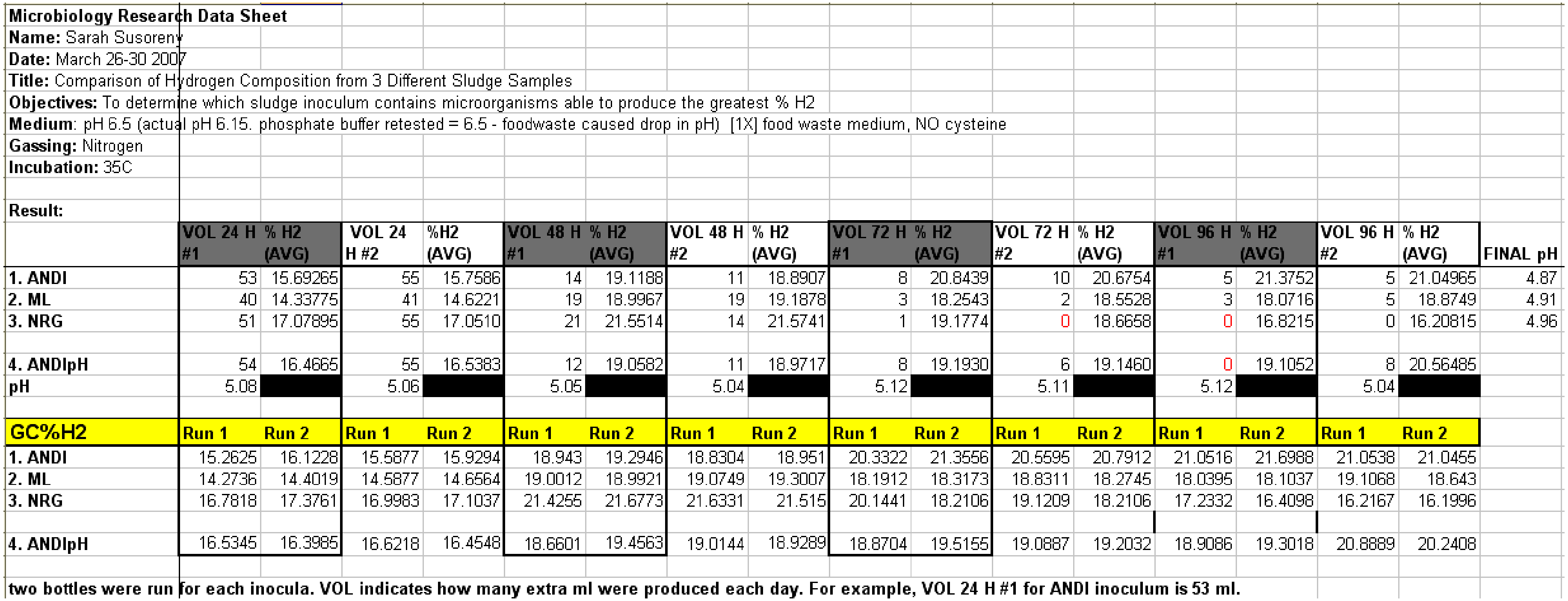
- It has been possible to produce up to ~20 volume % hydrogen from initial non optimized tests.
- A statistical optimization testing scheme is currently being implemented.
- Initial work started on multiple testing device to conduct automated testing
- Energy balance calculations are being modified to accommodate testing results and input from industrial advisors.
- Semi continuous testing device is under construction.
- Progress is consistent with project milestones and objectives

Accomplishments/Progress/Results



Accomplishments/Progress/Results

Example of Test Data



Microbiology Research Data Sheet
Name: Sarah Susoreny
Date: March 26-30 2007
Title: Comparison of Hydrogen Composition from 3 Different Sludge Samples
Objectives: To determine which sludge inoculum contains microorganisms able to produce the greatest % H2
Medium: pH 6.5 (actual pH 6.15. phosphate buffer retested = 6.5 - foodwaste caused drop in pH) [1X] food waste medium, NO cysteine
Gassing: Nitrogen
Incubation: 35C

Result:

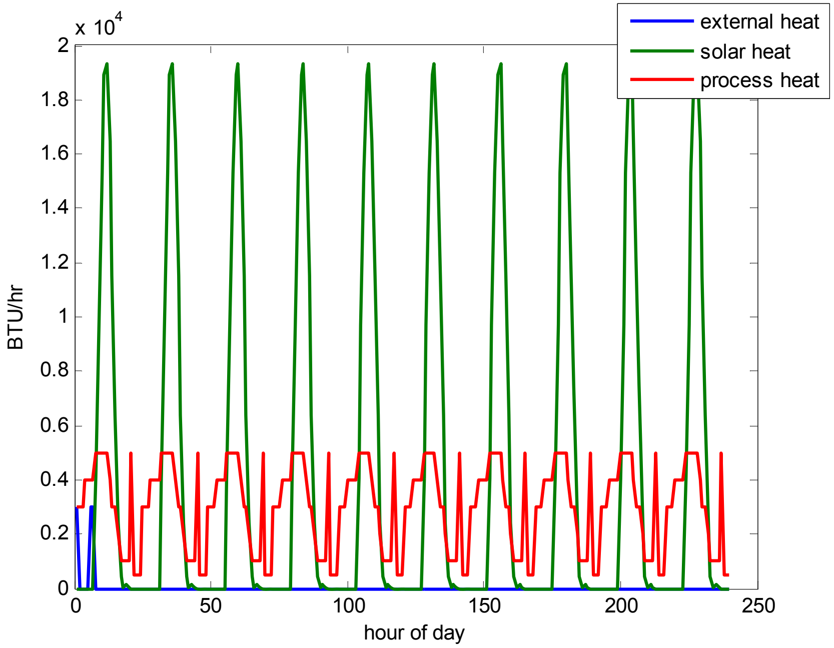
	VOL 24 H #1	% H2 (AVG)	VOL 24 H #2	%H2 (AVG)	VOL 48 H #1	% H2 (AVG)	VOL 48 H #2	% H2 (AVG)	VOL 72 H #1	% H2 (AVG)	VOL 72 H #2	% H2 (AVG)	VOL 96 H #1	% H2 (AVG)	VOL 96 H #2	% H2 (AVG)	FINAL pH
1. ANDI	53	15.69265	55	15.7586	14	19.1188	11	18.8907	8	20.8439	10	20.6754	5	21.3752	5	21.04965	4.87
2. ML	40	14.33775	41	14.6221	19	18.9967	19	19.1878	3	18.2543	2	18.5528	3	18.0716	5	18.8749	4.91
3. NRG	51	17.07895	55	17.0510	21	21.5514	14	21.5741	1	19.1774	0	18.6658	0	16.8215	0	16.20815	4.96
4. ANDIpH	54	16.4665	55	16.5383	12	19.0582	11	18.9717	8	19.1930	6	19.1460	0	19.1052	8	20.56485	
pH	5.08		5.06		5.05		5.04		5.12		5.11		5.12		5.04		

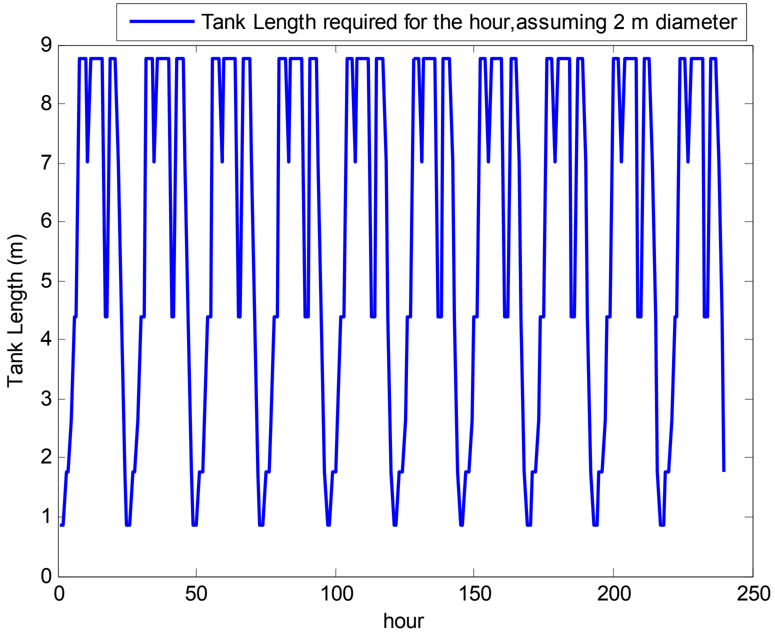
GC%H2	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**	**Run 1**	**Run 2**
1. ANDI	15.2625	16.1228	15.5877	15.9294	18.943	19.2946	18.8304	18.951	20.3322	21.3556	20.5595	20.7912	21.0516	21.6988	21.0538	21.0455
2. ML	14.2736	14.4019	14.5877	14.6564	19.0012	18.9921	19.0749	19.3007	18.1912	18.3173	18.8311	18.2745	18.0395	18.1037	19.1068	18.643
3. NRG	16.7818	17.3761	16.9983	17.1037	21.4255	21.6773	21.6331	21.515	20.1441	18.2106	19.1209	18.2106	17.2332	16.4098	16.2167	16.1996
4. ANDIpH	16.5345	16.3985	16.6218	16.4548	18.6601	19.4563	19.0144	18.9289	18.8704	19.5155	19.0887	19.2032	18.9086	19.3018	20.8889	20.2408

two bottles were run for each inocula. VOL indicates how many extra ml were produced each day. For example, VOL 24 H #1 for ANDI inoculum is 53 ml.

Accomplishments/Progress/Results

- **Energy Balance Calculations**





Future Work

- Determination of optimal parameters for hydrogen production from fermentation of food waste will continue.
- Multiple testing device is being developed.
- Energy balance will continue to be developed.
- Feasibility of production of potable water as a byproduct will be considered.
- Concept for capture of carbon dioxide to produce marketable chemical product will be considered.

Summary

- 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.
- This approach holds promise to provide an environmentally friendly means to produce electricity in remote or third world applications.
- Identification of optimal operating parameters and consortia for hydrogen production is producing positive results.
- Statistical experimental design testing is underway.
- Energy balance is being refined to accommodate information from testing and commercialization concerns of industry advisors.
- New concepts to maximize value as a local energy source, consistent with DOE goals, are being considered such as production of potable water as a by product. CO2 capture is being considered using organometallic nanocatalyst.
- As the technology is developed there is the opportunity to scale up the size of the energy production.