Clean Energy Research

Project III: Hydrogen Storage Using Chemical Hydrides

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STP38

Overview

Timeline

- 10/31/2004-10/31/2006
- 55% complete

Budget

- Total project funding
  - $559,875 DOE
  - $134,250 contractor
- FY05 funding
  - $365,000 DOE
  - $91,250 contractor
- Funding for FY06
  - $194,875 DOE
  - $43,000 contractor

Barriers

- System Weight and Volume
- Thermal Management
- Discharging Rates

Partners

Millennium Cell, Inc

Eatontown NJ

Dr. Ying Wu, Director R&D

Objectives

- Develop hydrogen storage and delivery technology based on steam + chemical hydrides for automotive fuel cell applications

$$NaBH_4 + (2+x)H_2O \rightarrow 4H_2\,(g) + NaBO_2 \cdot x\, H_2O + \Delta H_{rxn}$$

- Quantify/optimize steam + solid chemical hydride reaction kinetics as basis for production of hydrogen
- Compare experimental data to FreedomCAR targets
  - Mass efficiency of reaction (8MAA)
  - Hydrogen production rate / kinetic data (12MAA)
  - Analysis of water utilization of reactor and hydration characteristics of products (14MAA)
  - Prototype design development (16 MAA)
- Develop prototype of steam hydrolysis reactor

Approach

- Hydrolyze chemical hydrides with dry steam, rather than aqueous catalytic process
  - Chemically simple reaction with humid H_2 gas product
  - Minimal water inventory in the reactor
  - Autothermal integration: use reaction heat to produce steam
- Operate reactor at low temperatures (100 – 150^{O}C) and pressures (~ atmospheric)
- Basic research to minimize water utilization and maximize H_2 delivery rate
- Apply research to design a prototype system

Critical Assumptions and Issues

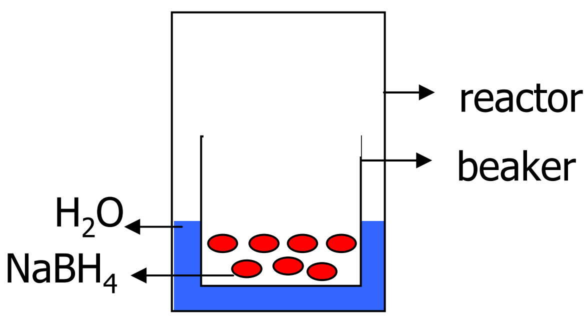
- Unreacted water from steam hydrolysis can be recovered & recycled to the reaction
- Heat of reaction can be recovered
- Cost and energy requirements of manufacturing and recycling $NaBH_4$ are crucial; research by others is addressing this.

Hydrogen Safety

- The most significant hydrogen hazards associated with this project are:
  - High reactivity of solid chemical hydrides when exposed to humidified air
  - Instability of aqueous $NaBH_4$ solutions
  - Toxicity and corrosivity of basic $NaBH_4$ solutions
- Our approach to deal with these hazards:
  - Steam/solid reaction minimizes water inventory in the reactor
  - Reactant is stored and transported in dry form
  - Reaction products are nearly dry, not an aqueous basic solution

1. Characterization of Hydrolysis Reaction Products (Hydrated Metaborates)

$$NaBH_{4(s)} + (2+x)H_2O_{(g)} \rightarrow 4H_{2(g)} + NaBO_2 \cdot x\, H_2O_{(s)}$$



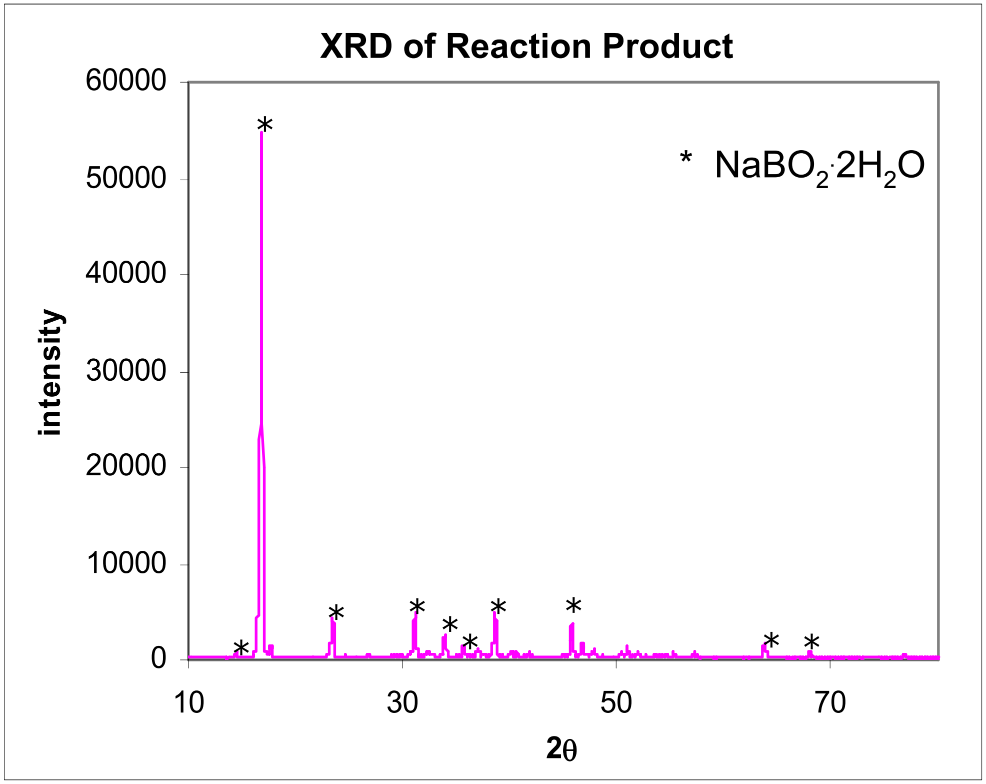
$NaBH_4$ was placed in the small beaker inside an isolated vessel as shown at left.

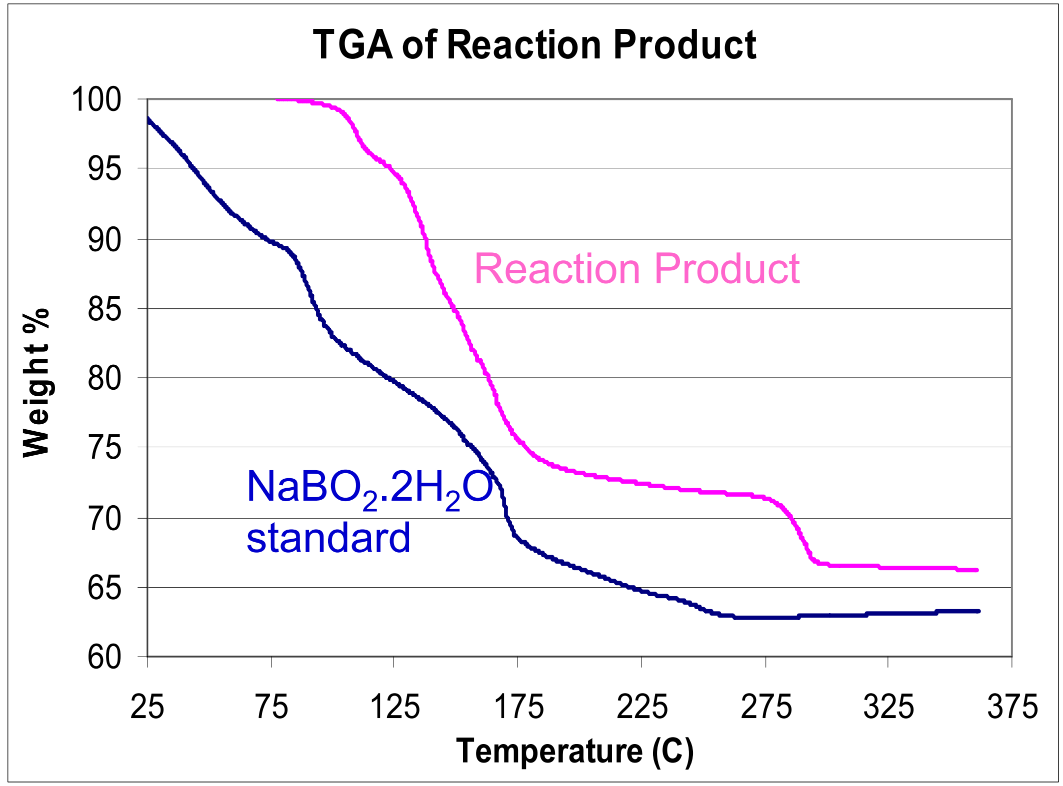
Hydrated metaborates, with unknown degree of hydration *x*, were generated by controlled exposure of $NaBH_4$ to H_2O vapor.

$NaBO_2 \bullet xH_2O$ were characterized using TGA and XRD; analyses were repeated for standard samples of $NaBO_2 \bullet 2\, H_2O$ and $NaBO_2 \bullet 4\, H_2O$.

Results are shown on the next two slides.

1. Characterization of Hydrolysis Products after Controlled Exposure to Steam



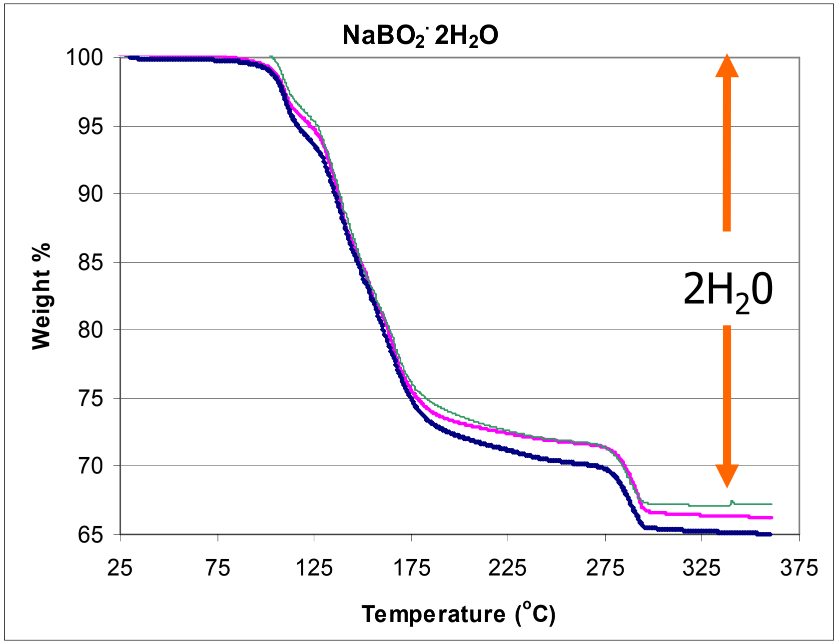


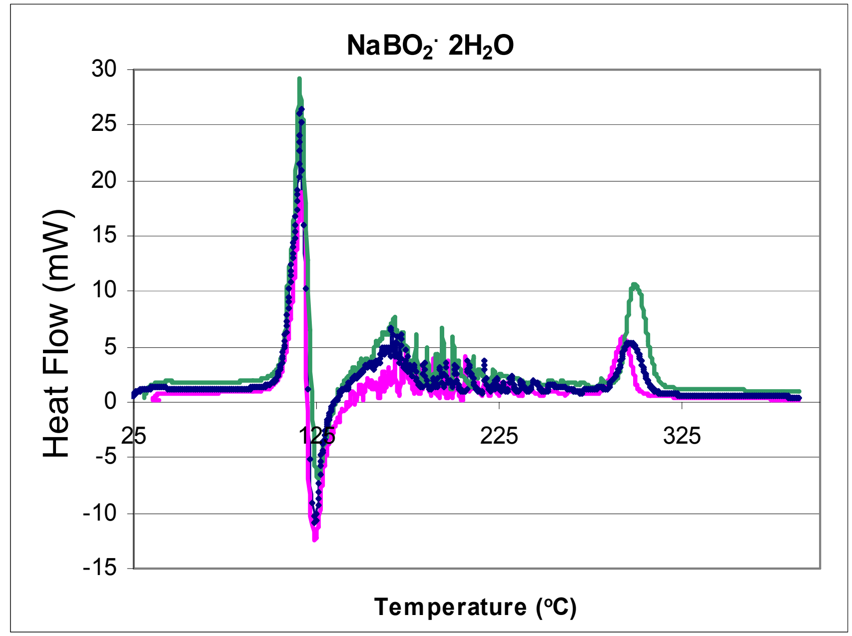
XRD of reaction product corresponds to $NaBO_2 \cdot 2H_2O$

TGA of reaction product is consistent with $NaBO_2 \cdot 2H_2O$ standard

$NaBO_2 \cdot 2H_2O$ was the primary product of the hydrolysis reaction. This translates to a decrease in the potential gravimetric and volumetric efficiencies of 33%

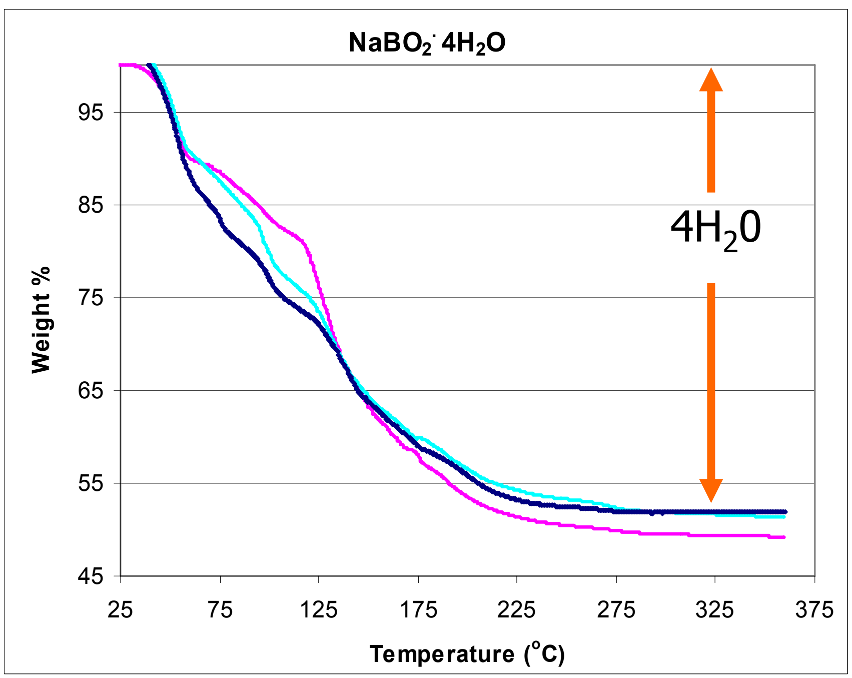
1. Characterization of Borate Standards

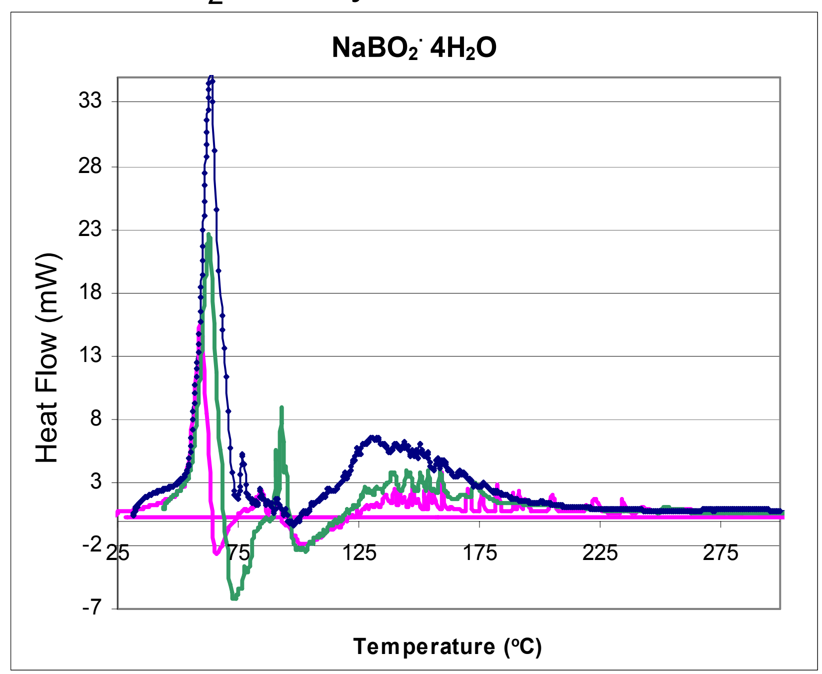




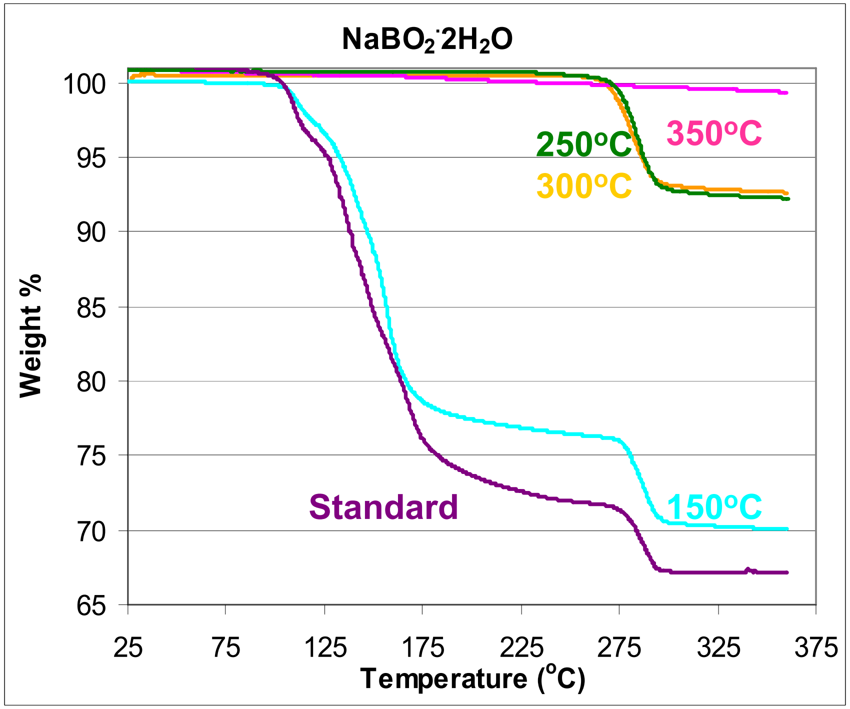
$NaBO_2 \cdot 2H_2O$ lost all its water (35%) before 400°C
$NaBO_2 \cdot 4H_2O$ lost all its water (52%) before 400°C

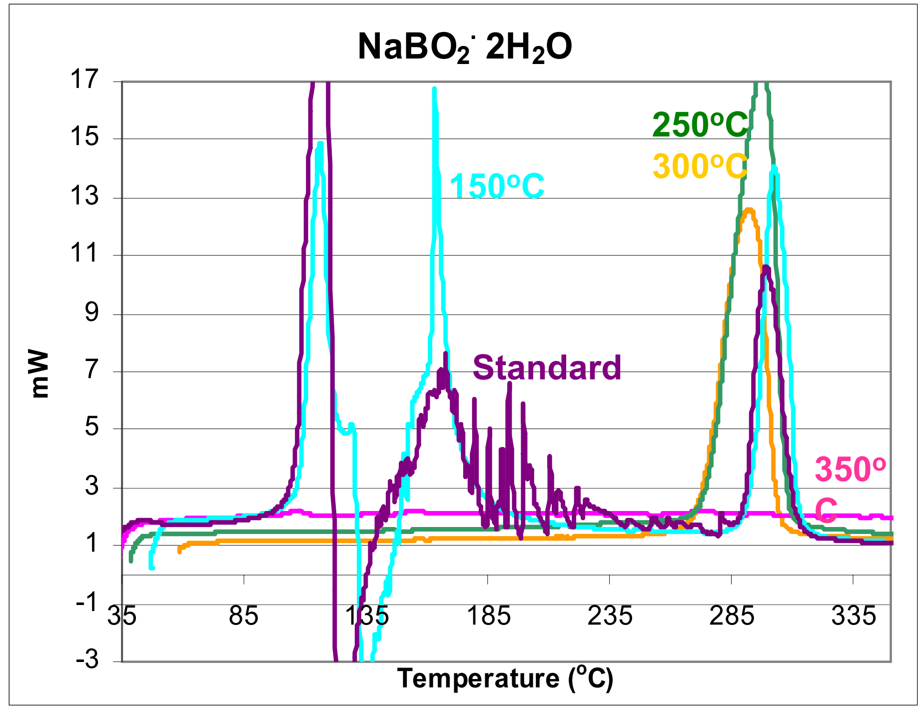
$NaBO_2 \cdot 2H_2O$ shows crystal transformation at 280 °C
$NaBO_2 \cdot 4H_2O$ is less reproducible due to larger amount of H_2O in crystal structure

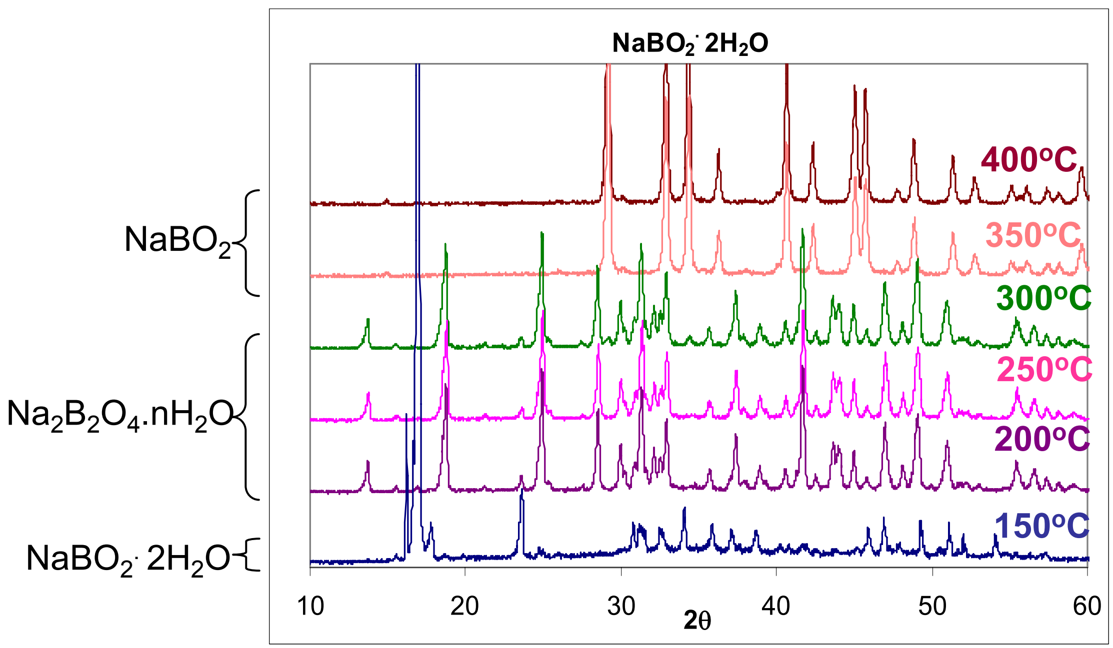




1. Thermal Dehydration of $NaBO_2{\cdot}2H_2O$ Standard







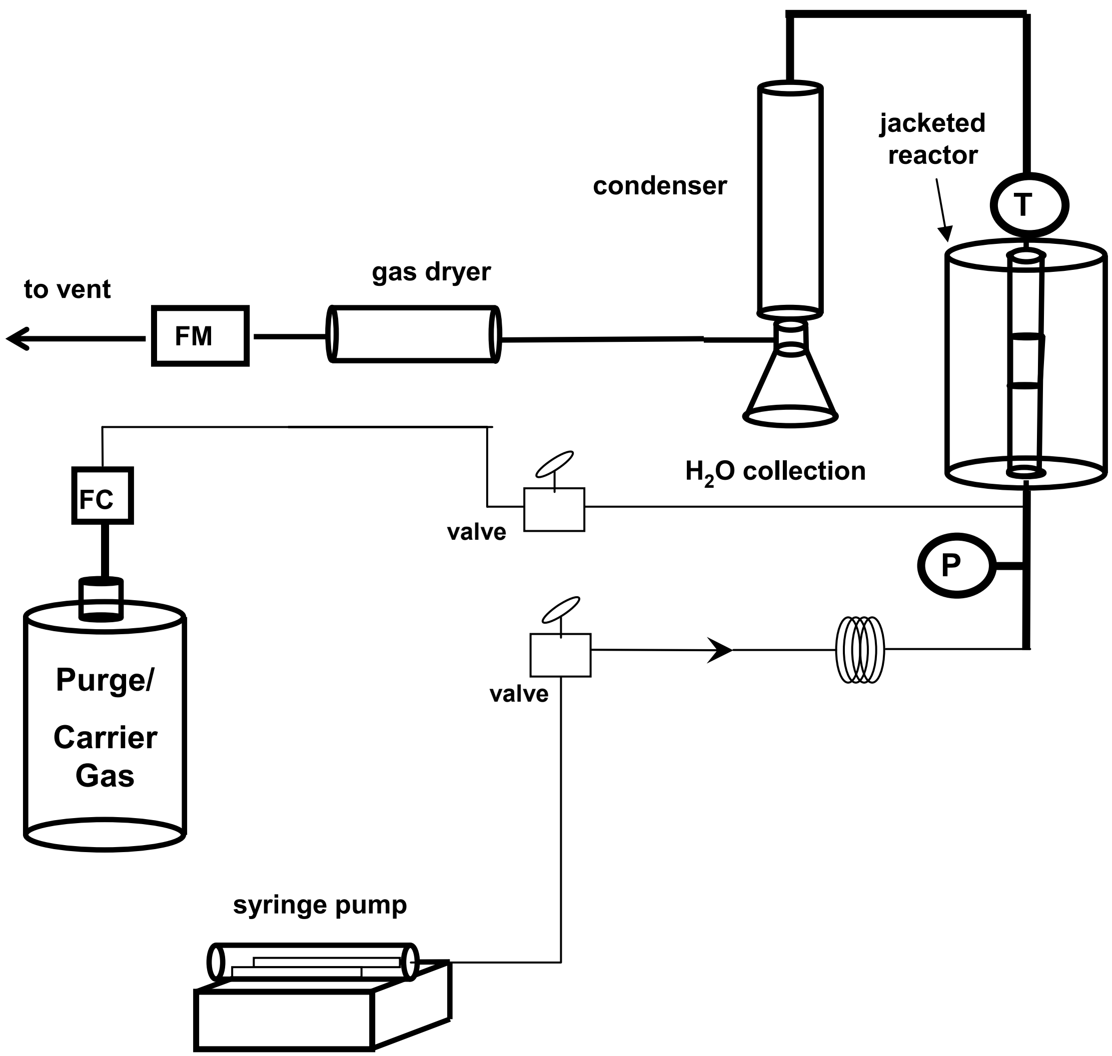
TGA: $NaBO_2{\cdot}2H_2O$ dehydrates in stages below 350°C

DSC: Peak at 280°C disappears after crystal structure transformation to $NaBO_2$ occurs

XRD: $NaBO_2{\cdot}2H_2O$ changes crystal structure with water loss

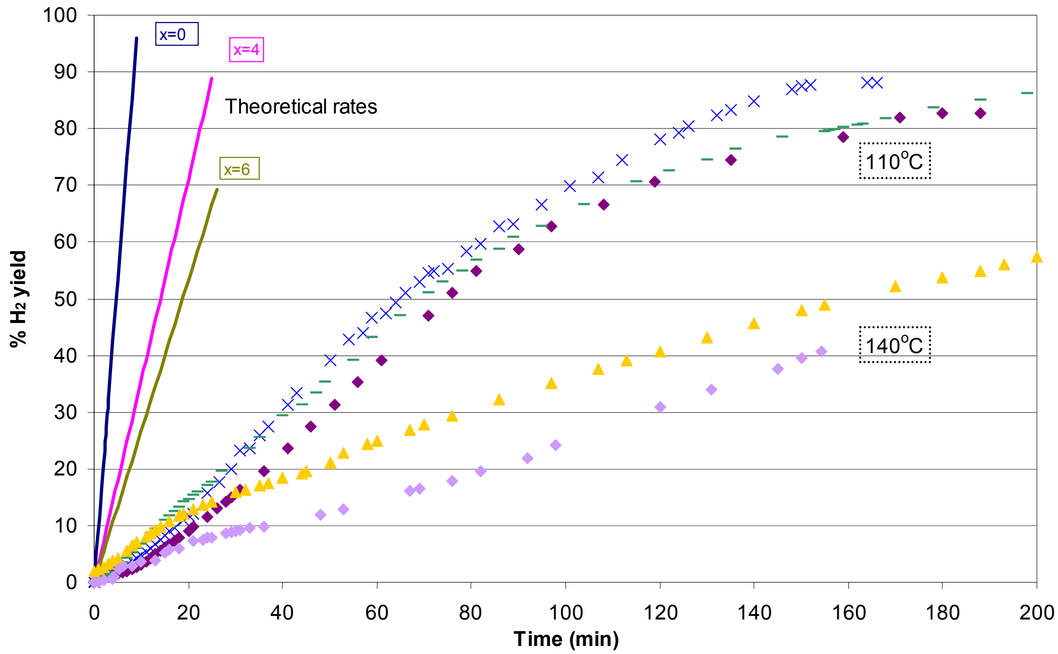
$NaBO_2{\cdot}2H_2O$ transforms into $NaBO_2$ above 300°C

2. Steam Hydrolysis Kinetics: Apparatus and Procedure

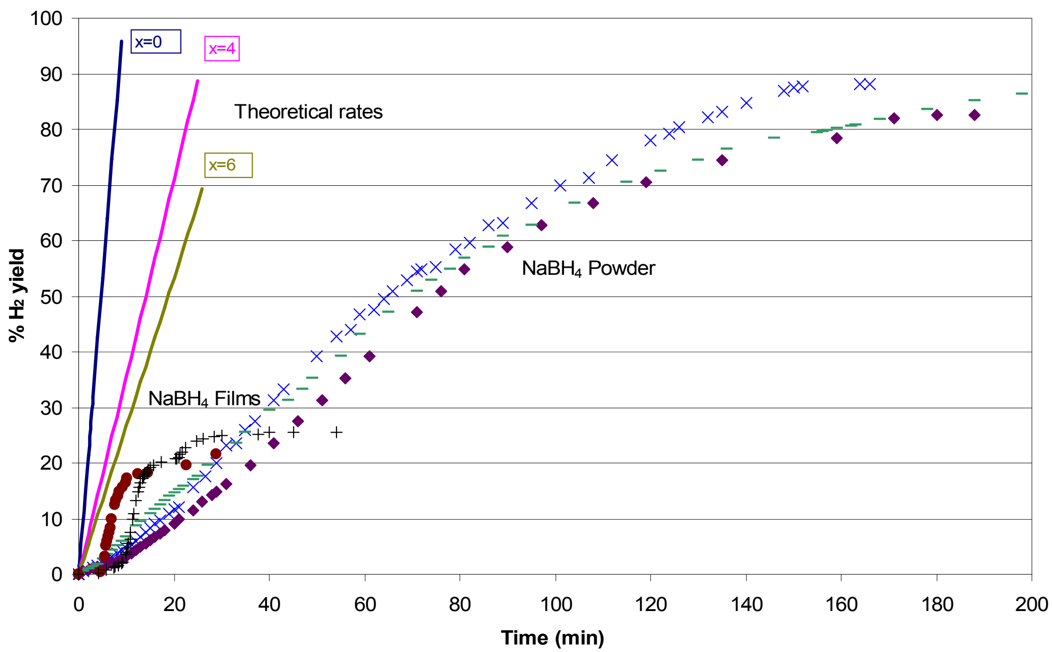


- Heated packed bed reactor in upflow configuration
  - FY05 used tilted orientation
- N_2 sweep gas is used for inert blanketing
- Product gas flow rate is measured with digital flow meters.
  - FY05 used H_2O displacement
- Water in the product stream is condensed and quantified
- Initial T_{rxr} = 110^{o}C
- Liquid water flow rate = 0.1 mL/min

2. Results from FY05



- Good yields, low rates at 110°C
- Poor yield and rates at 140°C
- Thin films give higher initial rates
- Decreased yields are attributable to insufficient reactant contact



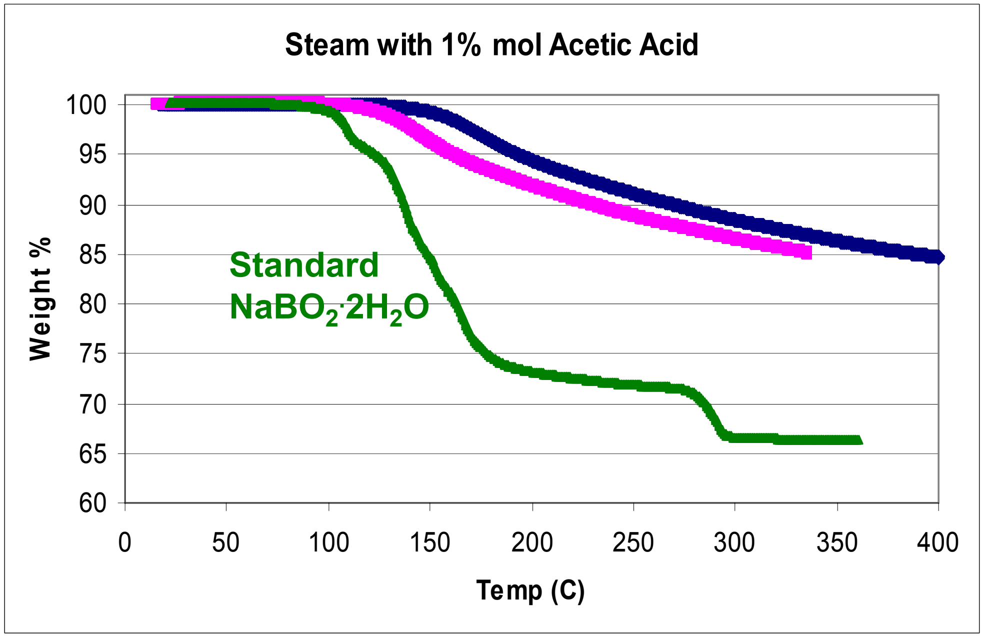
Description	T (°C)	Max Slope (mol/kg$_{NaBH4}$*min)	% of Theo. H_2 Yield
$NaBH_4$ powder	110	1.018	88.2
$NaBH_4$ powder	110	0.870	82.7
$NaBH_4$ powder	110	0.825	94.0
$NaBH_4$ powder	140	0.628	67.1
$NaBH_4$ powder	140	0.327	40.8
$NaBH_4$ on glass beads	110	4.42	19.7
$NaBH_4$ on glass beads	110	5.14	22.9
Theoretical Rates	x=0	11.1	100
	x=4	3.70	100
	x=6	2.78	100

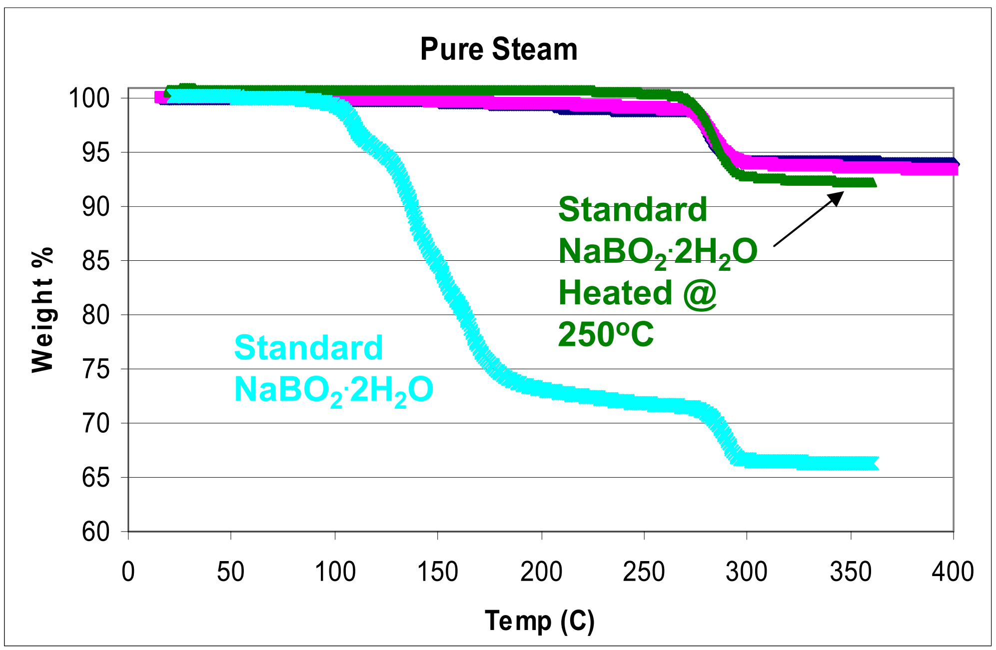
2. Representative Results, FY 06

Condition of Reactant Stream	Initial Rate (mol/kg*min)	Theoretical H_2 Yield %	H_2O Collected (% of amt fed)	Gravimetric Efficiency, % (mass H_2/(mass $NaBH_4$+ H_2O))
Pure Steam	0.843	72.5%	53%	1.34
Pure Steam	0.892	85.4%	92.5%	7.31
Pure Steam	0.906	90.3%	87.5%	5.01
1mol% HAc	0.790	92.4%	75%	3.0
1mol% HAc	1.044	92.7%	90%	6.6
15 mol% MeOH	0.629	72.9%	90%	4.85

Gravimetric efficiency assumes that condensed water can be recovered and recycled.

2. TGA of Products from Reactor





Reaction products allowed to dry for several hours under inert N_2 atmosphere prior to characterization analysis

Reaction with acetic acid vapor solution generates product other than $NaBO_2{\cdot}2H_2O$

Reaction with pure steam yields product similar to $NaBO_2{\cdot}2H_2O$ that was preheated to 250^oC

3. ^{11}B NMR Analysis

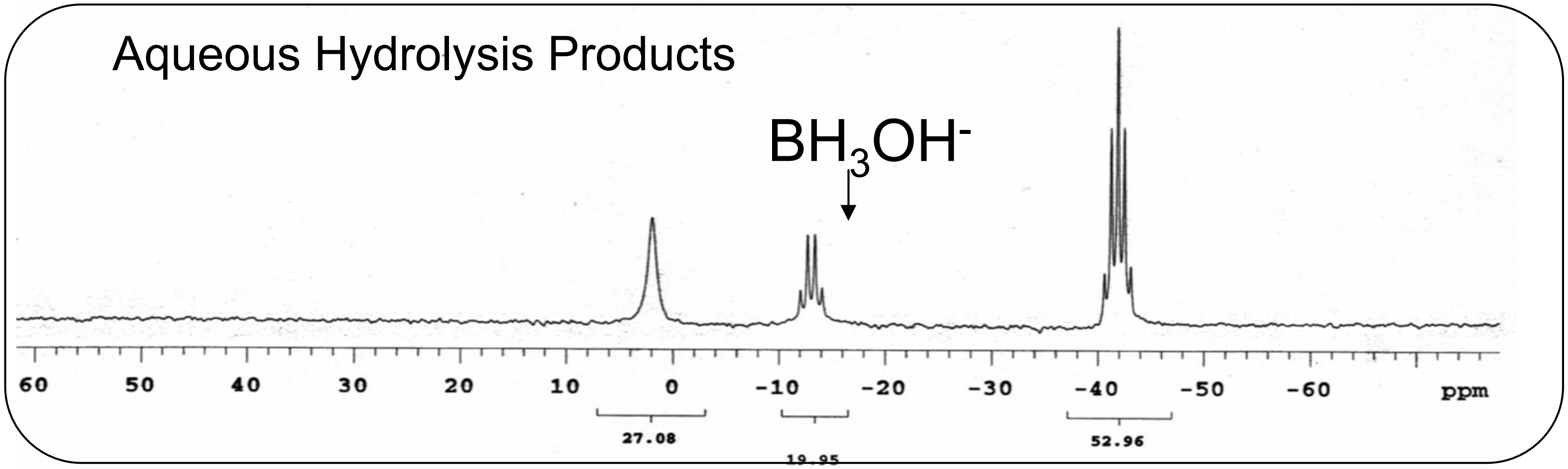
Objectives

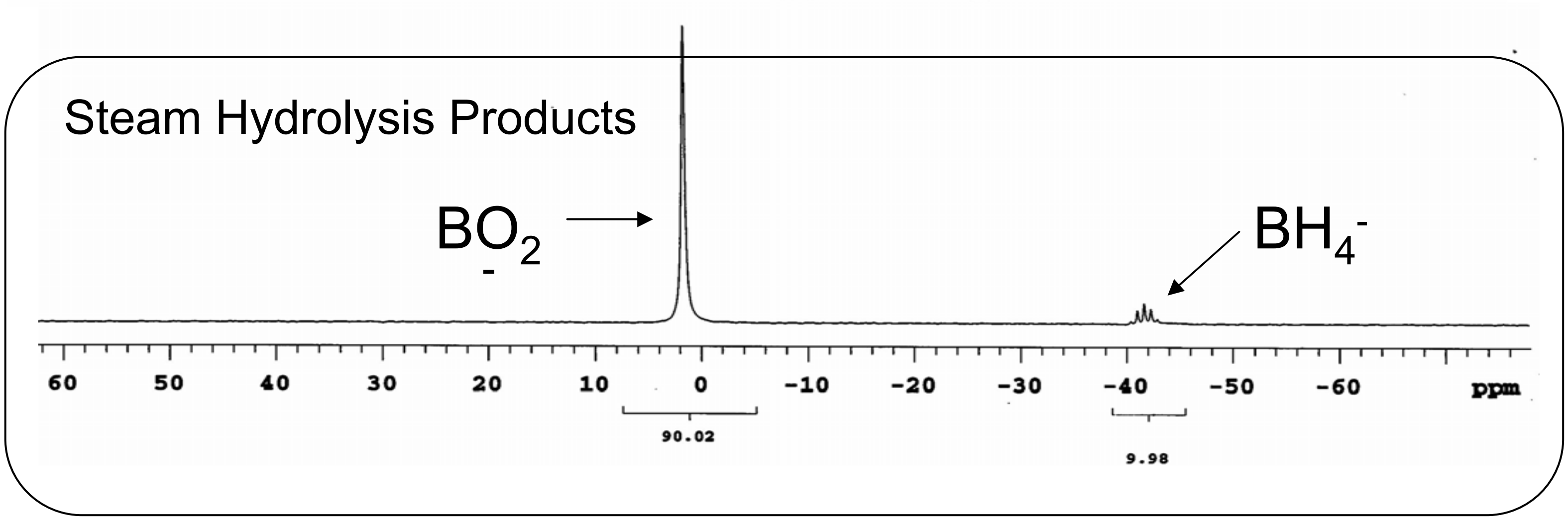
- Characterize solid reaction products from steam hydrolysis; compare to liquid-phase reaction intermediates
  - Detect BO_2^- and unreacted BH_4^- in solid products
- Analyze condensate from product stream
  - Detect carry-over of boron-containing species (if any)
- Use these results to help interpret steam hydrolysis reaction pathway and differences from aqueous hydrolysis pathway

Procedure

- 1mL of sample dissolved in 0.1M NaOH in 5mm NMR tubes
- Analyzed using a Varian Mercury/VX 400 with a $BF_3 \cdot O(C_2H_5)_2$ reference

3. ^{11}B NMR Analysis





BH_3OH^- intermediate does not appear in analysis of steam reaction indicating a different reaction mechanism than the aqueous reaction. Understanding the steam hydrolysis mechanism may lead to strategies to reduce water usage and lower system weight.

4. Commercial / Industrial Application Development

- Steam hydrolysis of $NaBH_4$ is the basis of a start-up company DEnergy LLC.
- 3 invention disclosures have been filed with the University of South Carolina.
- Prototype design is currently being tested and developed for preliminary portable power applications
  - Gateway approach to automotive technologies
- More information is available at http://ip.research.sc.edu/

5. Future Research Directions

FY06

- Steam/solid $NaBH_4$ system
  - Measure intrinsic kinetic rate of reaction under different operating temperatures and partial pressures of steam
  - Determine hydration characteristics of products in order to improve gravimetric efficiency and understand kinetic limitations
- Investigate additional solid hydride systems
  - Evaluate additional hydrides and mixtures to meet FreedomCAR requirements
- Submit description of prototype system design
  - Design will be based on laboratory-scale experiments
  - Design will be evaluated according to FreedomCar targets such as mass and volumetric efficiency and startup dynamics

Summary

- Yields approach 100% with $NaBH_4$ in powder form with pure steam, and also with addition of acetic acid and MeOH
- Acetic acid and MeOH additives give consistent high H_2 yields
- Reaction product, $NaBO_2 \cdot 2H_2O$, corresponds to an excess hydration factor of 2 (x=2)
  - Potential limitation on gravimetric/volumetric efficiency
- Hydration and crystal structure of $NaBO_2 \cdot 2H_2O$ are affected by reaction temperature and post-treatment.
  - Complete dehydration of $NaBO_2 \cdot 2H_2O$ occurs at $T < 350^oC$

Publications and Presentations

1. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, "Hydrogen storage in chemical hydrides". ***ACS National Meeting***, Philadelphia. (Aug. 2004)
2. Michael A. Matthews, Thomas A. Davis, and Eyma Y. Marrero-Alfonso, "Production of hydrogen from chemical hydrides via hydrolysis with steam". ***AIChE Annual Meeting***, Austin. (Nov 2004)
3. Steam Hydrolysis of Chemical Hydrides: Meeting the Challenge of Hydrogen Storage. Marrero-Alfonso, E.Y., Gray, J., Matthews, M.A., Davis, T.A. 230th ACS National Meeting, Washington, DC, Aug 28-Sept 1, 2005.
4. New method for hydrolysis of chemical hydrides. Marrero-Alfonso, E.Y., Gray, J.R., Davis, T.H., and Matthews, M.A. Second International Conference on Green and Sustainable Chemistry, and Ninth Annual Green Chemistry and Engineering Conference, Washington D.C. June 20-24, 2005.
5. J.R. Gray, E.Y. Marrero, T.A. Davis, and M.A. Matthews, "Steam Hydrolysis of Chemical Hydrides : Meeting the Challenge of Hydrogen Storage". ***42nd Power Sources Conference*** Philadelphia, Pennsylvania. June 12-15, 2006.