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System Level Analysis of Hydrogen Storage Options

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U.S. Department
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Project ID: ST2

Overview

Timeline

- Project start date: Oct 2004
- Project end date: Sep 2009
- Percent complete: 70%

Budget

- FY07: \$430 K
- FY08: \$525 K

Barriers

- H₂ Storage Barriers Addressed:
 - A: System Weight and Volume
 - B: System Cost
 - C: Efficiency
 - E: Charging/Discharging Rates
 - J: Thermal Management
 - K: System Life-Cycle Assessments

Interactions

- FreedomCAR and Fuel Partnership
- Storage Systems Analysis Working Group, MH COE, CH COE
- BNL, LANL and PNNL, LLNL, MCEL and RH, TIAX, H2A, and other industry

Objectives

- Perform independent systems analysis for DOE
 - Provide input for go/no-go decisions
- Provide results to CoEs for assessment of performance targets and goals
- Model and analyze various developmental hydrogen storage systems
 - On-board system analysis
 - Off-board regeneration
 - Reverse engineering
- Identify interface issues and opportunities, and data needs for technology development

Approach

- Develop thermodynamic and kinetic models of processes in cryogenic, complex metal hydride, carbon, and chemical hydrogen storage systems
- Calibrate, validate and evaluate models
- Work closely with the DOE Contractors, Centers of Excellence, Storage Tech Team, other developers, and Storage Systems Analysis Working Group
- Assess improvements needed in materials properties and system configurations to achieve H₂ storage targets

Technical Accomplishments

Cryo-Compressed Hydrogen (March 2008): Backup slides

- Updated the storage capacity of LLNL Gen-2 system

Carbon Storage (December 2007): Backup slides

- Revised analysis to reflect 2010 and 2015 delivery P targets

Metal Hydrides (June 2008)

- Performance of on-board system with alane slurries
- WTT efficiency for off-board regeneration of alane

Sodium Borohydride (Go/No-Go Decision: September 2007)

- Performance of on-board system with SBH hydrolysis
- WTT efficiency of regenerating SBH by MCEL and RH flowsheets

Hydrogen Storage in Liquid Carriers (December 2007)

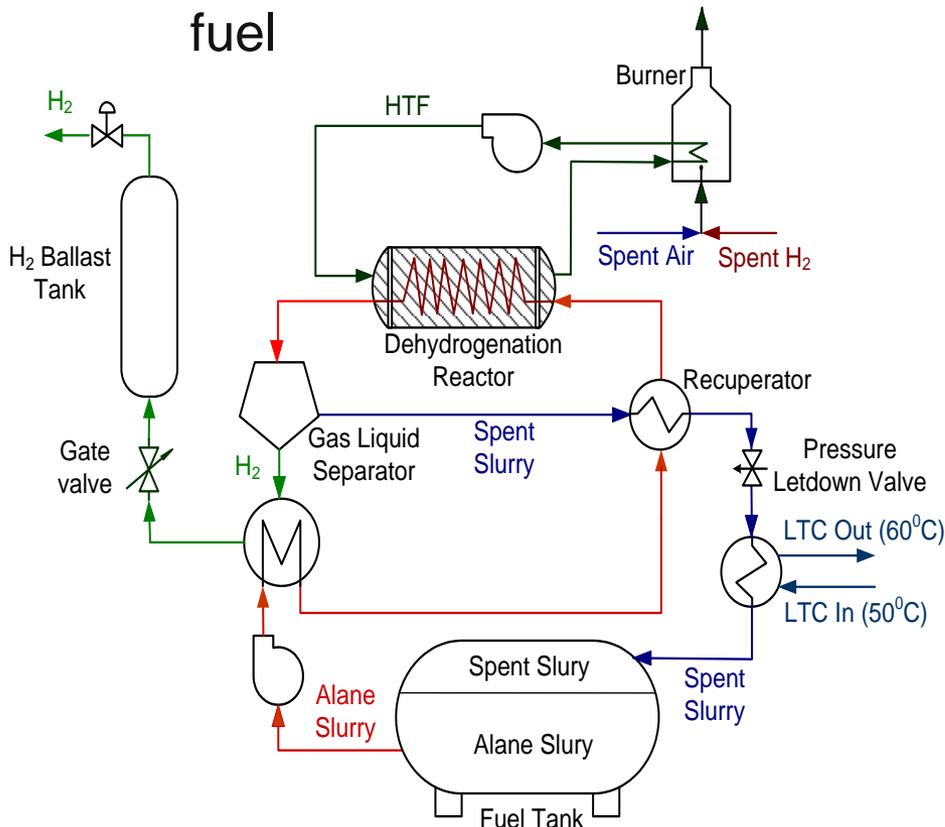
- WTT efficiency of rehydrogenation of organic liquid carriers

Hydrogen Storage in Amine Borane (October 2008)

- WTT efficiency of AB regeneration schemes being developed at the CHCoE

H₂ Storage as Alane Slurry

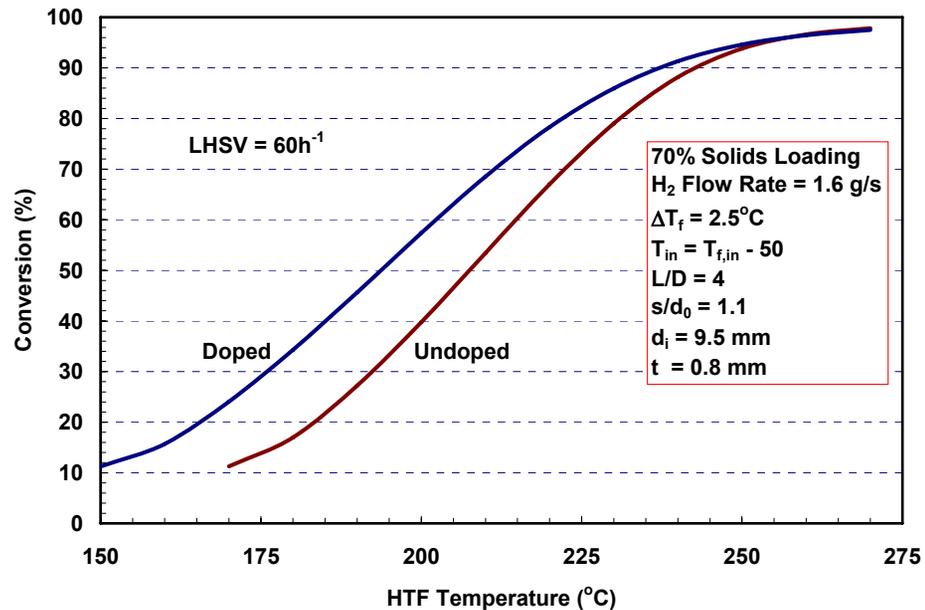
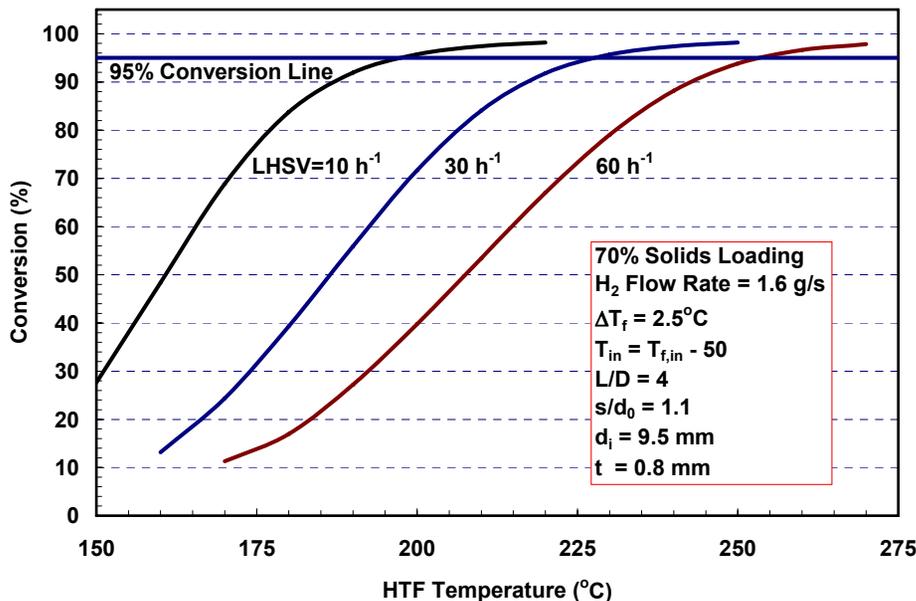
- Investigated several methods of storing alane in powder and liquid forms and selected slurry for initial evaluation
- Pros and cons of storing alane as slurry
 - Pros: heat transfer, easier refueling, liquid infrastructure, practical
 - Cons: reduced material capacity, added difficulty in recycling spent fuel



Component	Key Assumptions
Fuel Tank	Volume-exchange concept, 10% ullage, 5.6 kg usable H ₂
AlH ₃ Slurry	70 wt% AlH ₃ in light mineral oil
Heat Transfer Fluid	XCEL THERM ®
Dehydrogenation Reactor	Slurry on tube side, HTF on shell side, s/d=1.1, slurry at 100 bar, HTF at 3 bar, 1.6 g/s peak H ₂ consumption in FCS
AlH ₃ Dehydrogenation Kinetics	Avrami-Erofeyev rate expression
HEX Burner	50 kWt, non-catalytic, HTF pumped to stack P, 100°C approach T, 5% excess air
H ₂ Ballast Tank	100 bar, 75°C, AL-2219-T81 alloy tank, 2.25 SF
Recuperator, H ₂ Cooler, Spent Slurry Cooler	5 - 50°C approach T

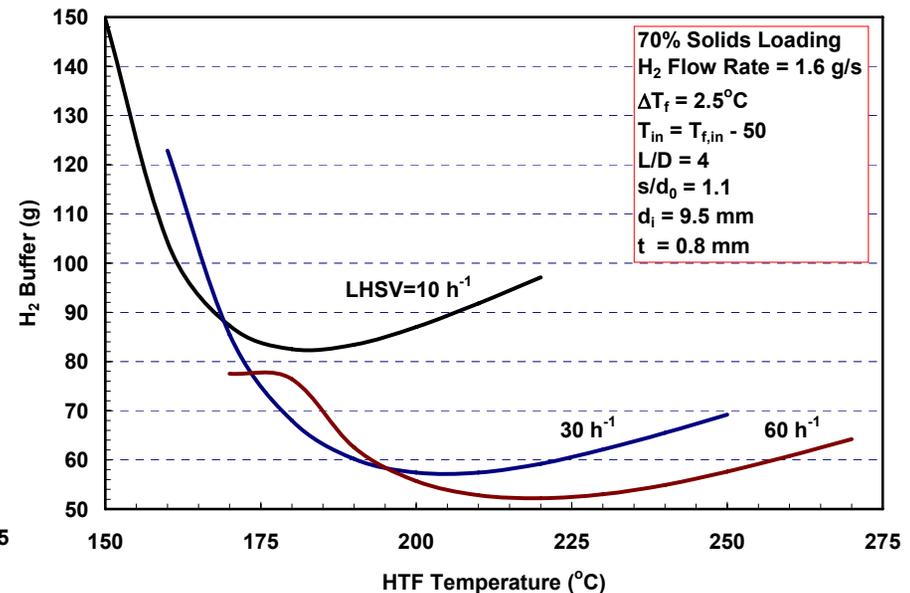
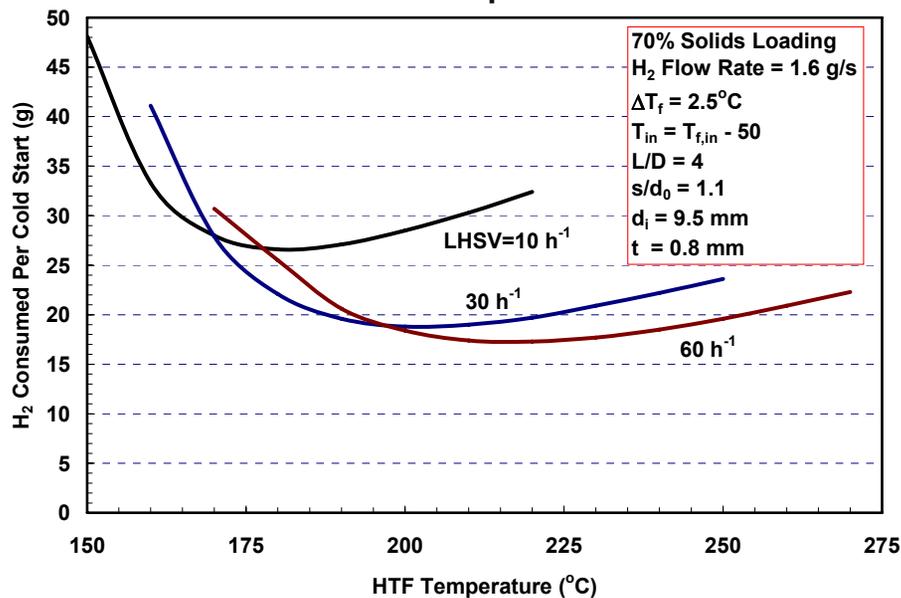
Conversion of Doped and Undoped Alane

- LHSV = Volumetric flow rate of slurry divided by the volume of slurry inside the dehydrogenation reactor, $\tau = 1/\text{LHSV}$
- Need to heat HTF to 200-260°C for 95% conversion at peak flow rate.
- Minimum heat load is 11.3 kW or 13.2 kJ/mol- H_2 , nearly double the heat of reaction at 298 K.
- Whereas doping (kinetic data from BNL) significantly destabilizes alane at low temperatures, effect is small at high conversion.



Start-up Energy, Time and H₂ Buffer

- Start-up transient defined as the time and energy needed to heat the components in the HTF circuit by burning H₂ stored in the buffer tank (50-kW burner)
- Minimum start up time and energy are about 30 s and 2.2 MJ. Start-up time can be reduced by employing a larger burner but at the expense of start-up energy.
- H₂ buffer stores sufficient H₂ for start-up and provide H₂ to the fuel cell at 50% of peak flow rate



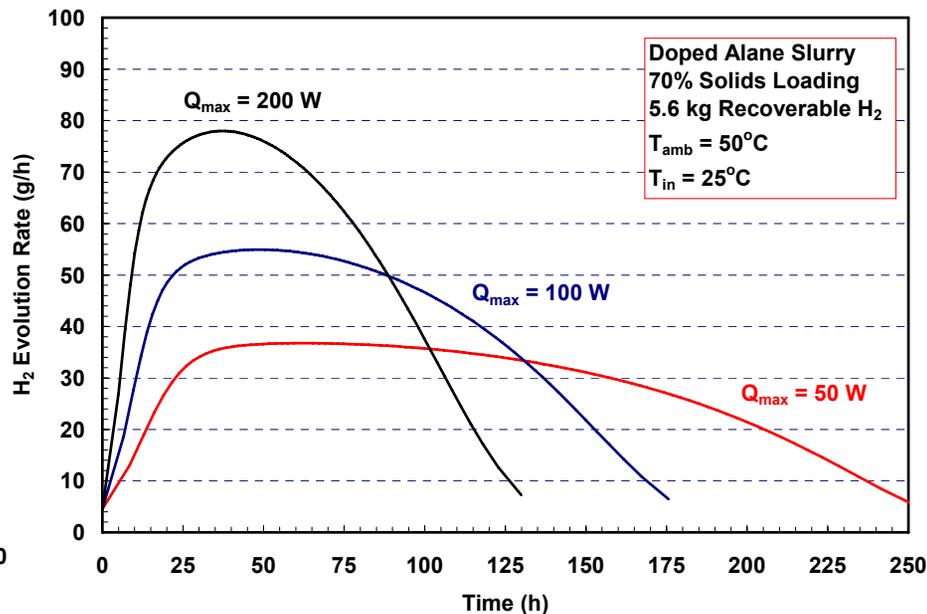
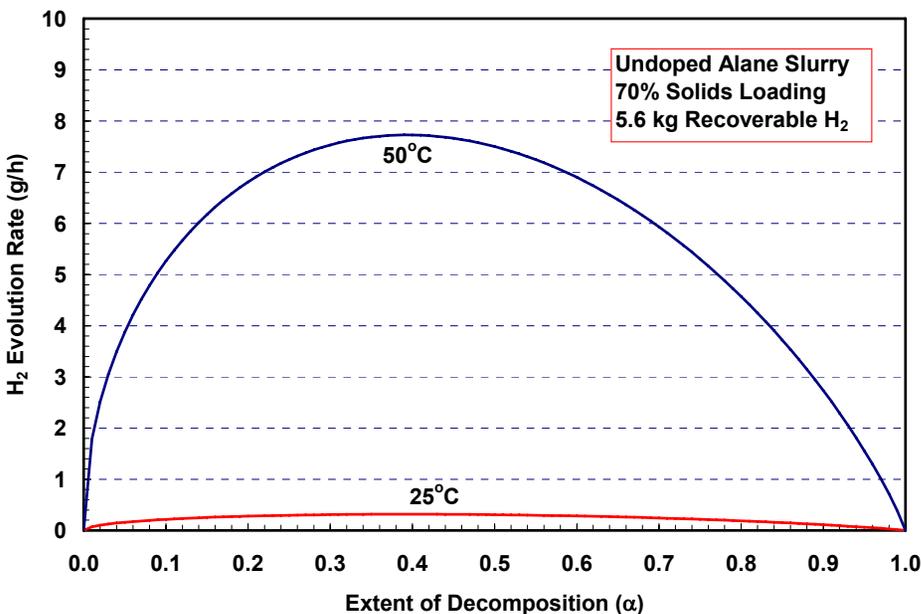
Stability of Doped and Undoped Alane

Undoped

- Peak H₂ loss rate is ~8 g/h at 50°C, <0.4 g/h at 25°C
- H₂ loss is limited by kinetics
- Autonomy time of fully-charged tank is >1500 h at 50°C

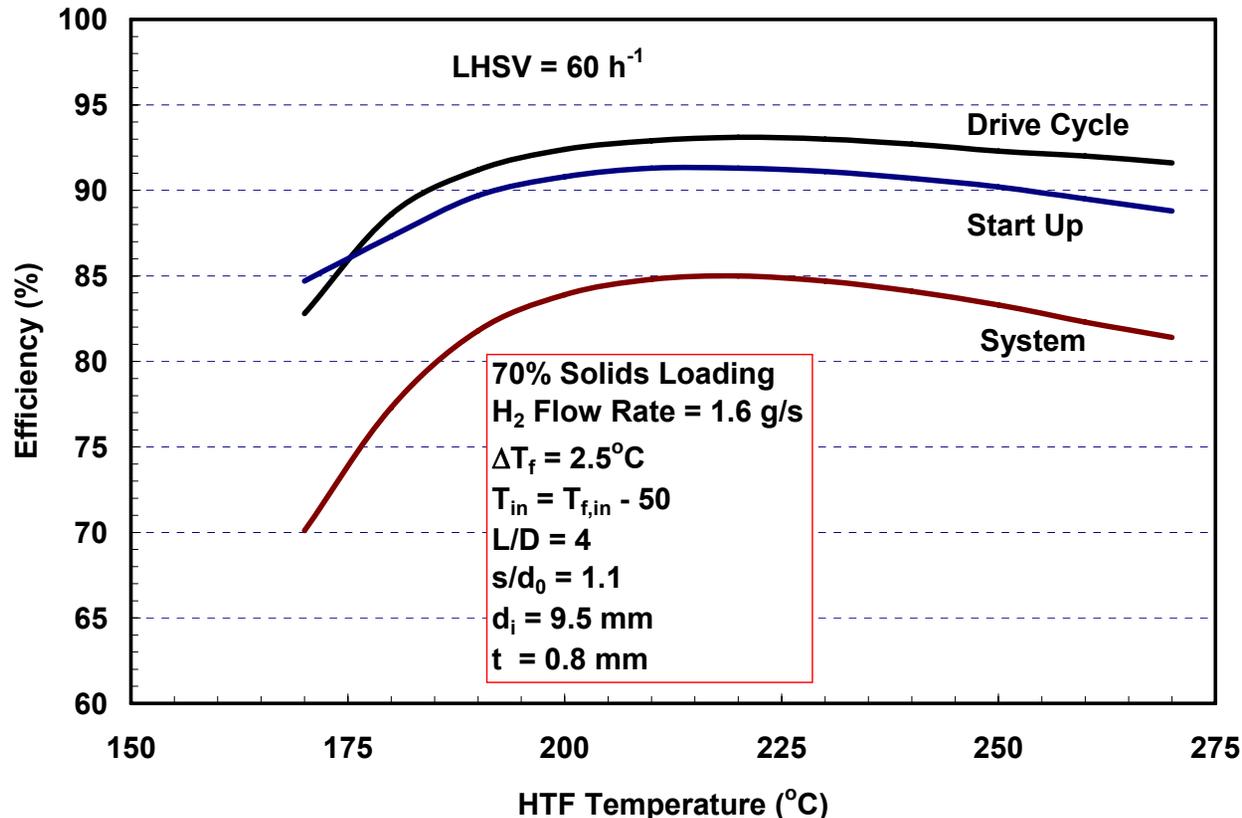
Doped

- Peak H₂ loss rate is 35-75 g/h.
- H₂ loss is limited by heat transfer as well as kinetics
- Autonomy time of fully-charged tank at 50°C is 550-1050 W-d.



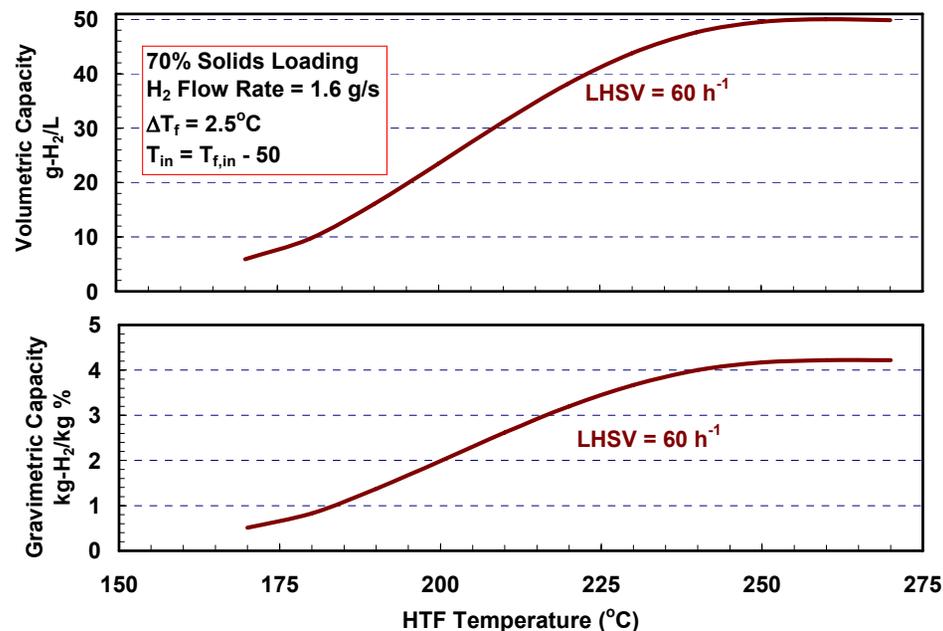
Storage Efficiency

- Start-up efficiency determined assuming 100,000 miles driven, 50 mpgge fuel economy and 10,000 cold starts over 10 years
- Drive cycle efficiency defined as the fraction of H₂ released (after the start-up transient) that is available to the fuel cell
- System efficiency is the product of drive cycle and start-up efficiencies



Assessment of Results

- Under optimum conditions, ~80% of H₂ stored in slurry is available for use in fuel cell system.
- Usable gravimetric capacity <4.25 wt% H₂, ~75% gravimetric efficiency
- Usable volumetric capacity ~50 g-H₂/l, 73% volumetric efficiency



Data Needs

- Preparation of 70-wt% AlH₃ slurry, effect of particle size distribution, surfactants, etc
- DeH₂ kinetics of AlH₃ slurry, fluid dynamics of slurry in micro-channel HX
- H₂ recovery from fuel tank

	Value	Units	Range
Intrinsic Material Capacity	10.0	g-H ₂ /g-AlH ₃ %	Variable T _{HTF} ,
H ₂ Capacity in Slurry	7.0	g-H ₂ /g-slurry, %	Fixed LHSV
Recoverable H ₂ Capacity	6.9	g-H ₂ /g-slurry, %	(: 11.3-97.9%
Available H ₂ Capacity	6.3	g-H ₂ /g-slurry, %	(_{DC} : 82.8-93.1%
Usable H ₂ Capacity	5.6	g-H ₂ /g-slurry, %	(_{SU} : 84.7-91.3%
Usable Gravimetric Capacity	4.2	g-H ₂ /g-system, %	0.5-4.2
Usable Volumetric Capacity	49.8	g-H ₂ /L-system	5.9-50.0
Peak H ₂ Loss at 25°C	0.3	g-H ₂ /h	0-0.3
Peak H ₂ Loss at 50°C	7.7	g-H ₂ /h	0-7.7

Key Results for SBH On-board System

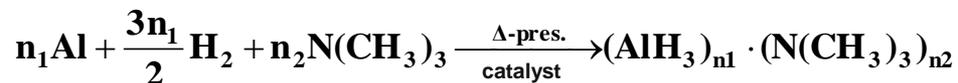
- On-board SBH system may not meet the 2007 storage capacity targets with 24-wt% formulation
- No clear pathway to meet the 2010 or 2015 storage targets

Material Capacity	5.1 wt% H ₂ for 24-wt% SBH formulation 6.4 wt% H ₂ for 30-wt% SBH formulation
Gravimetric Capacity	3.3 wt% H ₂ for 24-wt% SBH formulation 4.3 wt% H ₂ for 30-wt% SBH formulation
Volumetric Capacity	27.6 g-H ₂ /l for 24-wt% SBH formulation 36.4 g-H ₂ /l for 30-wt% SBH formulation
Reactor Operating Conditions	165-177°C at 9-12 bar for adiabatic operation
Reactor Heat Management	Need on-board water for >24-wt% SBH formulations
Freeze Issues	Yes, for both on-board water and spent NaBO ₂ solution
Precipitation Issues	Tank must be above 90°C for 24-wt% SBH formulation Slurry handling and precipitate recovery options not explored
Heat Rejection Issues	Major problem common to exothermic reactions with large ΔH

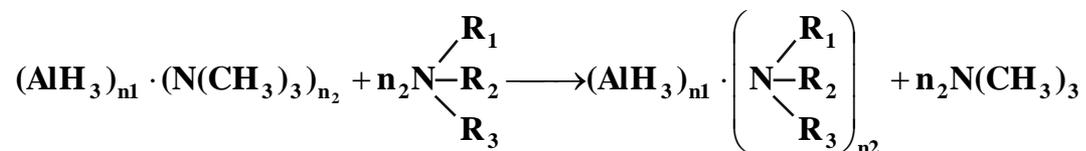
Note: Loss in capacity due to tank heating and condenser heat rejection not included.

Regeneration of Alane - ANL Reference Flowsheet

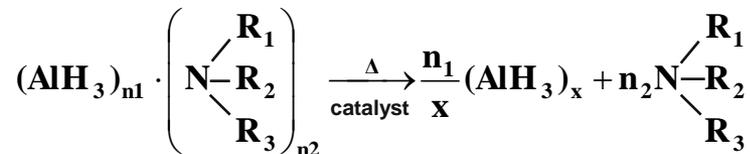
- Form AlH_3 as adduct to TMA in ether in the presence of LiAlH_4 .



- Displace TMA from TMAA in ether by TEA (transamination).



- Decompose TEAA in presence of LiAlH_4 (thermal decomposition)

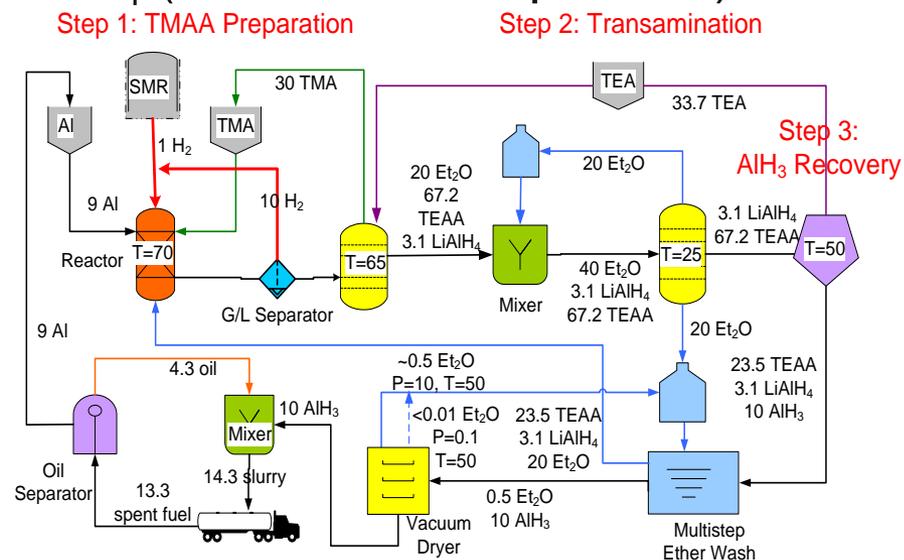


- For high conversion, use excess amounts of reagents.

H_2 Stoichiometry: Φ_{H_2}

TMA Stoichiometry: Φ_{TMA}

TEA Stoichiometry: Φ_{TEA}



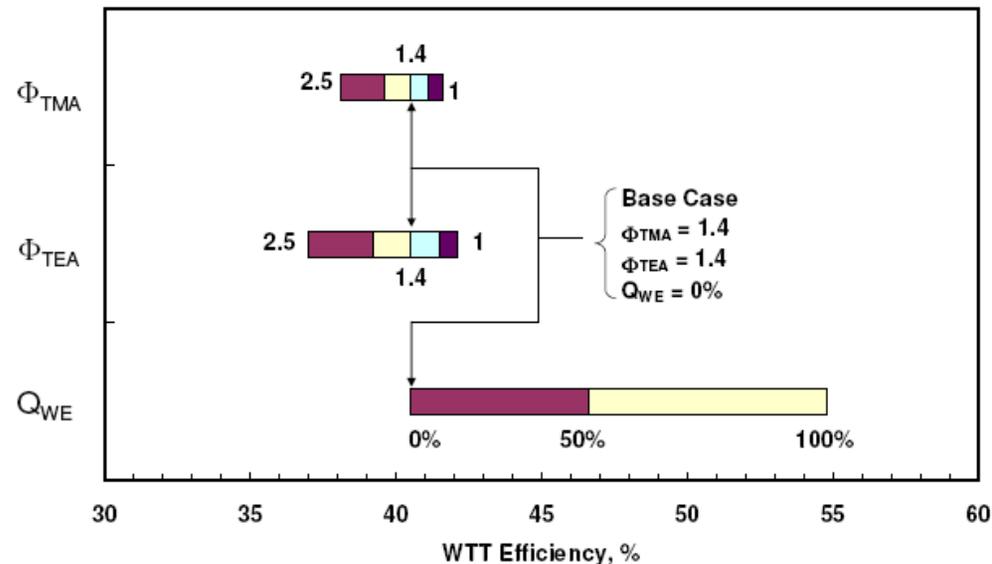
Ref: Murib and Horvitz, U.S. Patent 3,642,853 (1972)

FCHtool Analysis: Preliminary WTT Efficiency

- Without credit for availability of low-grade heat, the WTT efficiency is 40.5% ($\Phi_{H_2}=10$, $\Phi_{TMA}=1.4$, $\Phi_{TEA}=1.4$).
 - Q: 71.9 MJ/kg-H₂, E: 3.6 kWh/kg-H₂
- A single-variable parametric analysis indicates that WTT efficiency is most sensitive to the availability of low-grade waste heat.
- We are working with BNL to verify the process steps and determine the operating conditions.

Q: MJ/kg-H₂, E: kWh/kg-H₂

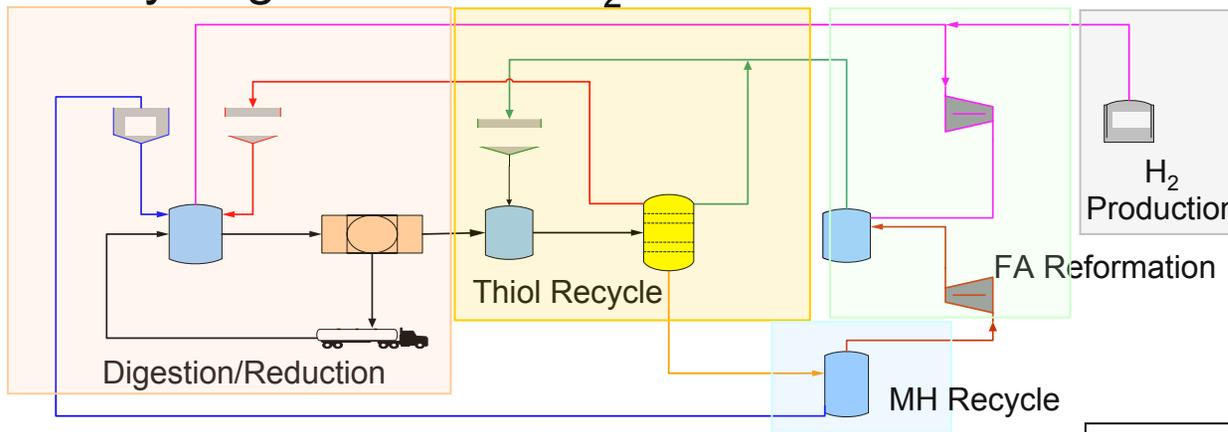
Process	T °C	P bar	Q MJ	E kWh
Compress H ₂ from SMR	70	30		0.3
Compress circulating H ₂	70	30		0.6
Distill TMA	65	5	28.6	
Distill ether	25	0.3	22.9	1.1
Decompose TEAA	50	0.2	20.2	1.4
Vacuum dry AlH ₃	50	<10 ⁻¹	0.2	0.2
Total			71.9	3.6



Regeneration of BH_3NH_3 from BNH_2

Collaborating with CHCoE to develop flowsheets for estimating η_{WTT} .

- Completed preliminary evaluation of one of three schemes.
- Single reactor for digesting BNH_2 and reducing products using excess amounts of thiol (α) and tin MH (γ)
- Solid AB recovered as precipitate and thiol recycled by reacting with excess amount of formic acid (β)
- Thiol and excess formic acid recovered by fractional distillation
- MH is recovered by thermally decomposing MH-COOH products
- Direct hydrogenation of CO_2 for reformation of formic acid



Digestion/Reduction: $\text{BNH}_2 + 3/2 \alpha(\text{SCatH}_2) + \gamma\text{H}_2\text{SnBu}_2 + 1/2 \gamma\text{HSnBu}_3 \rightarrow \text{BH}_3\text{NH}_3 + 1/2 \text{H}_2 + 3/2 (\alpha-1)(\text{SCatH}_2) + (\gamma-1)\text{H}_2\text{SnBu}_2 + 1/2 (\gamma-1)\text{HSnBu}_3 + (\text{SCat})\text{SnBu}_2 + 1/2 (\text{SCatH})\text{SnBu}_3$

Thiol Recycle: $(\text{SCat})\text{SnBu}_2 + 1/2 (\text{SCatH})\text{SnBu}_3 + 5/2 \beta\text{HCOOH} + (\gamma-1)\text{H}_2\text{SnBu}_2 + 1/2 (\gamma-1)\text{HSnBu}_3 \rightarrow 3/2 (\text{SCatH}_2) + 5/2(\beta-1) \text{HCOOH} + (\text{COOH})_2\text{SnBu}_2 + 1/2 (\text{COOH})\text{SnBu}_3 + (\gamma-1)\text{H}_2\text{SnBu}_2 + 1/2 (\gamma-1)\text{HSnBu}_3$

MH Recycle: $(\text{COOH})_2\text{SnBu}_2 + 1/2 (\text{COOH})\text{SnBu}_3 + (\gamma-1)\text{H}_2\text{SnBu}_2 + 1/2 (\gamma-1)\text{HSnBu}_3 \rightarrow \gamma\text{H}_2\text{SnBu}_2 + 1/2 \gamma\text{HSnBu}_3 + 5/2 \text{CO}_2$

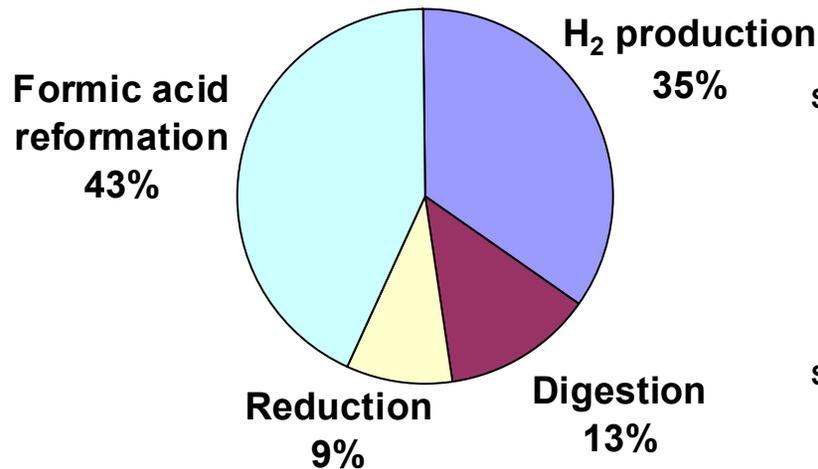
Formic Acid Reformation: $5/2 \text{CO}_2 + 5/2 \text{H}_2 \rightarrow 5/2 \text{HCOOH}$ (BP Patent)

Ref: Kevin Ott, Private Communication, LANL (2008)

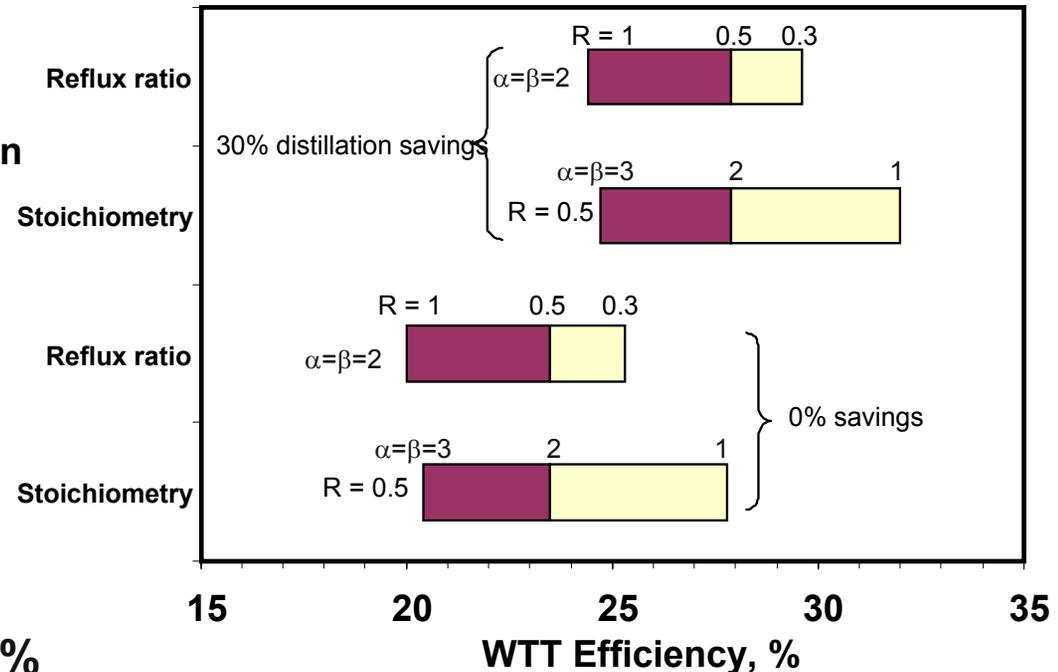
FCHtool Analysis: Primary Energy & WTT Efficiency

- Preliminary estimate of WTT efficiency for spent AB regeneration by LANL scheme is 17 – 34%
- Formic acid reformation of CO₂ consumes significant amount of energy in the MH recycle step of the overall scheme
- LANL is using ANL results to develop alternate schemes that may not require formic acid in the MH recycle step

Primary Energy Consumption



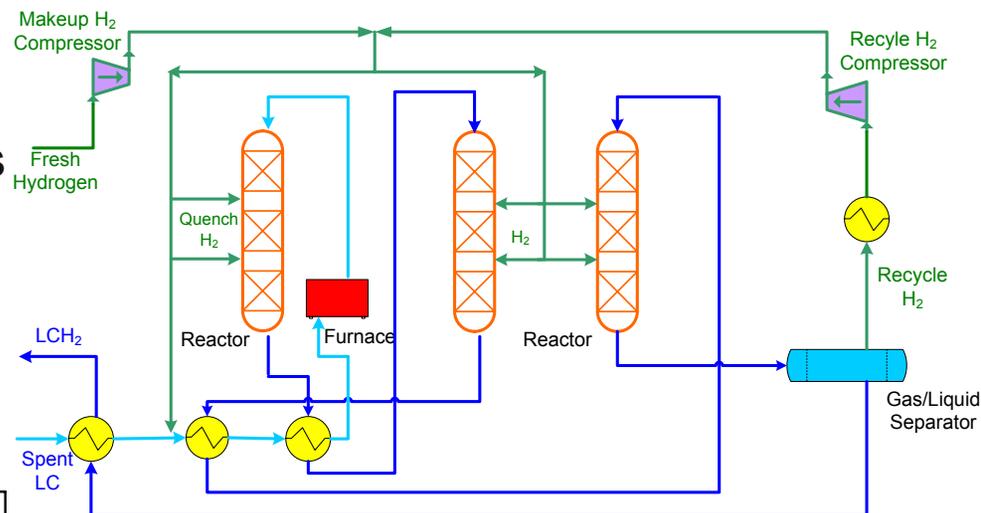
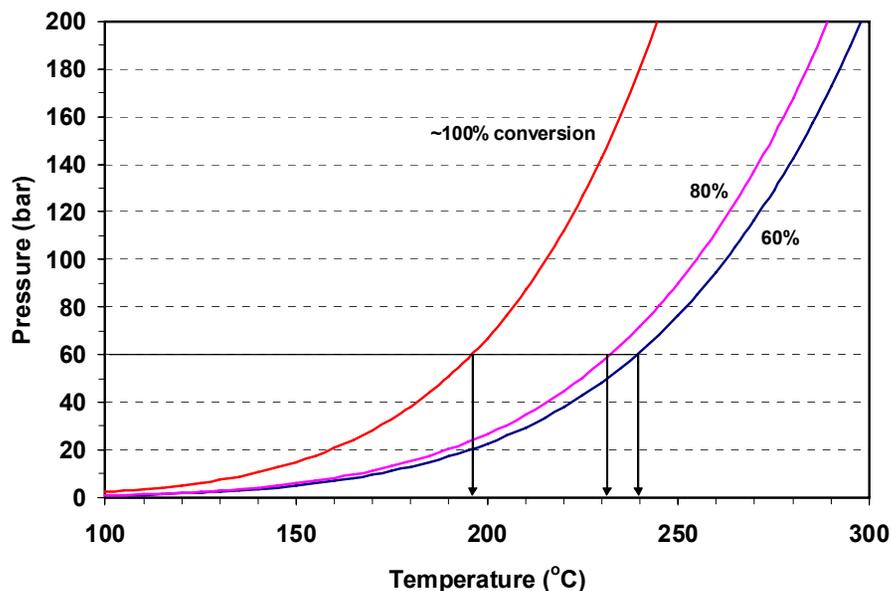
Total = 507 MJ/kg H₂, WTT=23.6%



Rehydrogenation of Organic Liquid Carriers

Multi-stage hydrogenation reactors

- Declining T profile: H₂ quench and inter-stage regenerative cooling
- Overall exothermic reaction: process fuel used in furnace, low-grade heat recovered in H₂ cooler
- Operating P is a function of conversion and T



N-ethylcarbazole

Parameter	1-Stage	3-Stage
Temperature, °C	196	240/232/196
Pressure, bar	60	60
Cumulative Conversion	1.0	0.6/0.8/1.0
H ₂ Circulation Ratio	21.7	16.2
Electricity, kWh/kg H ₂	2.02	1.68
Heat input, MJ/kg H ₂	0.8	0.8
WTT, %	59.8	60.9

Future Work

Continue to work with DOE contractors and CoE to model and analyze various developmental hydrogen storage systems.

Metal Hydrides

- Refine analysis for alane with experimental support from BNL
- Refine organometallic flowsheet and investigate electrochemical and supercritical CO₂ extraction routes

Sorbent Storage

- Extend work to metal organic frameworks and other sorbents

Chemical Hydrogen

- Evaluate energy consumption and fuel cycle efficiency of candidate materials and processes
- Liquid carrier option
 - Extension to the “best” APCI carrier with the “best” APCI catalyst
 - Refine off-board rehydrogenation analysis
 - Collaborate with TIAX on cost analysis