

Clean Energy Research

Project III: Hydrogen Storage Using Chemical Hydrides

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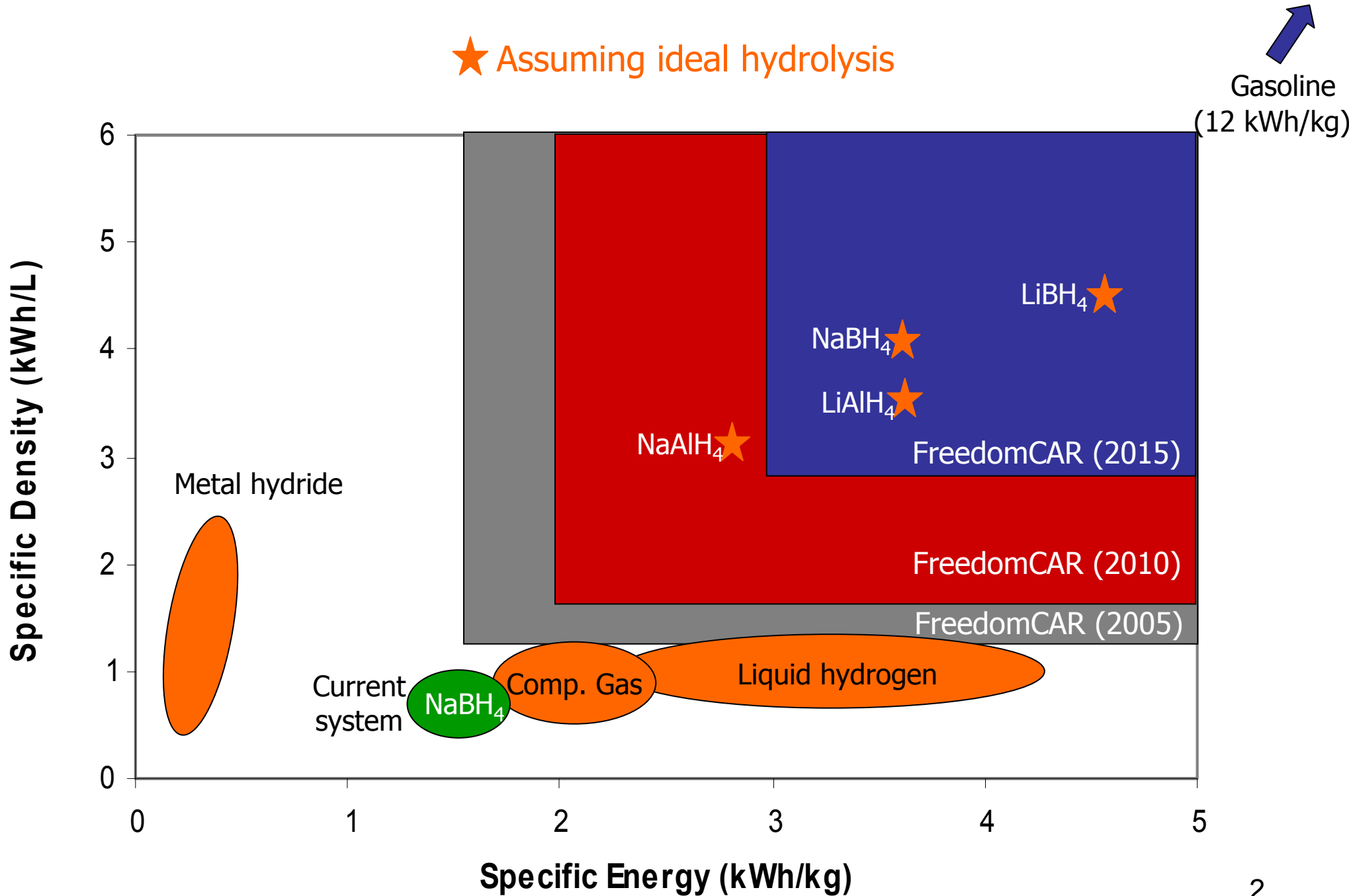
May 25, 2005

STP56

This presentation does not contain any proprietary or confidential information

Current Technologies

★ Assuming ideal hydrolysis



Hydrogen Storage Using Chemical Hydrides

Objectives

- **Develop hydrogen storage and delivery technology based on steam + chemical hydrides for automotive fuel cell applications**
 - Evaluate novel steam + solid chemical hydride reaction as basis for on-demand 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 characterization of hydration characteristics of products (14MAA)
 - Prototype design development (16 MAA)

DOE FreedomCAR Technical Targets

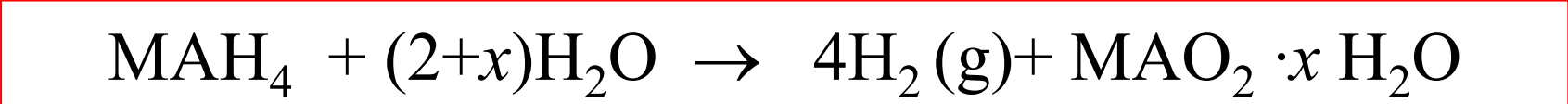
Year	2005	2010	2015
Usable Specific Energy from Hydrogen			
Target (kWh/kg system)	1.5	2.0	3.0
Target (kg H ₂ /kg system)	0.045	0.06	0.09
Usable Energy Density from Hydrogen			
Target (kWh/L system)	1.2	1.5	2.7
Target (kg H ₂ /L system)	0.036	0.045	0.081

DOE FreedomCAR Technical Targets

Year	2005	2010	2015
Fuel Cost [\$ per gasoline equiv. at pump]			
Target	3	1.5	1.5
Projection	2.5	1.8	1.8
Minimum full-flow rate [g/sec/kW]			
Target	0.02	0.02	0.02
Projection	0.025-0.03	0.025-0.03	0.025-0.03

Gravimetric Efficiency (kg H₂/kg reactants) Fuel Only

Hydride	x=0	x=1	x=2	x=3
NaBH₄	0.108	0.087	0.073	0.063
LiBH ₄	0.139	0.106	0.085	0.072
LiAlH ₄	0.108	0.087	0.073	0.063
NaAlH ₄	0.089	0.074	0.063	0.056



$x = 3$ is the lowest excess hydration factor obtained so far in our lab; optimization continues.

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Gravimetric Efficiency (kg H₂/kg reactants)

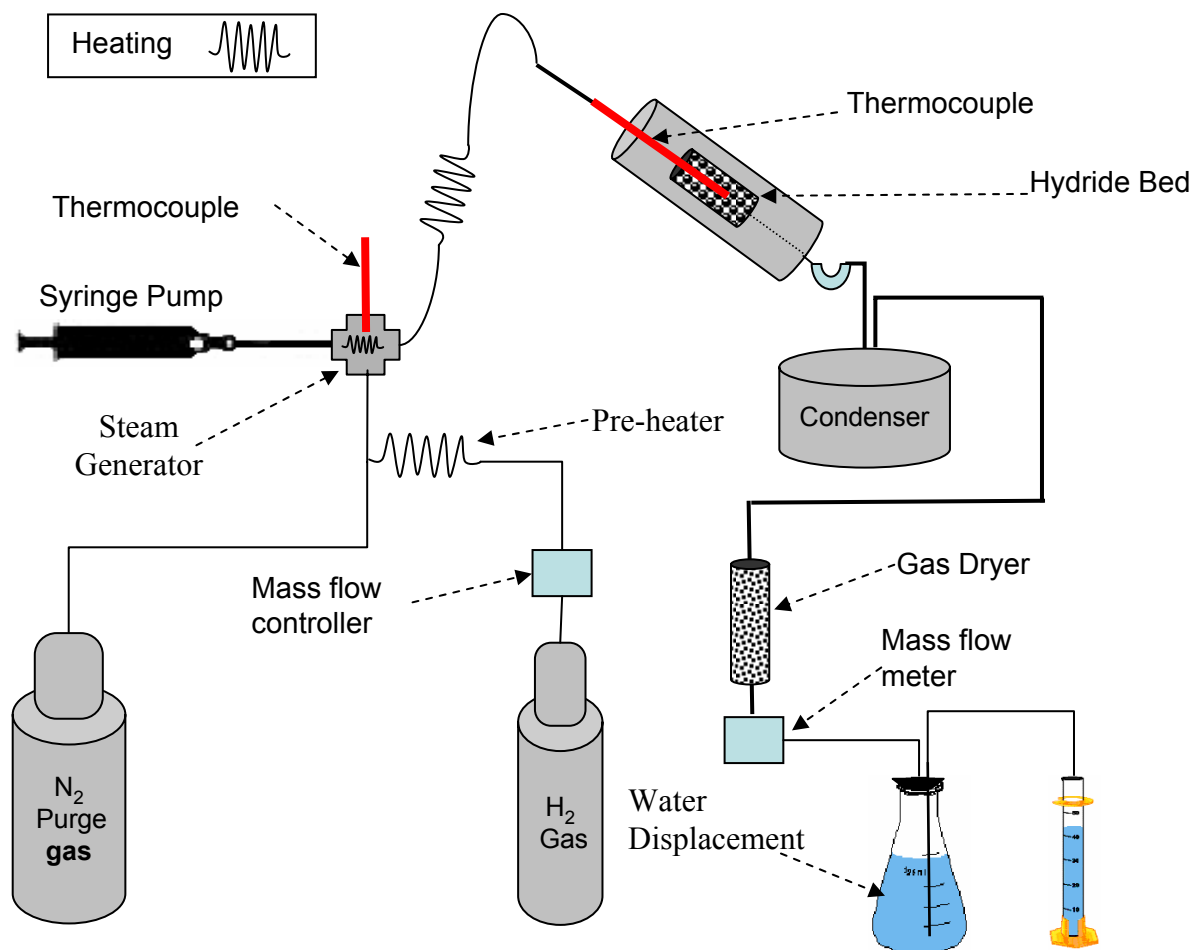
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If $x=3$, mass allowed for reactor = -0.429 kg reactor/kg system
Not possible to meet 2015 target
 0.05 kg reactor/kg system
To meet 2010 target for
 0.286 kg reactor/kg system
To meet 2005 target

Approach

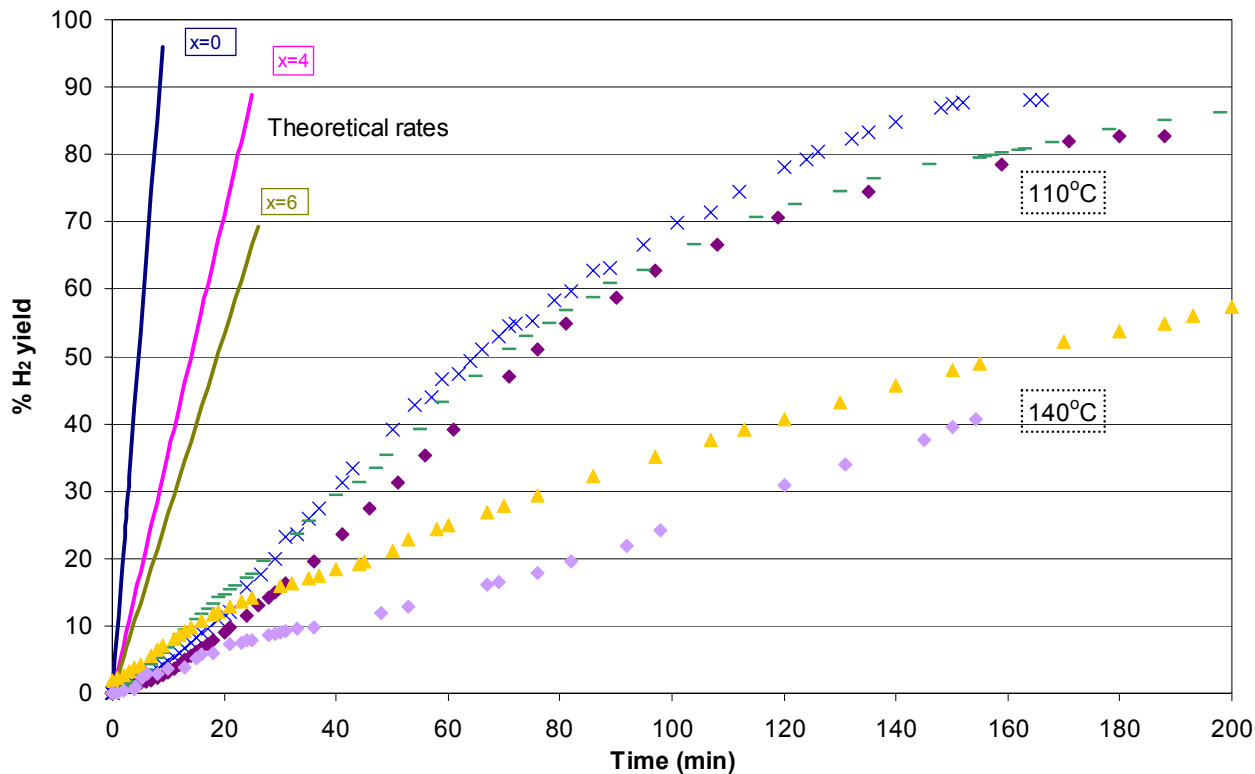
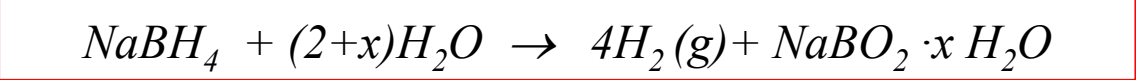
- Hydrolyze chemical hydrides with dry steam, rather than aqueous catalytic process
 - Chemically simple reaction
 - Humid H₂ gas product
 - Hydride reactants and products are dry
 - Minimal water inventory in the reactor
 - Autothermal integration: use heat of reaction to produce steam
- Operate reactor at low temperatures (100 °C – 150 °C) and pressures
- Conduct basic research on the reaction to utilize water efficiently and maximize H₂ delivery rate
 - Translate results to prototype design via mathematical model

Data Collection From First Generation Screening Reactor



- Advantages
 - Screen different chemical hydrides
 - Investigate reactant preparation methods
- Disadvantages
 - Significant dead volume
 - Limited control over steam flow rate
 - Insufficient reactant contact
 - Channeling

NaBH₄ Powder Reacts Slowly



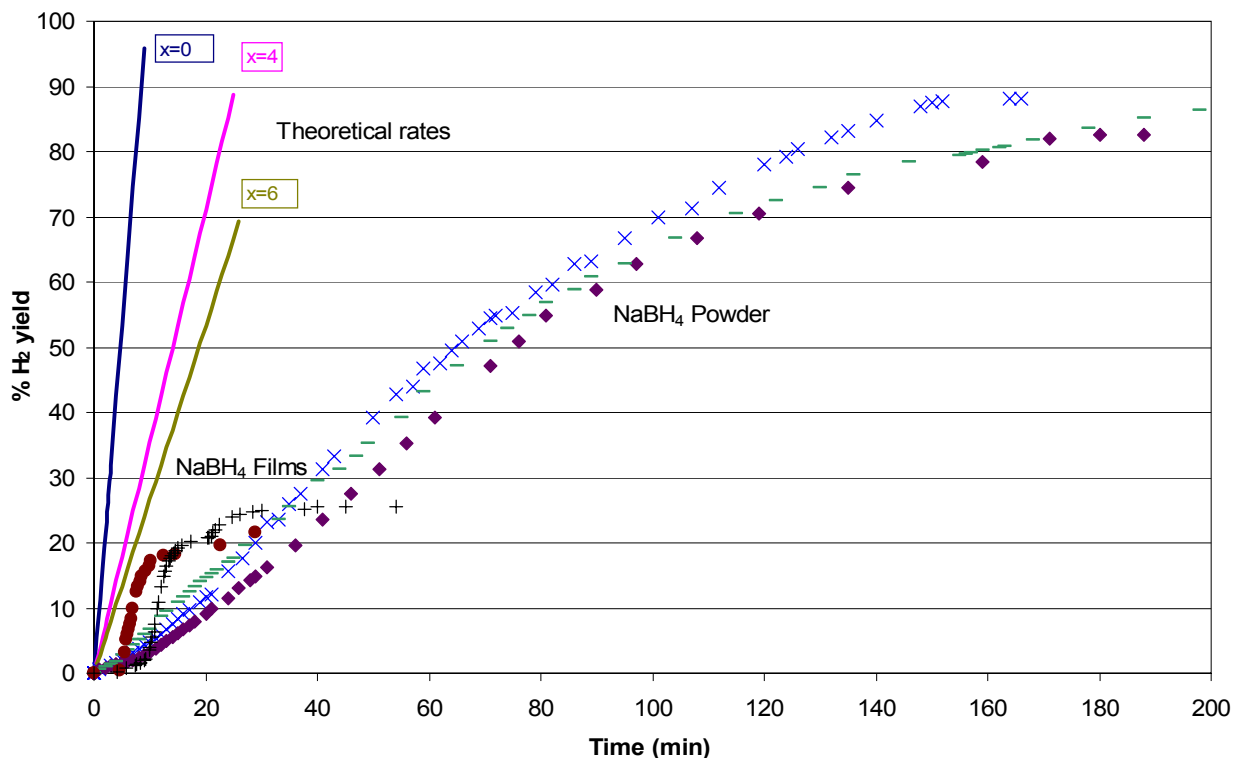
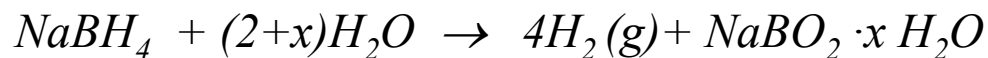
- Good yields, low rates at 110 °C ($x > 10$)
- Poor yield and rates at 140 °C likely related to NaBO₂·xH₂O by-product

x is the “excess hydration factor,” representing the degree of hydration of the borate products

FreedomCar Gravimetric Efficiency

	Target (wt%)	Equiv. x
2005	4.5	4
2010	6.0	3
2015	9.0	1

Films of Recrystallized NaBH₄ Give Improved Initial Rates



x is an indirect measurement of the efficiency of water utilization of the reaction

- Thin films give higher initial rates ($x = 2-3$)
- Decreased yields are attributable to channeling within reactor and insufficient reactant contact at longer times.

FreedomCar Gravimetric Efficiency

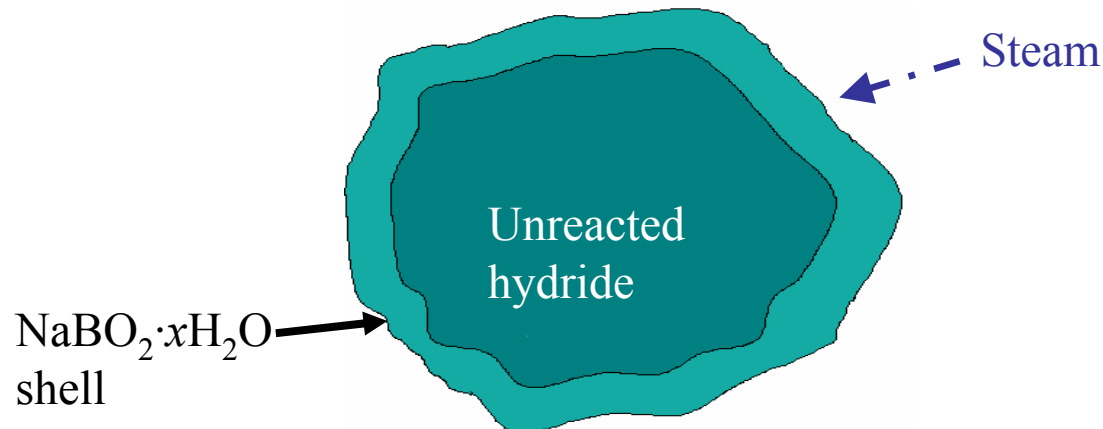
	Target (wt%)	Equiv. x
2005	4.5	4
2010	6.0	3
2015	9.0	1

Summary of Steam-Solid Hydrolysis Data From Screening Reactor

Description	T (°C)	Max Slope (mol/kgNaBH ₄ *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 film	110	4.42	19.7
NaBH ₄ film	110	5.14	22.9
Theoretical Values (assuming instantaneous rxn)		11.1 (x=0)	100
		3.70 (x=4)	100
		2.78 (x=6)	100

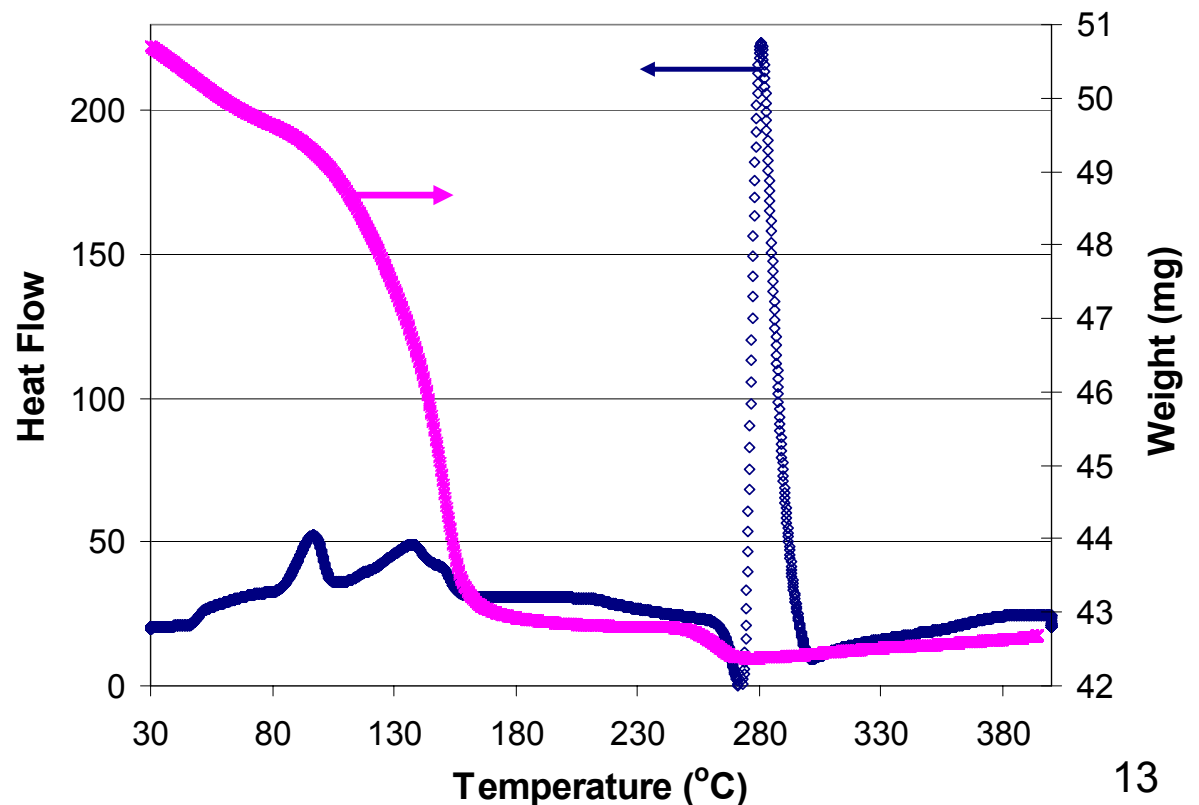
- Powder data
 - Rate at higher temp ~ 53% of rate for lower temp
 - Yield at high temp ~61% of yield for lower temp
- Thin film data
 - Rate for thin film ~5x rate for powder data
 - Yield for thin film ~25% of yield for powder data

Water Utilization and Product Characterization



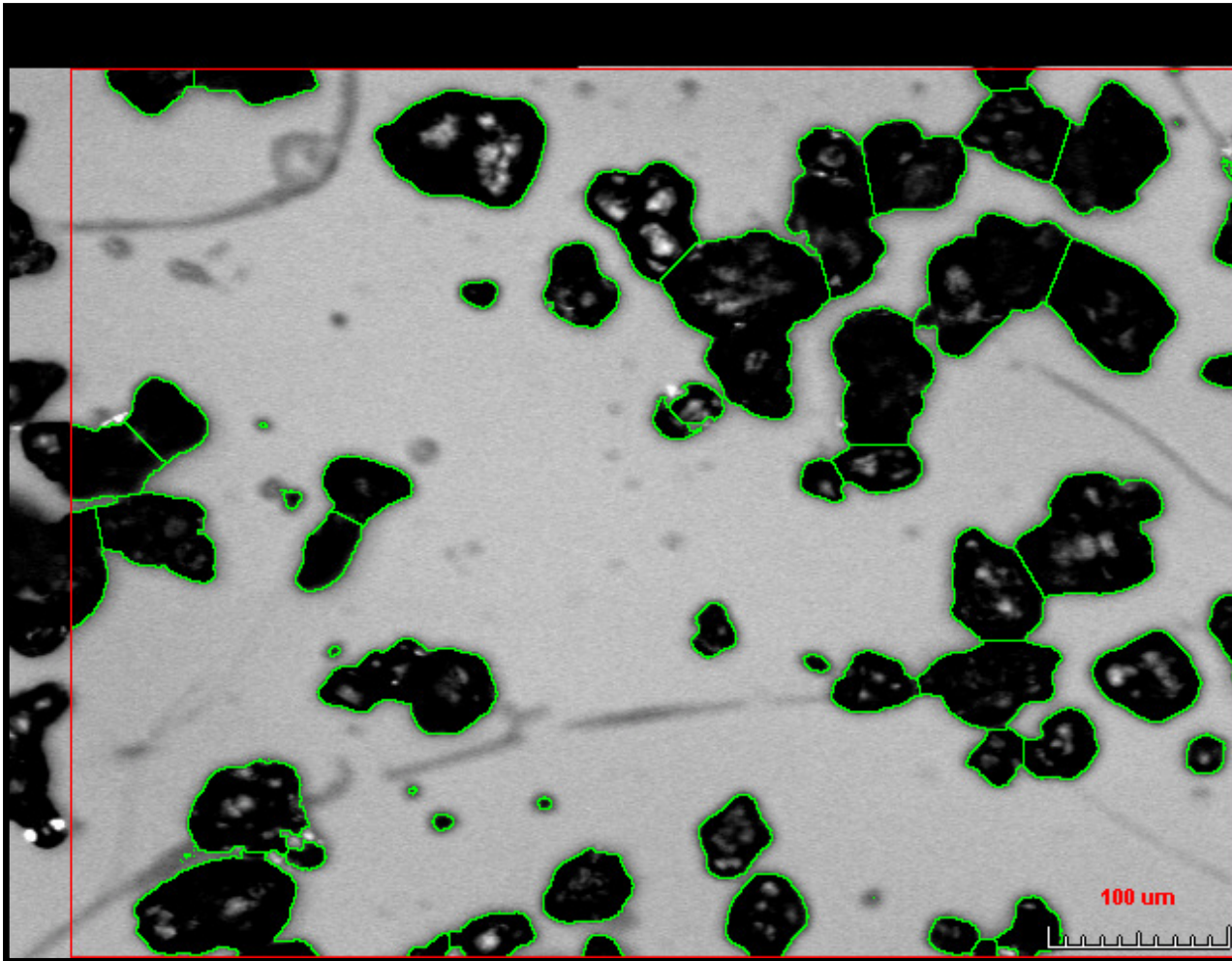
- NaBO₂·xH₂O product is a dense solid
 - Dense by-product causes mass transfer limitation
 - Highly hydrated byproducts
- Waste water and decrease gravimetric efficiency

- Investigate hydration properties of products with Thermal Gravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC)
 - TGA: 17 wt% loss associated with H₂O loss by borate product
 - DSC: peak indicates phase transition in products



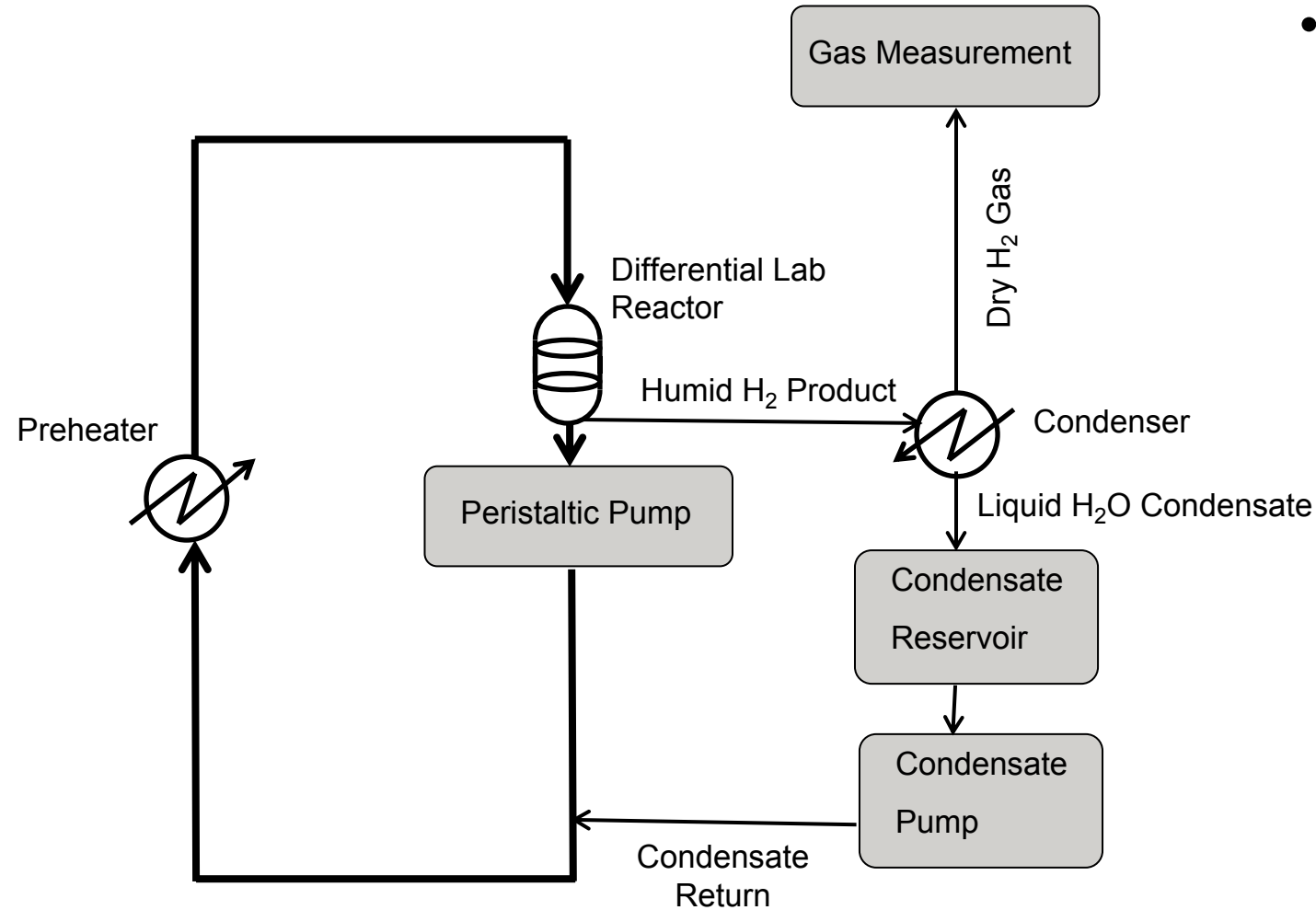
Particle Size Distribution

Microscope image of NaBH_4 powder



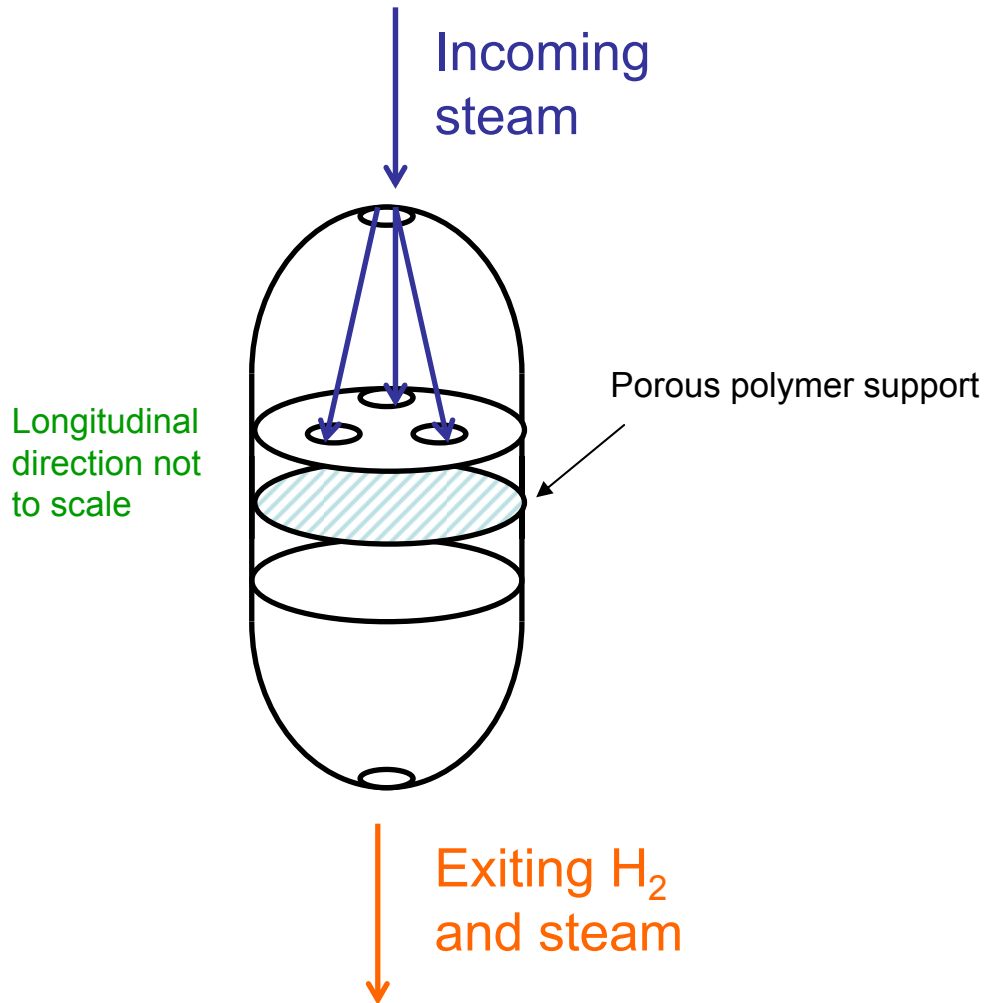
- Determine effect of particle size
 - Kinetic rates and H_2 production
 - Reduce shell inhibition
- Optical method with digital analysis to measure PSD

Construction of Differential Reactor with Water Recirculation



- Differential lab reactor
 - Uniform steam/solid contact
 - More compact
 - Controlled steam flow rates
 - Water utilization tracked by closed condensate loop

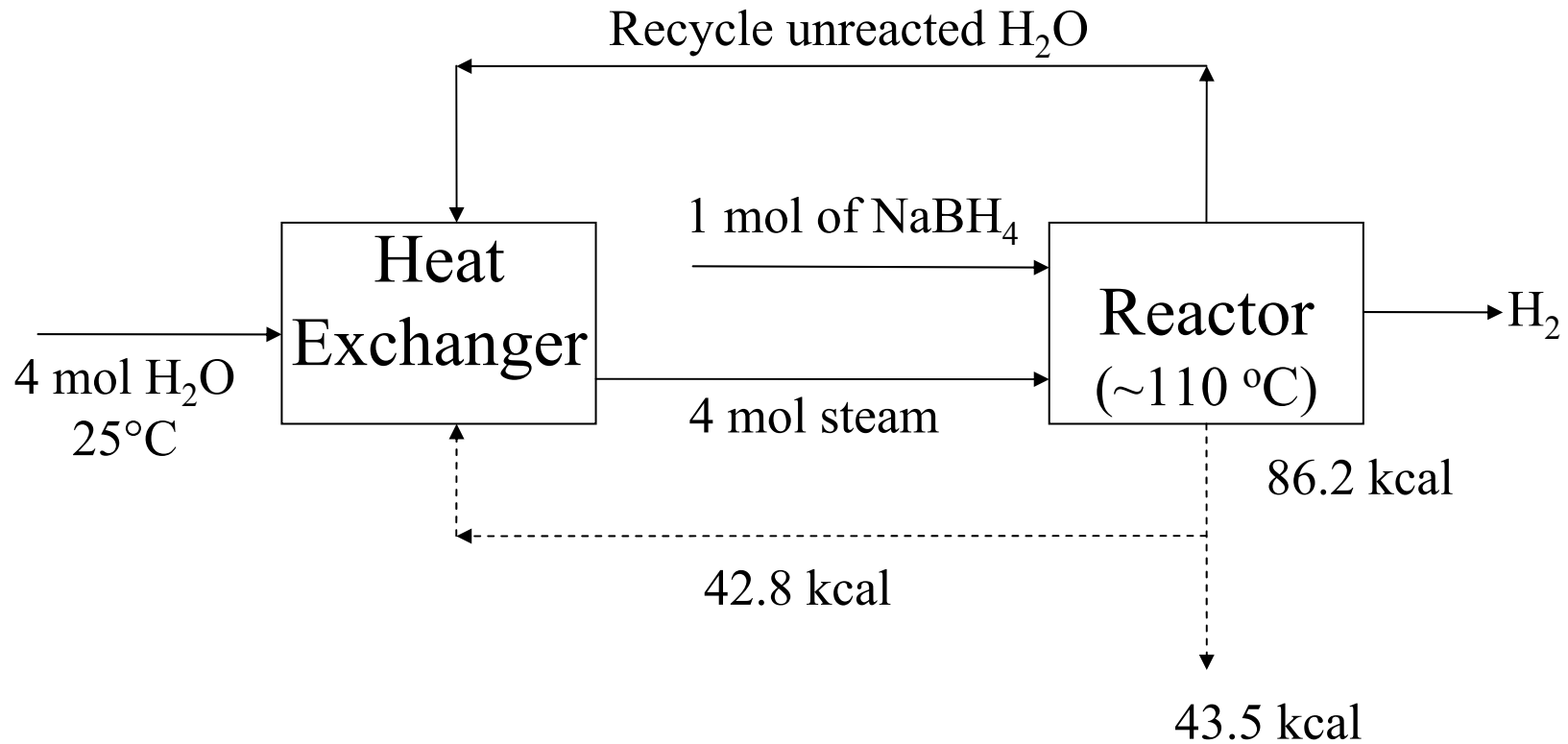
Differential Lab Reactor Details



- NaBH₄ powder dispersed on porous polymer support
 - Particles $\approx 150 \mu\text{m}$
 - Pore size $\approx 0.50 \mu\text{m}$
- Achieve uniform contact
 - Reduce agglomeration and shell formation
 - Reduce mass transport limitations
 - De-couple kinetics from transport

Thermally Neutral Hydrogen Generator

(Energy balances for $x=2$)



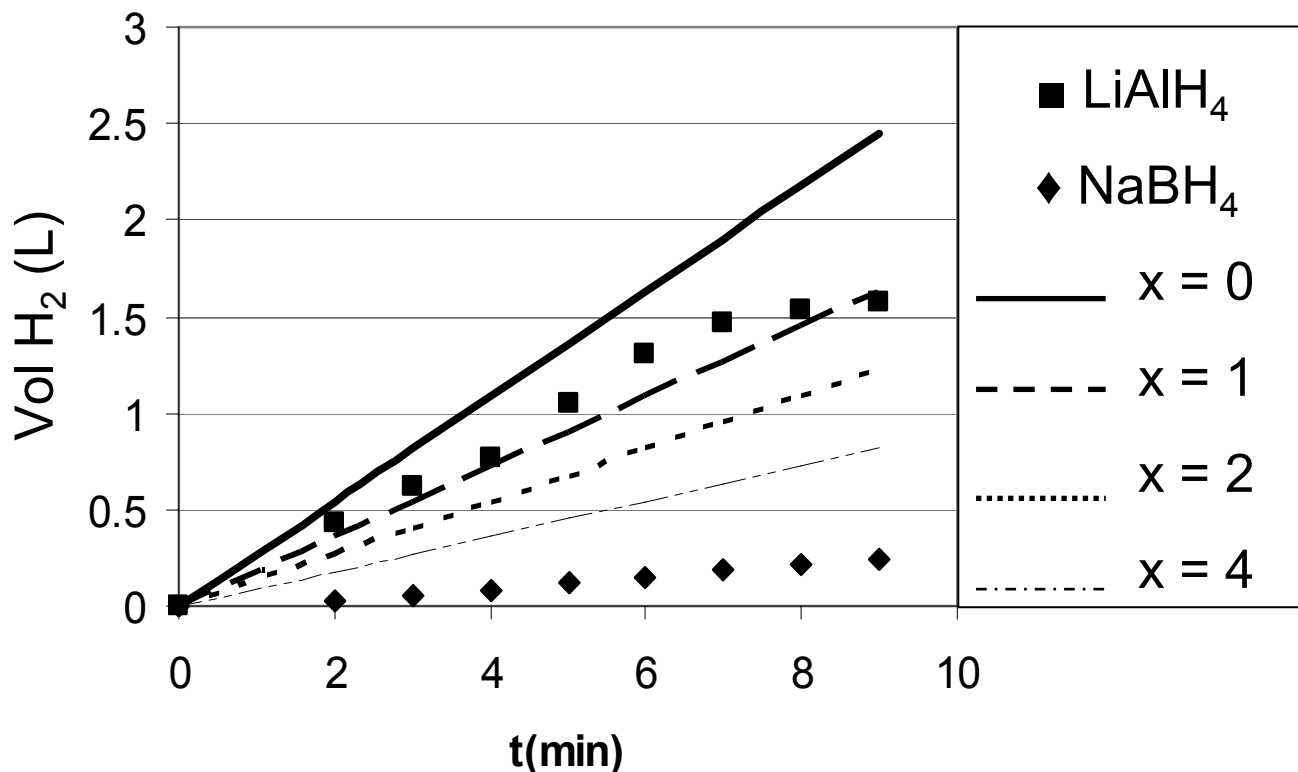
Increased Range of T_{rxn}

- Objective is to design thermally-integrated storage and delivery reactor
- Reaction is currently more efficient at lower T_{rxn}
- Need techniques to operate at higher temperature for efficient heat transfer
 - $Q = UA\Delta T_{\text{lm}}$
- Better understanding of reaction kinetics and product formation is crucial

Potential for Other Hydrides



H₂ Production from NaBH₄ and LiAlH₄



- Other hydrides more reactive
 - May be difficult to control reaction
 - May be unstable for extended shelf-life
- NaBH₄ *could be* benchmark for prototype development

Responses to Previous Year Reviewers' Comments

- Not applicable – first year project.

Future Research Directions

FY05

- Steam/solid NaBH₄ system
 - Obtain improved gravimetric efficiency of reaction
 - Liberate H₂ wt% > 4.5 by 4/30/2005
 - Measure intrinsic kinetic rate of reaction under different operating temperatures, pressures and reactant preparations
 - Full flow of H₂ in < 10 sec by 10/30/2005
 - Clarify the effect of particle size on reactant contact and mass transfer
 - Determine hydration characteristics of products in order to improve gravimetric efficiency and understand shell formation
- Investigate additional solid hydride systems
 - Evaluate additional hydrides based on FreedomCAR requirements

FY06

- 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

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)

Hydrogen Safety

- The most significant hydrogen hazards associated with this project are:
 - High reactivity of solid chemical hydrides when exposed to humidified air
 - Toxicity: Avoid ingestion or contact with eyes and mucous membranes
- Our approach to deal with this hazard is:
 - Handle hydrides in an inert atmosphere within a glove box
 - Use small quantities for laboratory experiments
 - Blanket reactor with inert gas