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System Level Analysis of Hydrogen Storage Options

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2008 DOE Hydrogen Program Review
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Arlington, VA

Project ID: ST2

Overview

Timeline

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

Barriers

- H_2 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

Budget

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

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 H_2 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)

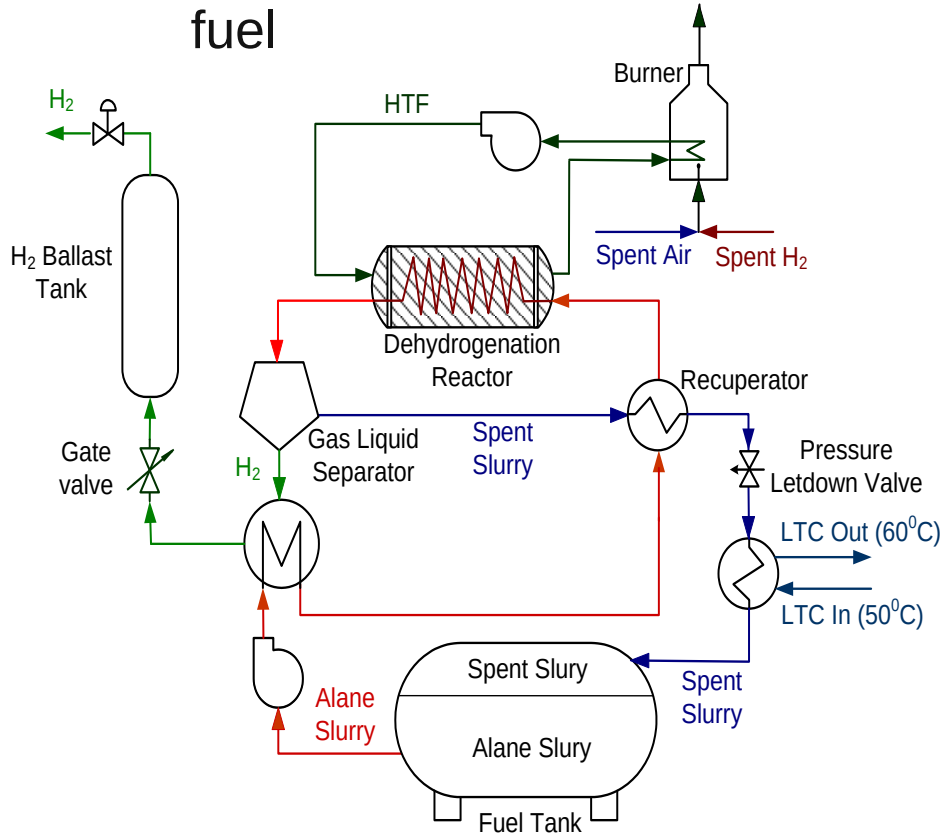
- WTT efficiency of rehydrogenation of organic liquid carriers

Hydrogen Storage in Amine Borane (October 2008)

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

H_2 Storage as Alane Slurry

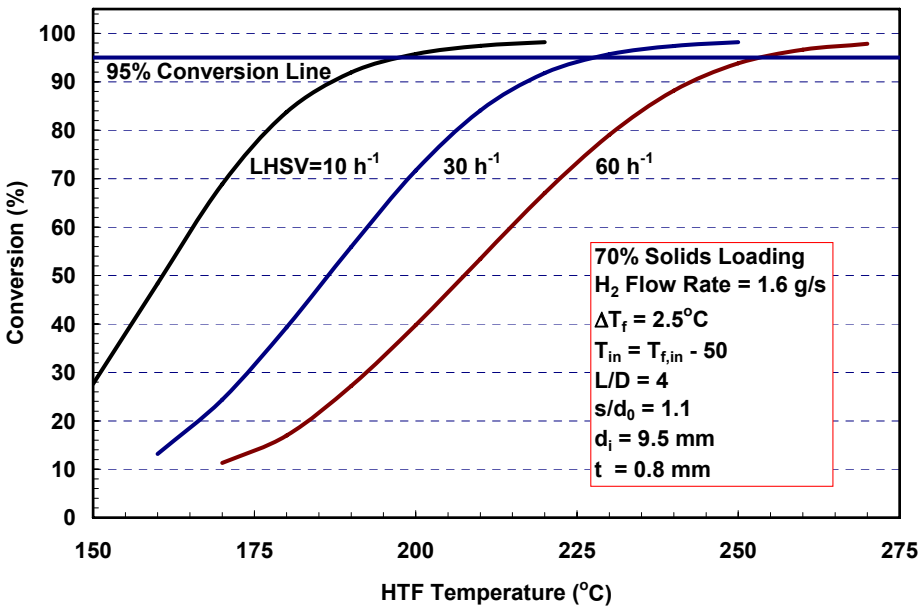
- Investigated several methods of storing alane in powder and liquid forms and selected slurry for initial evaluation
- Pros and cons of storing alane as slurry
  - Pros: heat transfer, easier refueling, liquid infrastructure, practical
  - Cons: reduced material capacity, added difficulty in recycling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

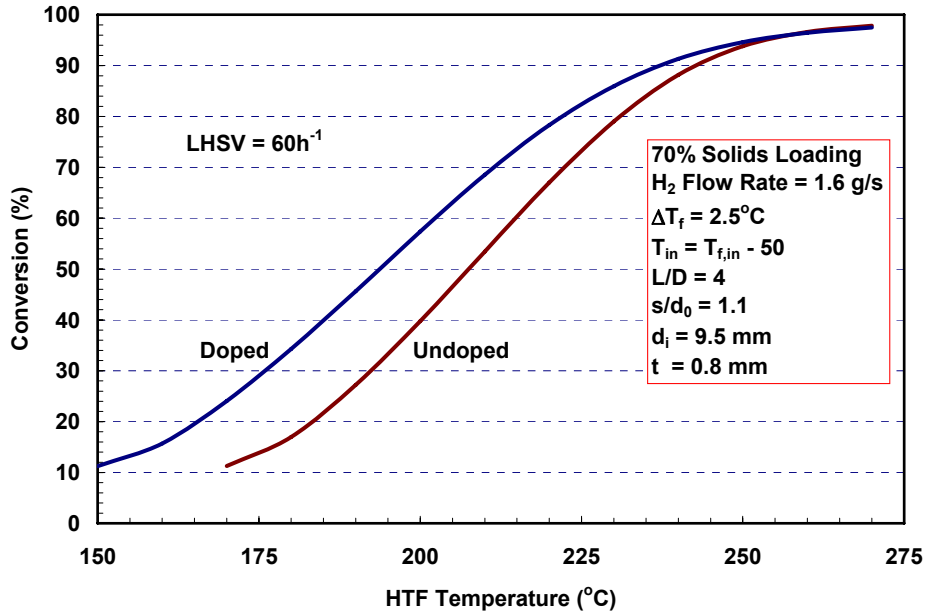


Component	Key Assumptions
Fuel Tank	Volume-exchange concept, 10% ullage, 5.6 kg usable H_2
AlH_3 Slurry	70 wt% AlH_3 in light mineral oil
Heat Transfer Fluid	XCELTHERM ®
Dehydrogenation Reactor	Slurry on tube side, HTF on shell side, s/d=1.1, slurry at 100 bar, HTF at 3 bar, 1.6 g/s peak H_2 consumption 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

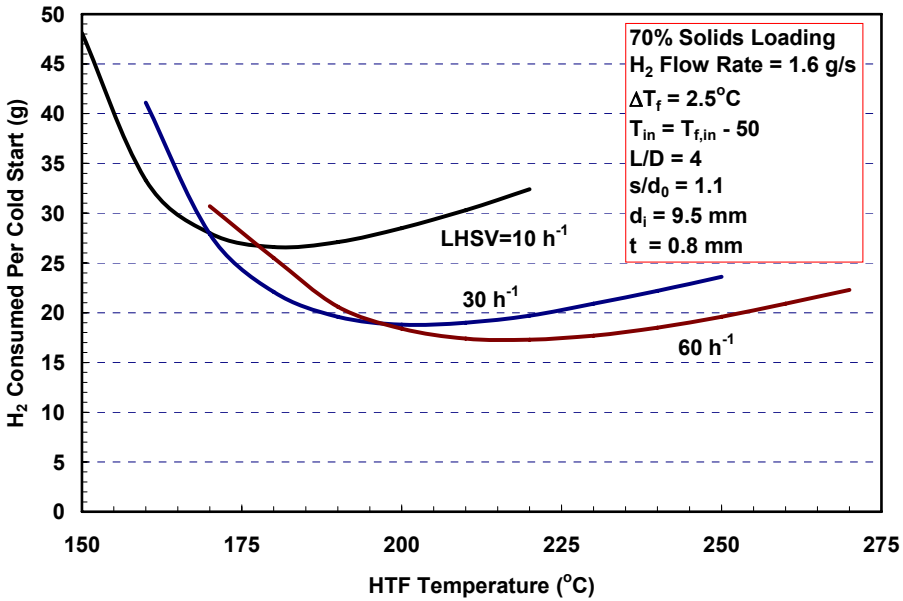
- LHSV = Volumetric flow rate of slurry divided by the volume of slurry inside the dehydrogenation reactor, τ = 1/LHSV
- Need to heat HTF to 200-260°C for 95% conversion at peak flow rate.
- Minimum heat load is 11.3 kW or 13.2 kJ/mol-H_2, nearly double the heat of reaction at 298 K.
- Whereas doping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

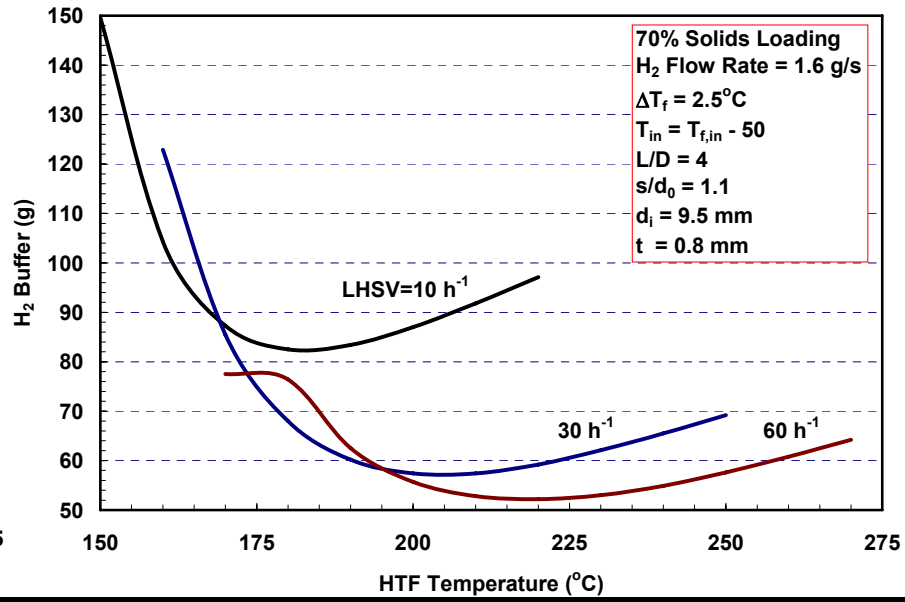




Start-up Energy, Time and H_2 Buffer

- Start-up transient defined as the time and energy needed to heat the components in the HTF circuit by burning H_2 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.
- H_2 buffer stores sufficient H_2 for start-up and provide H_2 to the fuel cell at 50% of peak flow rate





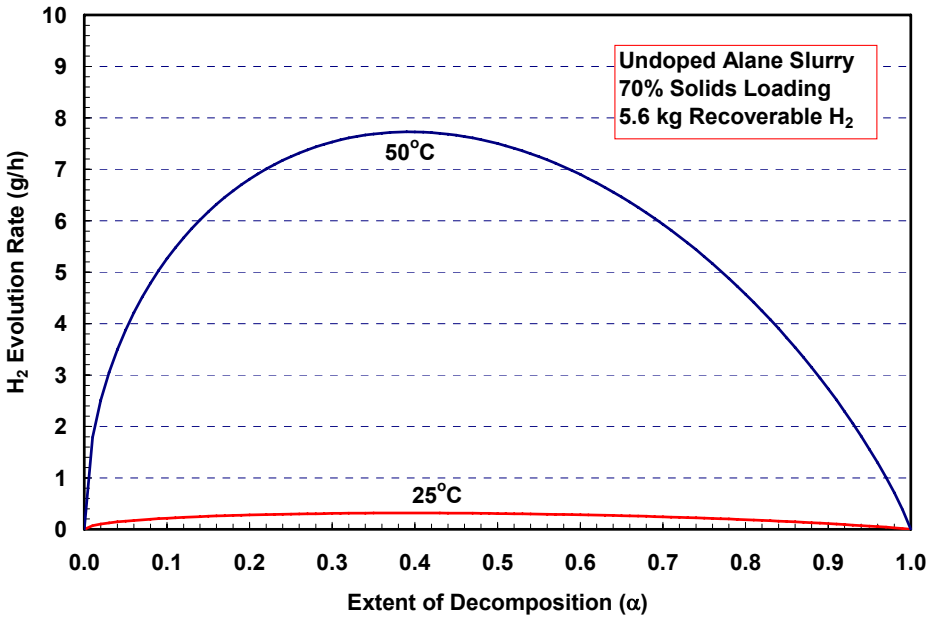
Stability of Doped and Undoped Alane

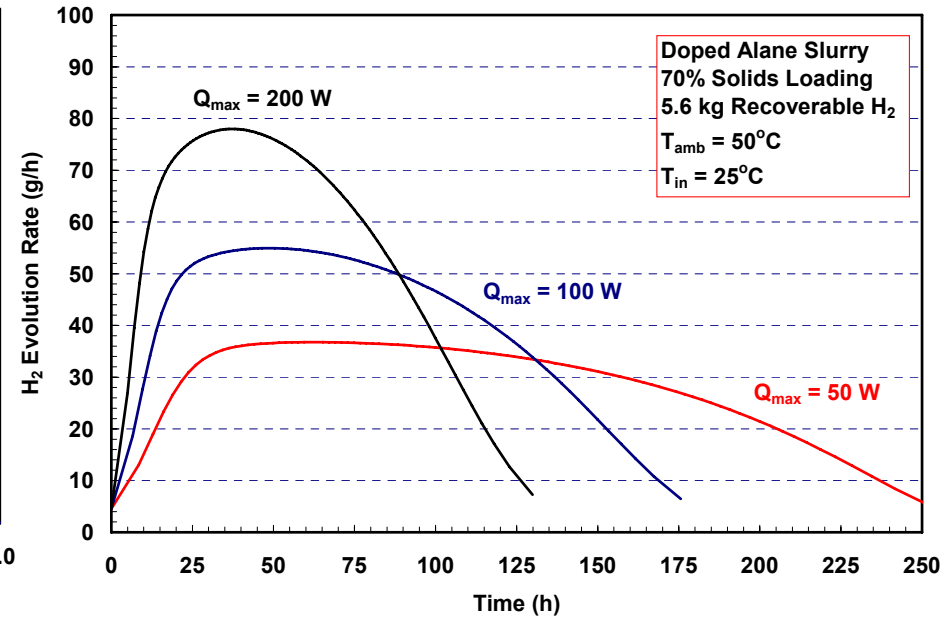
Undoped

- Peak H_2 loss rate is ~8 g/h at 50°C, <0.4 g/h at 25°C
- H_2 loss is limited by kinetics
- Autonomy time of fully-charged tank is >1500 h at 50°C

Doped

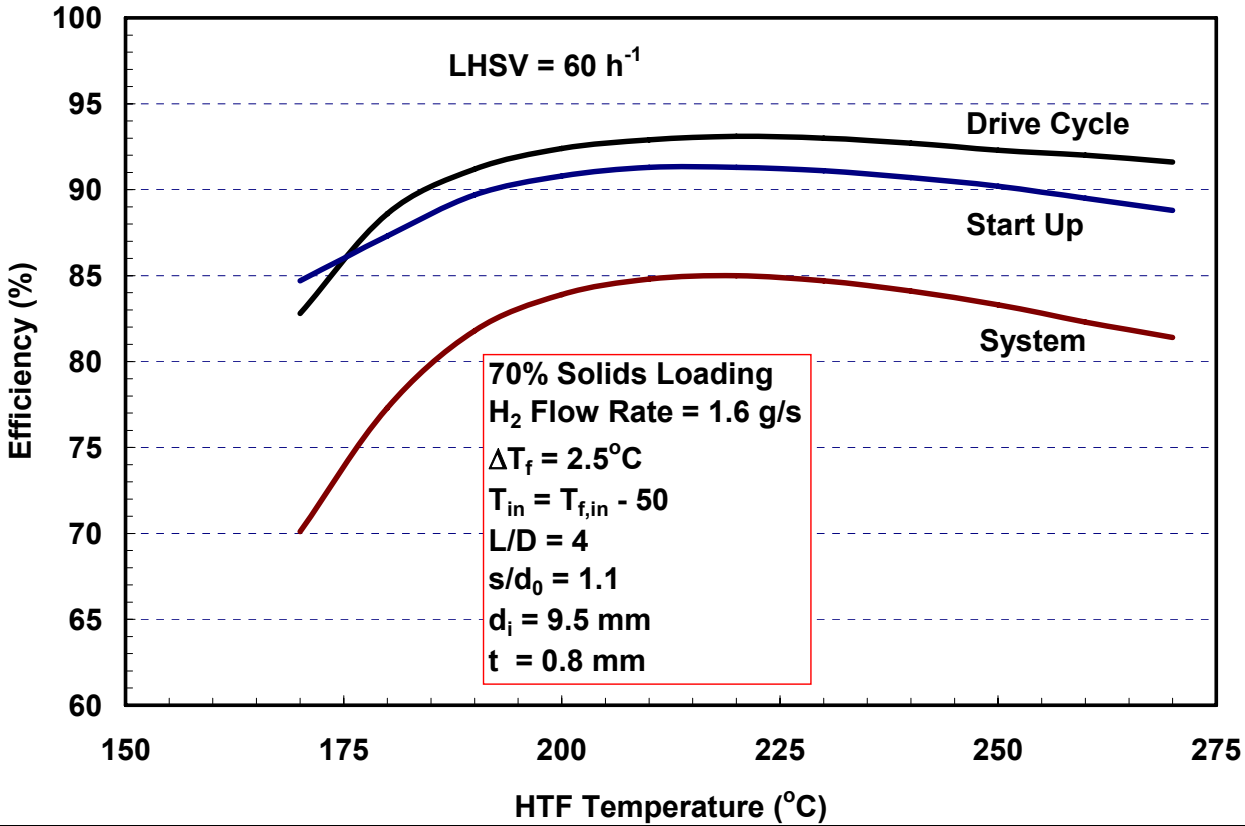
- Peak H_2 loss rate is 35-75 g/h.
- H_2 loss is limited by heat transfer as well as kinetics
- Autonomy time of fully-charged tank at 50°C is 550-1050 W-d.





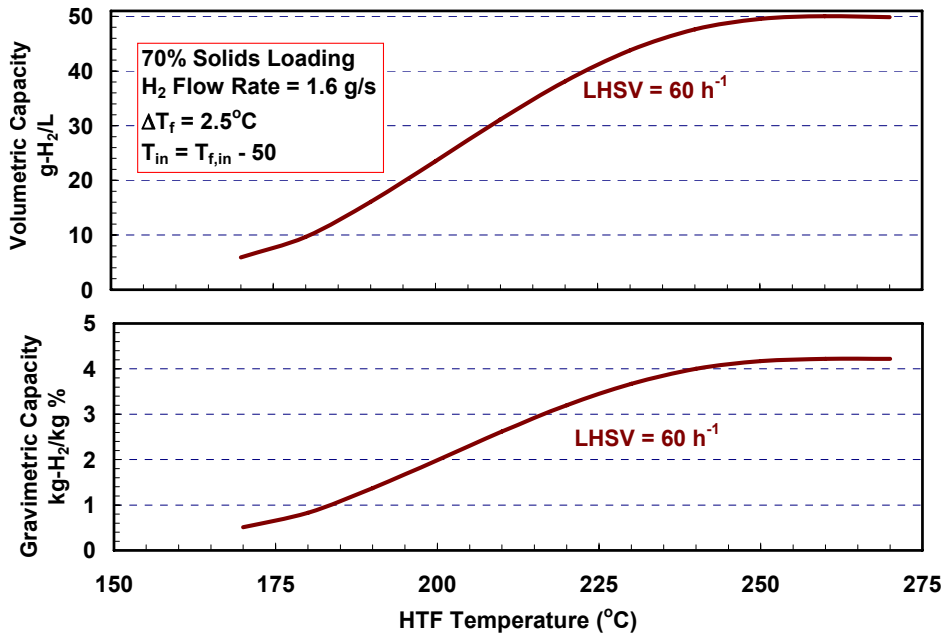
Storage Efficiency

- 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 H_2 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 H_2 stored in slurry is available for use in fuel cell system.
- Usable gravimetric capacity <4.25 wt% H_2, ~75% gravimetric efficiency
- Usable volumetric capacity ~50 g-H_2/l, 73% volumetric efficiency



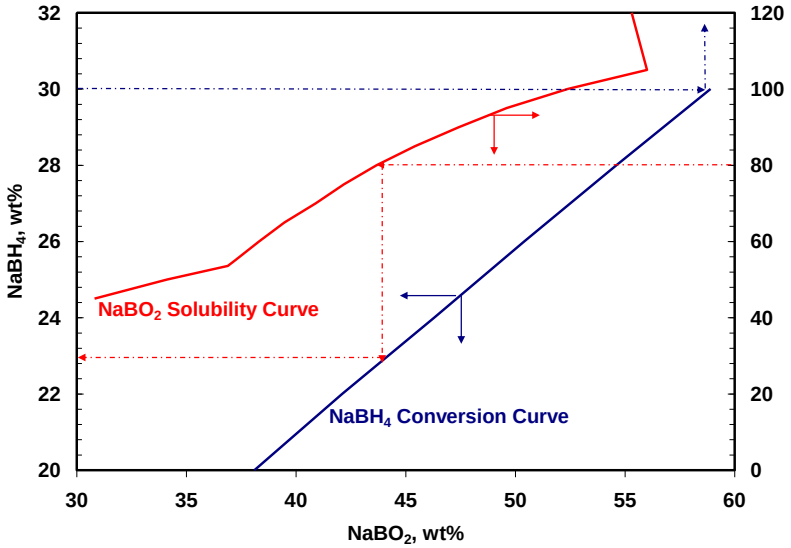
Data Needs

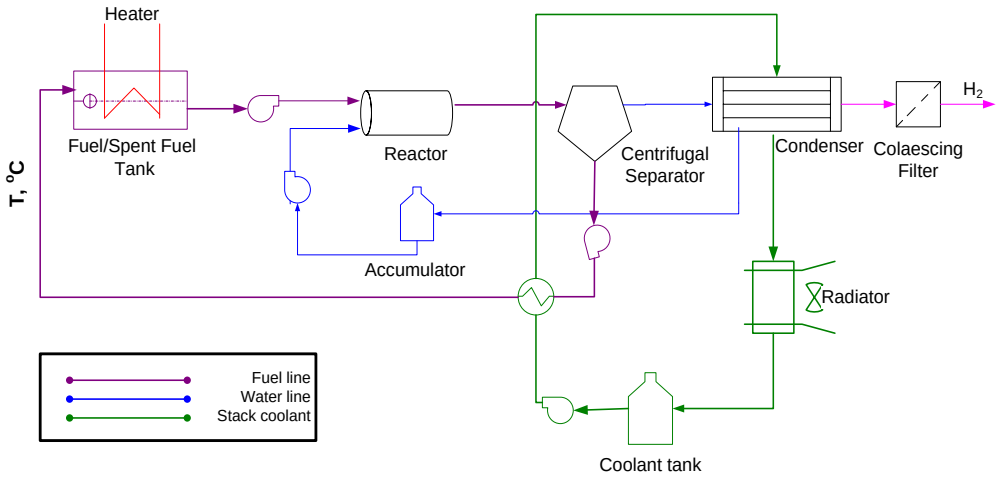
- Preparation of 70-wt% AlH_3 slurry, effect of particle size distribution, surfactants, etc
- DeH_2 kinetics of AlH_3 slurry, fluid dynamics of slurry in micro-channel HX
- H_2 recovery from fuel tank

	Value	Units	Range
Intrinsic Material Capacity	10.0	g-H_2/g-AlH_3, %	Variable T_{HTF}, Fixed LHSV
H_2 Capacity in Slurry	7.0	g-H_2/g-slurry, %	
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

SBH On-Board System

- Reactor is cooled evaporatively with on-board water, steam recovered in condenser: fixed relationship between P, T and SBH concentration
- Theoretical minimum water: Amount of water that boils off (function of reactor P and T) and the amount consumed in SBH reaction
  - On-board water required for 24-wt% and 30-wt% SBH formulations
- Minimum tank temperature to prevent precipitation of $NaBO_2$ determines allowable $NaBH_4$ concentration in fuel
- SBH system heat load (56 kW for 1.6 g/s of H_2) comparable to heat duty on FCS main radiator.





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^{o}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^{o}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 $LiAlH_4$.

$$n_1Al + \frac{3n_1}{2}H_2 + n_2N(CH_3)_3 \xrightarrow[\text{catalyst}]{\Delta\text{-pres.}} (AlH_3)_{n1}\cdot(N(CH_3)_3)_{n2}$$

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

$$(AlH_3)_{n1}\cdot(N(CH_3)_3)_{n_2} + n_2N\begin{matrix}R_1\\ \diagup\\ -R_2\\ \diagdown\\ R_3\end{matrix} \longrightarrow (AlH_3)_{n1}\cdot\left(N\begin{matrix}R_1\\ \diagup\\ -R_2\\ \diagdown\\ R_3\end{matrix}\right)_{n2} + n_2N(CH_3)_3$$

- Decompose TEAA in presence of $LiAlH_4$ (thermal decomposition)

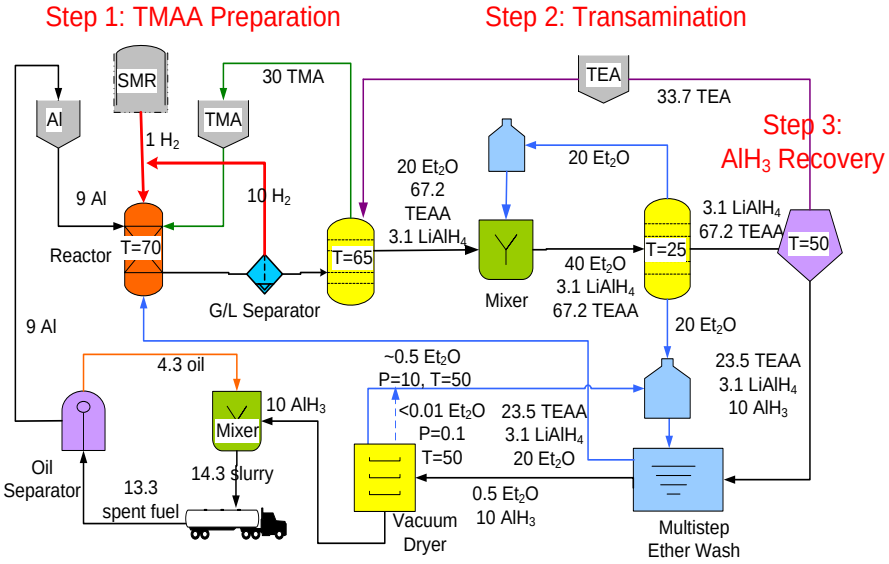
$$(AlH_3)_{n1}\cdot\left(N\begin{matrix}R_1\\ \diagup\\ -R_2\\ \diagdown\\ R_3\end{matrix}\right)_{n2} \xrightarrow[\text{catalyst}]{\Delta} \frac{n_1}{x}(AlH_3)_x + n_2N\begin{matrix}R_1\\ \diagup\\ -R_2\\ \diagdown\\ R_3\end{matrix}$$

- For high conversion, use excess amounts of reagents.

  H_2 Stoichiometry: Φ_{H2}

  TMA Stoichiometry: Φ_{TMA}

  TEA Stoichiometry: Φ_{TEA}



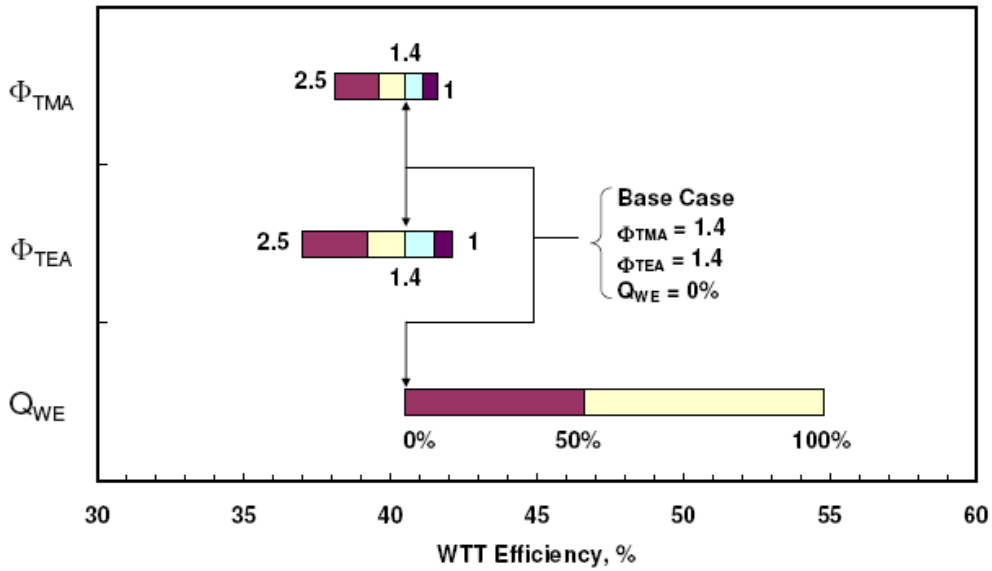
Ref: Murib and Horvitz, U.S. Patent 3,642,853 (1972)

FCHtool Analysis: Preliminary WTT Efficiency

- Without credit for availability of low-grade heat, the WTT efficiency is 40.5% (Φ_{H2}=10, Φ_{TMA}=1.4, Φ_{TEA}=1.4).
  - Q: 71.9 MJ/kg-H_2, E: 3.6 kWh/kg-H_2
- 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-H_2, E: kWh/kg-H_2

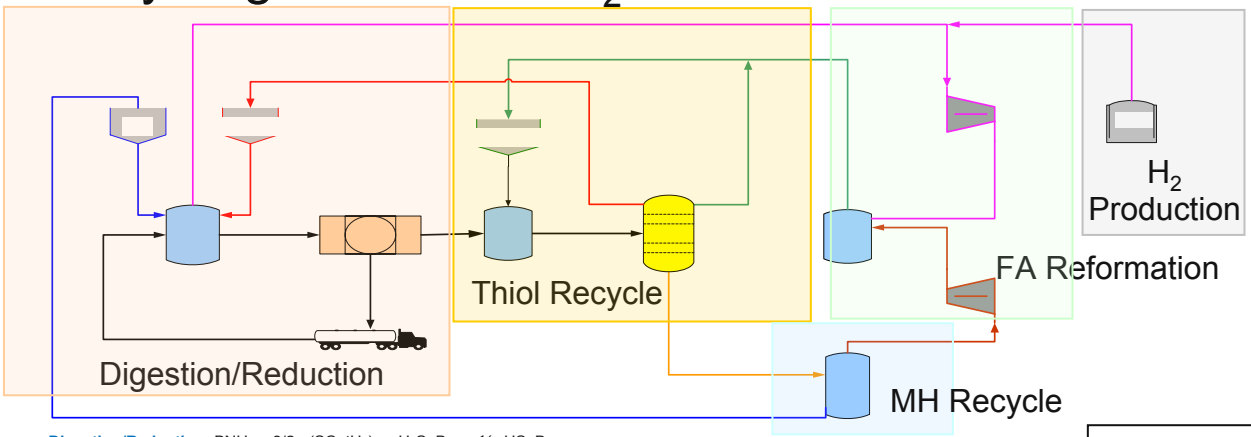
Process	T °C	P bar	Q MJ	E kWh
Compress H_2 from SMR	70	30		0.3
Compress circulating H_2	70	30		0.6
Distill TMA	65	5	28.6	
Distill ether	25	0.3	22.9	1.1
Decompose TEAA	50	0.2	20.2	1.4
Vacuum dry AlH_3	50	$<10^{-1}$	0.2	0.2
Total			71.9	3.6



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: $BNH_2 + 3/2\ \alpha(SCatH_2) + \gamma H_2SnBu_2 + ½\ \gamma HSnBu_3 \rightarrow BH_3NH_3 + ½\ H_2 + 3/2\ (\alpha\text{-}1)(SCatH_2) + (\gamma\text{-}1)H_2SnBu_2 + ½\ (\gamma\text{-}1)HSnBu_3 + (SCat)SnBu_2 + ½\ (SCatH)SnBu_3$

Thiol Recycle: $(SCat)SnBu_2 + ½\ (SCatH)SnBu_3 + 5/2\ \beta HCOOH + (\gamma\text{-}1)H_2SnBu_2 + ½\ (\gamma\text{-}1)HSnBu_3 \rightarrow 3/2\ (SCatH_2) + 5/2(\beta\text{-}1)\ HCOOH + (COOH)_2SnBu_2 + ½\ (COOH)SnBu_3 + (\gamma\text{-}1)H_2SnBu_2 + ½\ (\gamma\text{-}1)HSnBu_3$

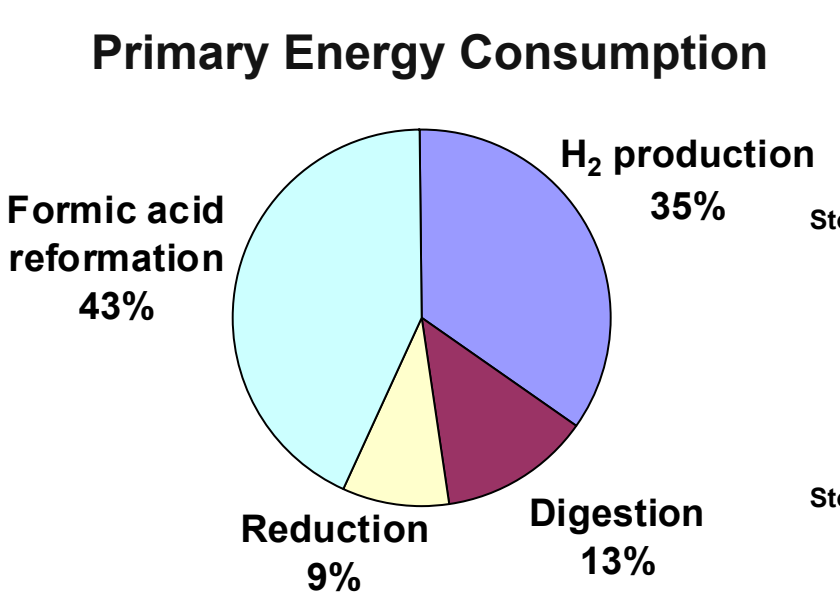
MH Recycle: $(COOH)_2SnBu_2 + ½\ (COOH)SnBu_3 + (\gamma\text{-}1)H_2SnBu_2 + ½\ (\gamma\text{-}1)HSnBu_3 \rightarrow \gamma H_2SnBu_2 + ½\ \gamma HSnBu_3 + 5/2\ CO_2$

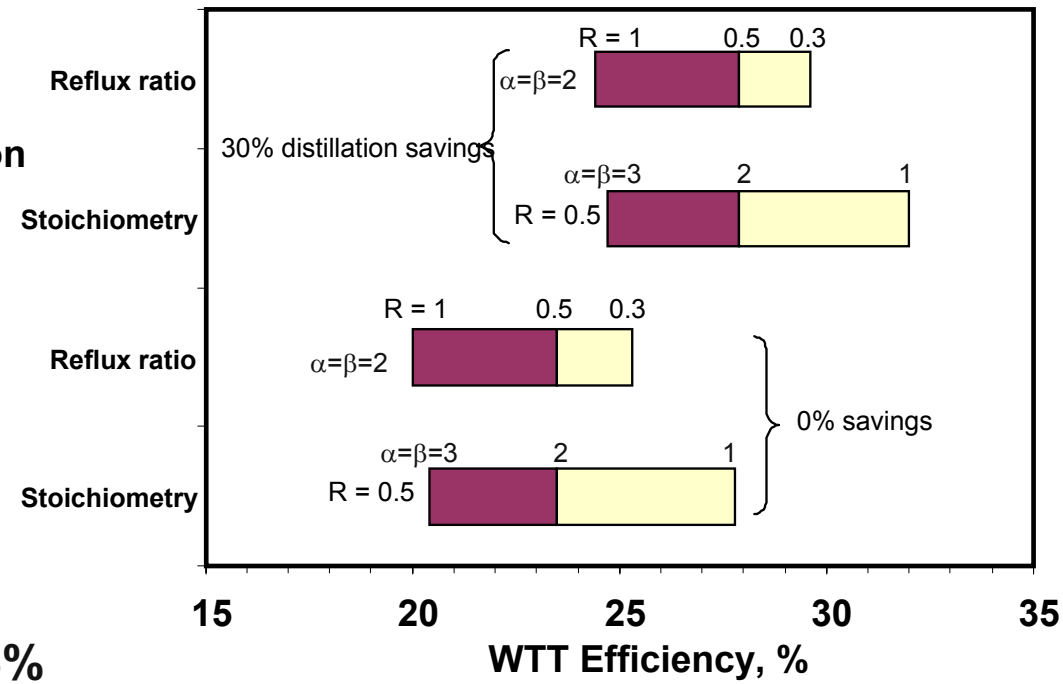
Formic Acid Reformation: $5/2\ CO_2 + 5/2\ H_2 \rightarrow 5/2\ HCOOH$ (BP Patent)

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 CO_2 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



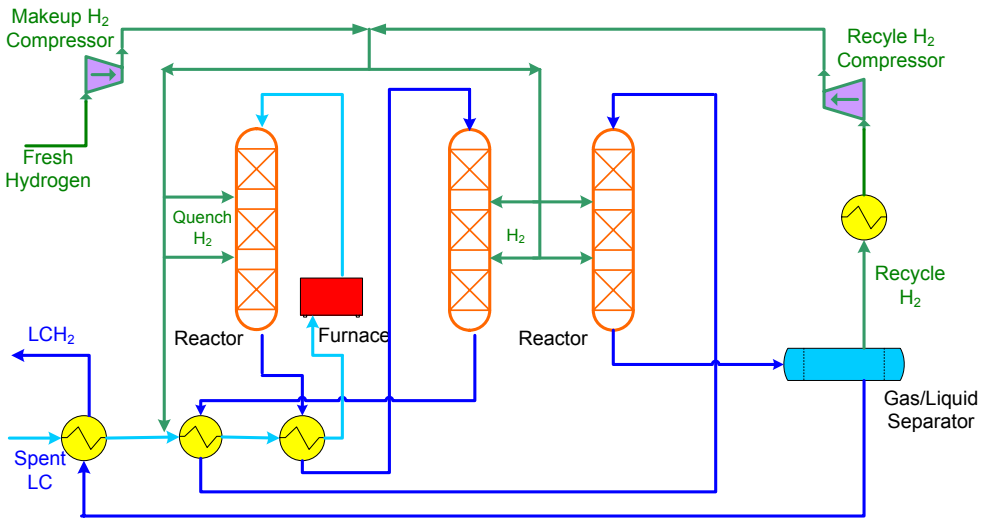


Total = 507 MJ/kg H_2, WTT=23.6%

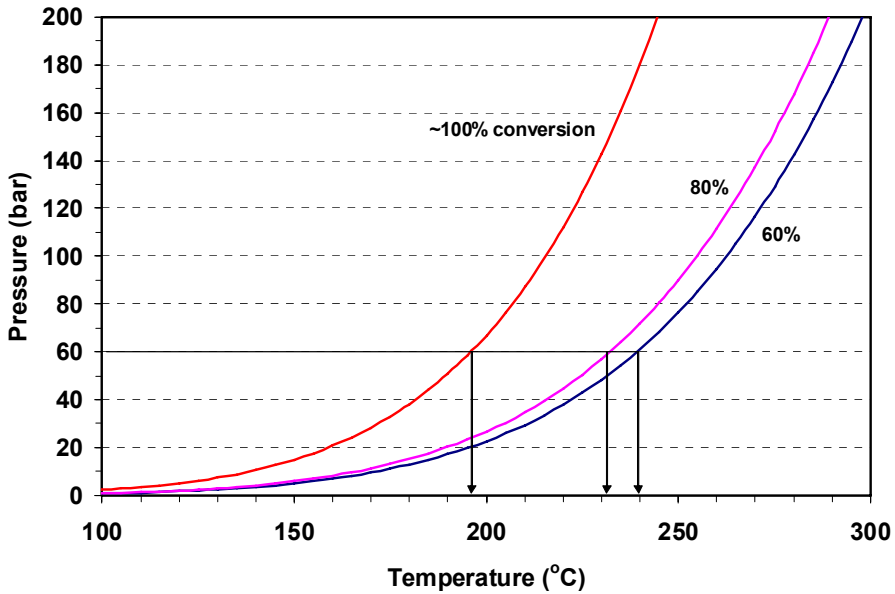
Rehydrogenation of Organic Liquid Carriers

Multi-stage hydrogenation reactors

- Declining T profile: H_2 quench and inter-stage regenerative cooling
- Overall exothermic reaction: process fuel used in furnace, low-grade heat recovered in H_2 cooler
- Operating P is a function of conversion and T



N-ethylcarbazole

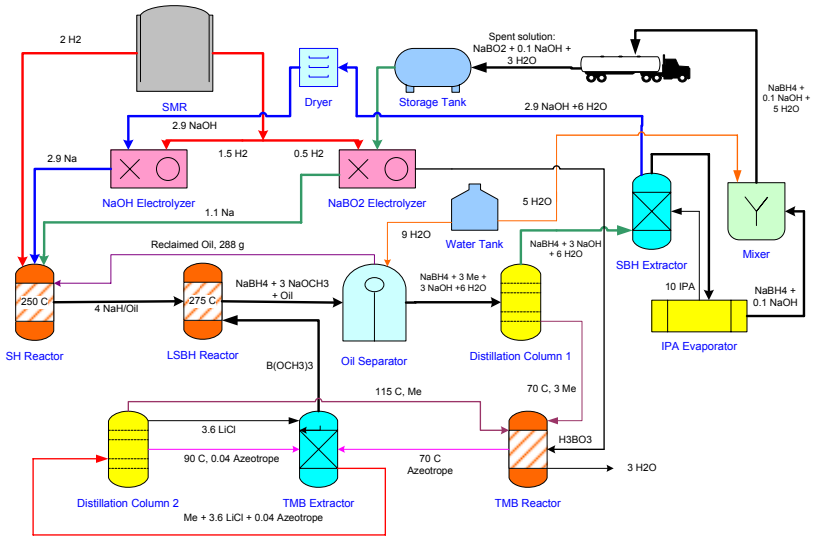


Parameter	1-Stage	3-Stage
Temperature, °C	196	240/232/196
Pressure, bar	60	60
Cumulative Conversion	1.0	0.6/0.8/1.0
H_2 Circulation Ratio	21.7	16.2
Electricity, kWh/kg H_2	2.02	1.68
Heat input, MJ/kg H_2	0.8	0.8
WTT, %	59.8	60.9

Regeneration of SBH from $NaBO_2$

Electrolysis with Na recovery (MCEL)

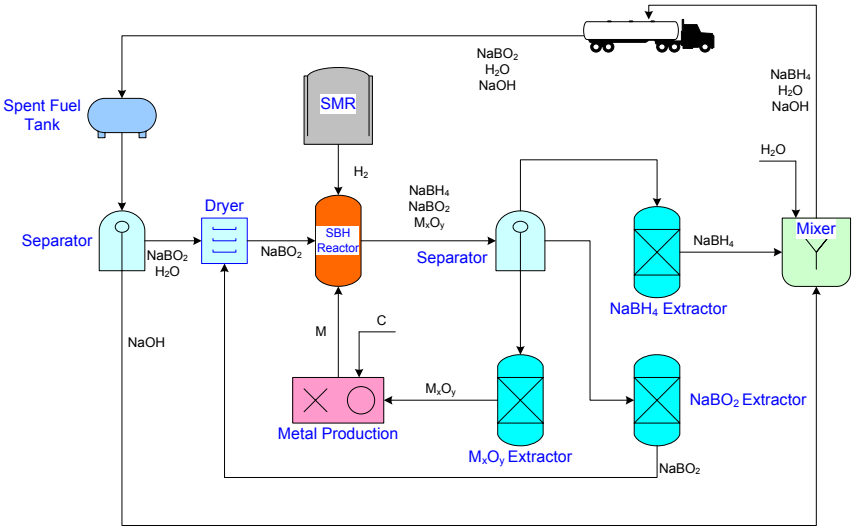
- NaOH and $NaBO_2$ electrolysis
- Na recovery is the most energy intensive step



Na Recovery Option	WTT Efficiency,%	
	Baseline	Sensitivity Analysis
AnH-AqH	21.3	19.3 - 23.1
AqH-AqH	18.6	17.2 - 20.2
An-Aq	17.7	16.4 - 19.2
Aq-Aq	15.6	14.6 - 16.7

Metal reduction (Rohm and Haas)

- Direct reduction of $NaBO_2$ with metal
- Regeneration of metal from its oxide accounts for 70-80% of total primary energy



Metal Reduction Option	WTT Efficiency, %
Option A	11.8
Option B	13.9
Option C	14.0
Option D	17.0

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 CO_2 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