System Level Analysis of Hydrogen Storage Options

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Project ID: ST001

Overview

Timeline

- Project start date: Oct 2009
- Project end date: Sep 2014
- Percent complete: 40%

Budget

- FY11: $600 K
- FY10: $700 K

Barriers

- H_2 Storage Barriers Addressed:
  - A: System Weight and Volume
  - B: System Cost
  - C: Efficiency
  - E: Charging/Discharging Rates
  - J: Thermal Management
  - K: Life-Cycle Assessments

Partners/Interactions

- Storage Systems Analysis Working Group (SSAWG)
- Hydrogen Storage Engineering Center of Excellence (HSECoE), NREL, SRNL
- BNL, LANL, Ford
- BMW, LLNL, TIAX, and other industry
- FreedomCAR and Fuel Partnership

Objectives and Relevance

- Conduct independent systems analysis for DOE to gauge the performance of H_2 storage systems
- Provide results to material developers for assessment against performance targets and goals and help them focus on areas requiring improvements
- Provide inputs for independent analysis of costs of on-board systems.
- Identify interface issues and opportunities, and data needs for technology development
- Perform reverse engineering to define material properties needed to meet the system level targets

Approach

- Develop thermodynamic and kinetic models of processes in physical, complex metal hydride, sorbent, and chemical H_2 storage systems
  - Address all aspects of on-board and off-board storage targets, including capacity, charge/discharge rates, emissions, and efficiencies
  - Assess improvements needed in materials properties and system configurations to achieve storage targets
- Select model fidelity to resolve system-level issues
  - On-board system, off-board spent fuel regeneration, reverse engineering
  - Conduct trade-off analyses, and provide fundamental understanding of system/material behavior
  - Calibrate, validate, and evaluate models
- Work closely with DOE technology developers, HSECoE and others in obtaining data
- Participate in SSAWG meetings and communicate modeling, analysis approach, and results to foster consistency among DOE-sponsored analysis activities

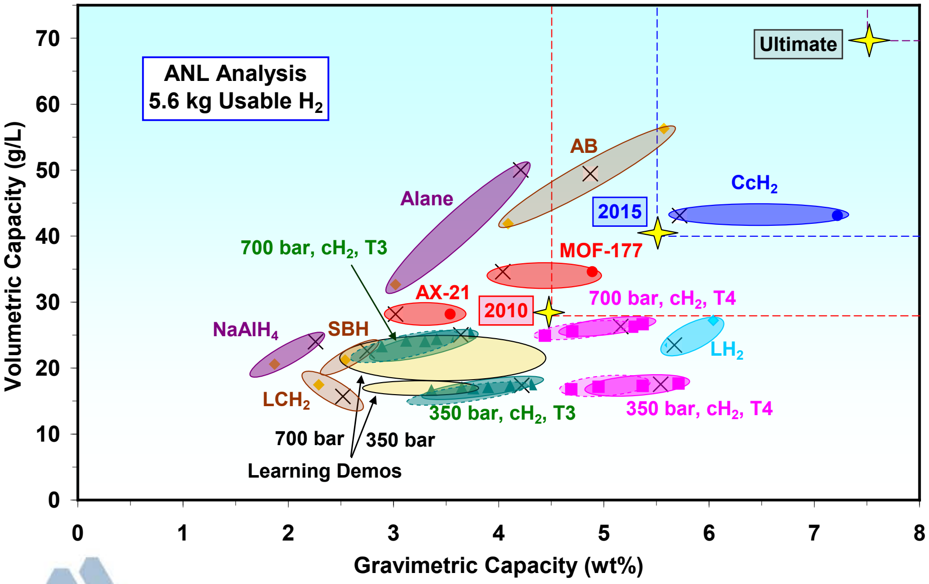
Collaborations

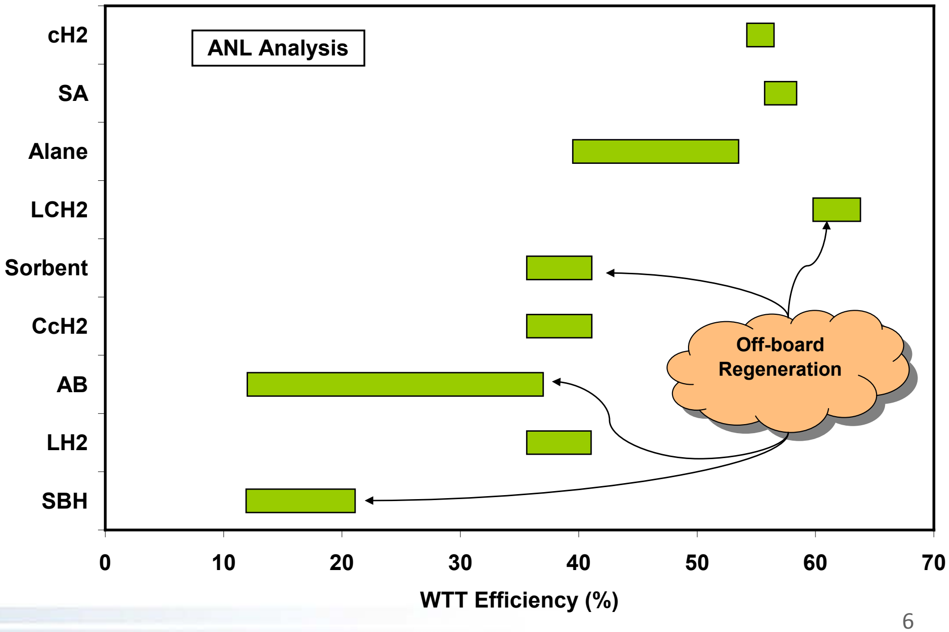
Compressed H_2 (cH2)	Lincoln Composites, Quantum
Cryo-Compressed H_2 (CcH2)	BMW, LLNL
Metal Hydrides	BNL
Chemical Hydrides	LANL
Sorbents	Ford
GHG Emissions	ANL (GREET)
Off-Board Spent Fuel Regeneration	BNL, LANL, Dow Chemicals
Off-Board Cost	ANL (H2A Group), ANL (HDSAM)
On-Board Cost	TIAX
SSAWG	HSECoE, DOE, LLNL, OEMs, SNL,Tank Manufactures,TIAX

- Argonne develops the storage system configuration, determines performance, identifies and sizes components, and provides this information to TIAX for manufacturing cost estimation

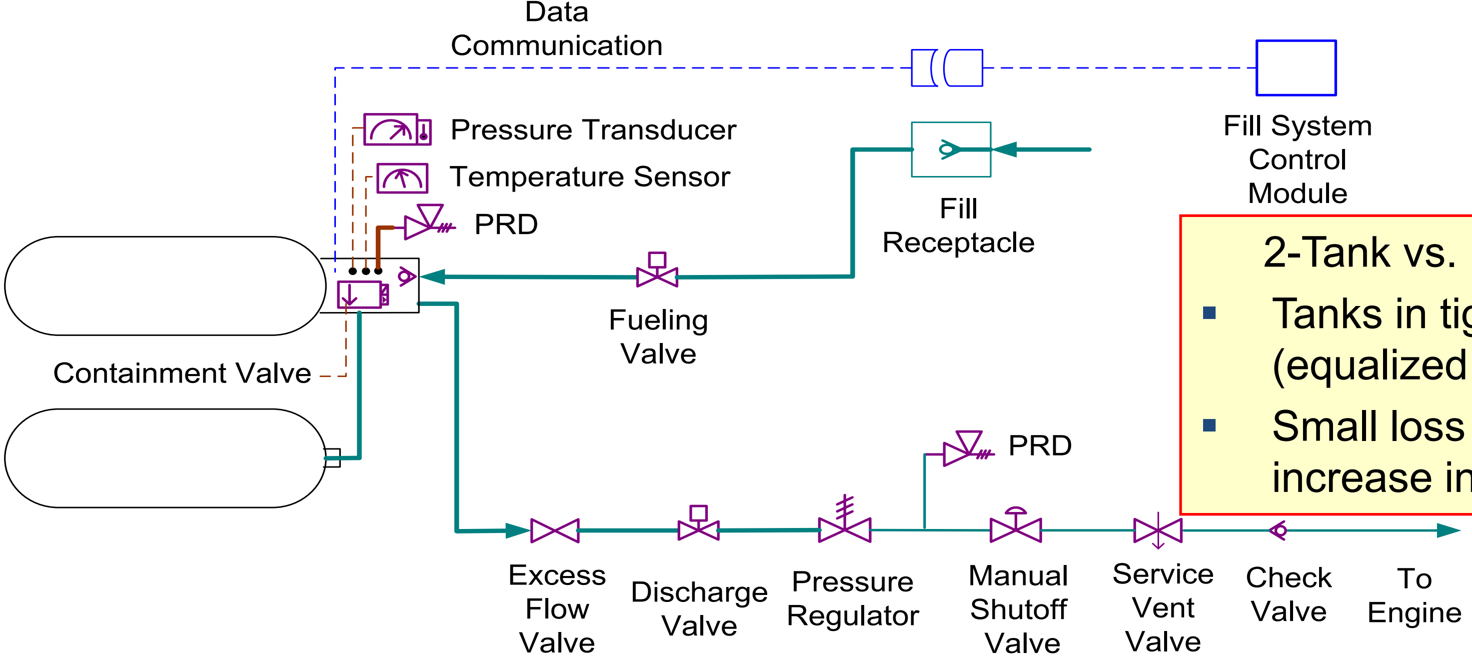
Summary: FY2011 Technical Accomplishments

- Systems analyzed or updated in FY 2011
  - Physical storage: Two-tank cH_2 system, supercritical CcH_2 system
  - Sorption storage: MOF-5 powder and pellets
  - Chemical storage: Ammonia borane in ionic liquid (AB/IL)
  - Metal hydride: Alane slurry
- Systems are at different stages of development and have been analyzed to different levels of sophistication
  - Results are continually updated



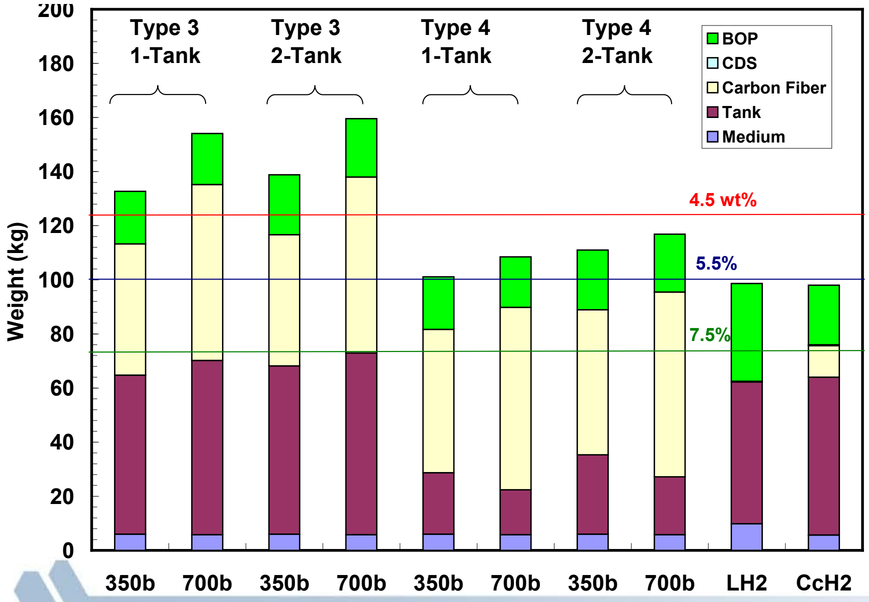


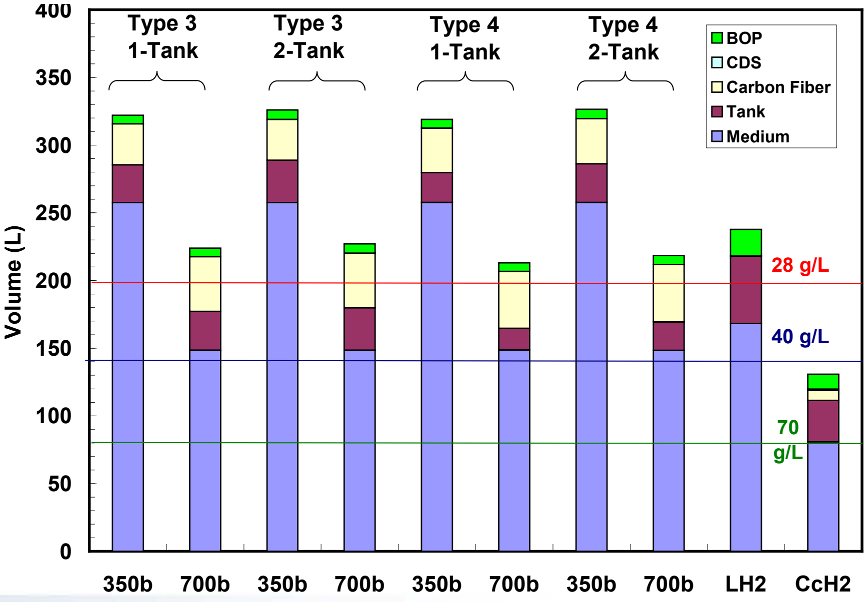
Physical Storage Systems



2-Tank vs. 1-Tank Systems

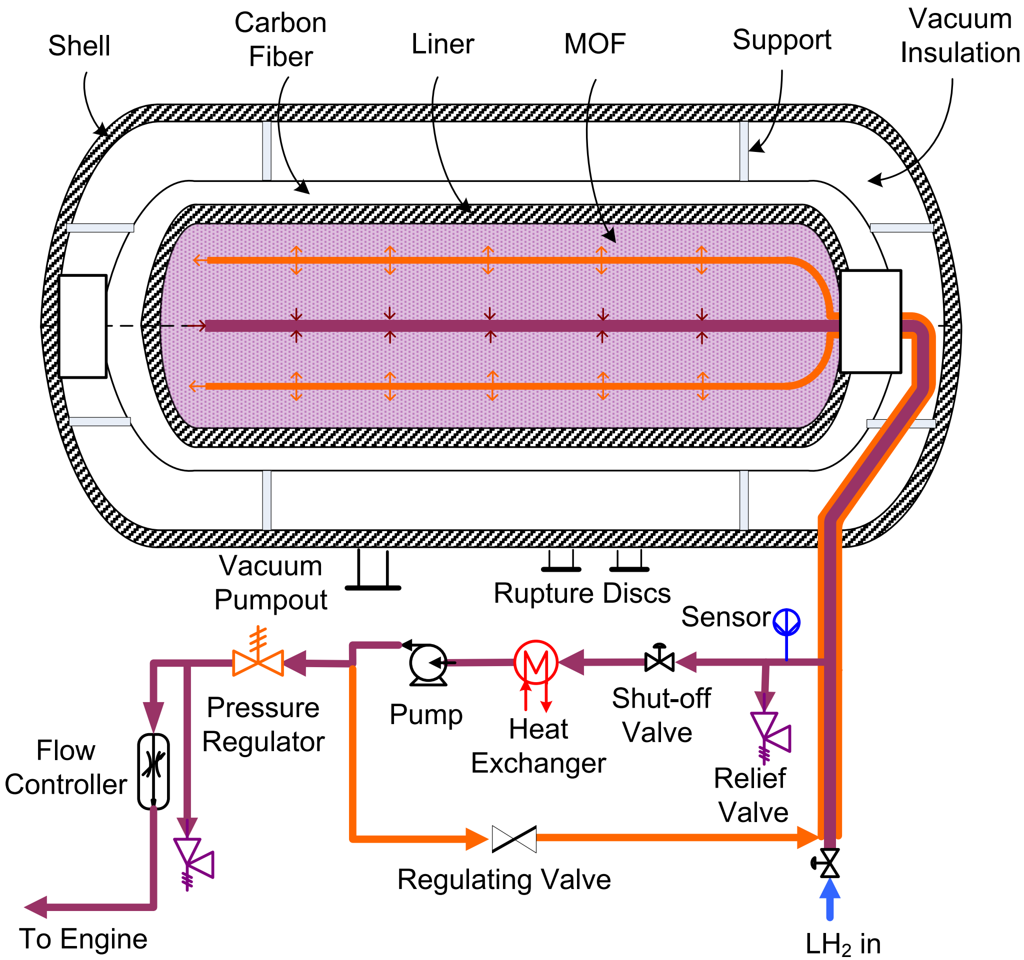
- Tanks in tight communication (equalized pressures)
- Small loss in capacity and increase in cost





CDS: Charge-Discharge System

Cryogenic Hydrogen Storage in MOF-5
Adiabatic Liquid H_2 Refueling



Key System Requirements

Storage Medium

- 5.6 kg recoverable H_2
- 5-bar minimum delivery P
- MOF-5 powder and pellets

Type-3 Containment Vessel

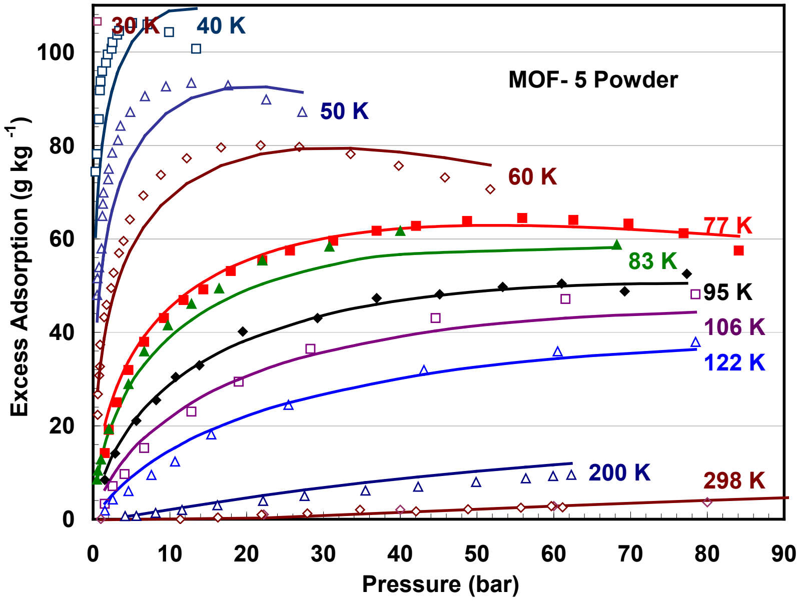
- 2.25 safety factor
- 5,500 P and T cycles
- Toray 2550 MPa CF
- Al 6061-T6 alloy liner

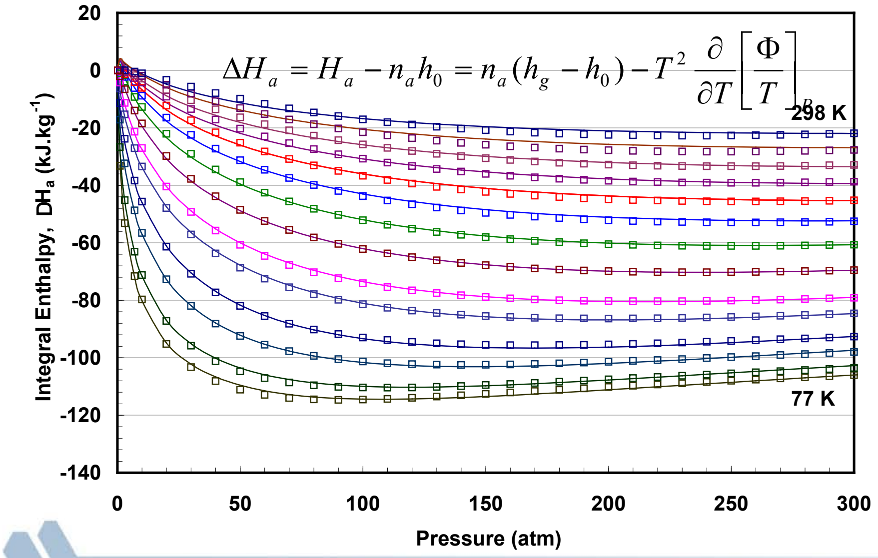
Heat Transfer System

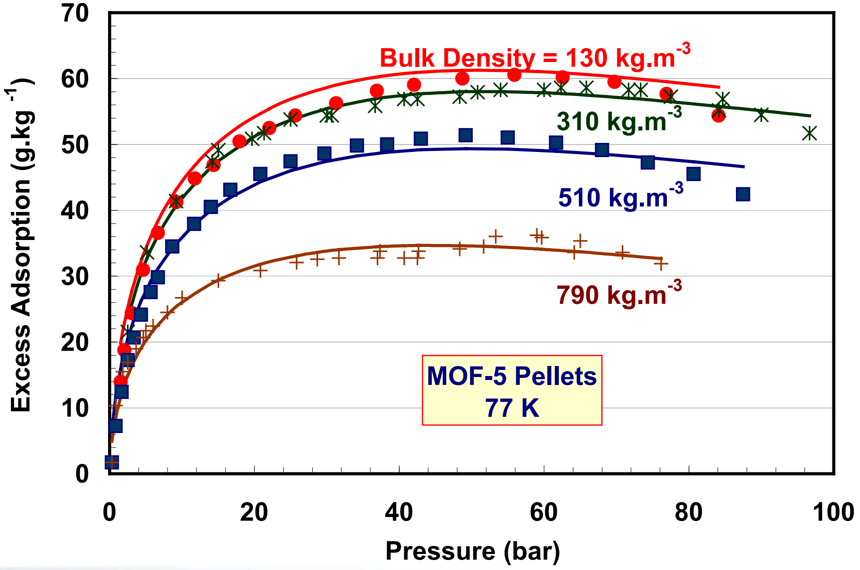
- 1.5 kg/min H_2 refueling rate
- 1.6 g/s H_2 min flow rate
- 5 W heat in-leakage

Modeled Adsorption Isotherms: MOF-5 Powder and Pellets

- Sudik et al (2010 Annual AIChE Meeting)
  - MOF-5 (Basolite Z100-H) loose powder, 130 kg.m^{-3} bulk density
  - 6 wt% surface excess at 77 K, 55 bar
  - Pelletization causes ~12% loss in excess gravimetric but ~300% gain in volumetric capacity at 77 K
- Sorption fitted to Dubinin-Astakhov (D-A) isotherm, solution thermodynamics for integral enthalpy of adsorption



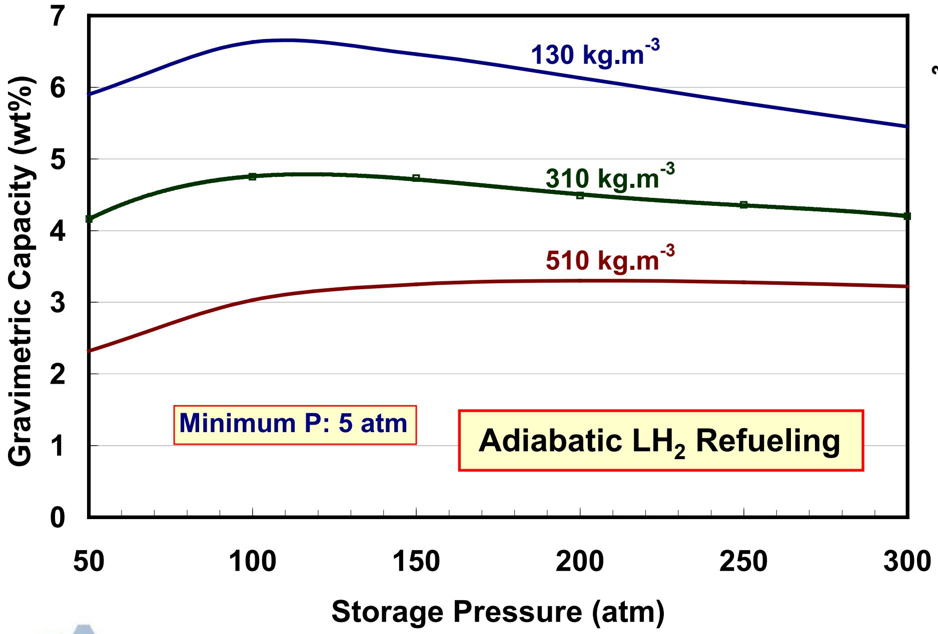


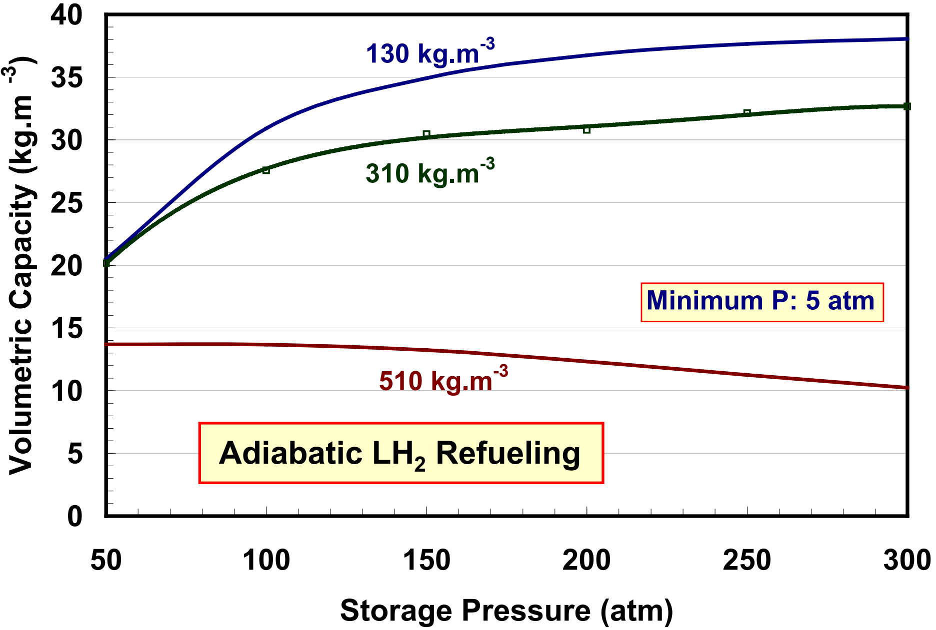


Optimum Pressures and Temperatures: MOF-5 Pellets

All results for LH_2 refueling

- Optimum P and T for maximum gravimetric capacity are 100-120 atm and ~60 K for powder and 310 kg.m^{-3} bulk density, higher for 510 kg.m^{-3} bulk density
- Optimum T lower than the T at which recoverable excess uptake is maximum
- System volumetric capacity increases with P for 130-310 kg.m^{-3} bulk densities, but does not reach the 40-g.L^{-1} target

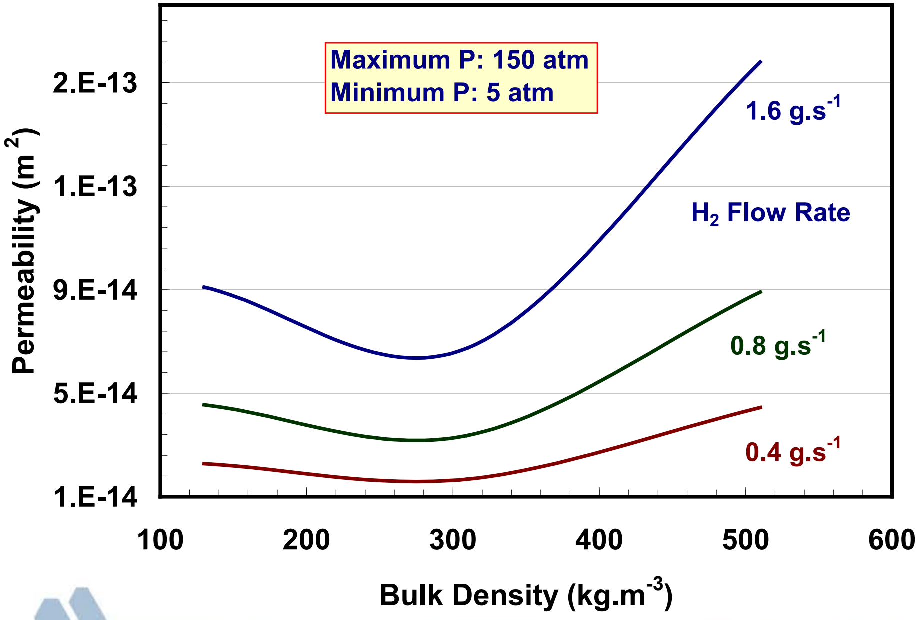


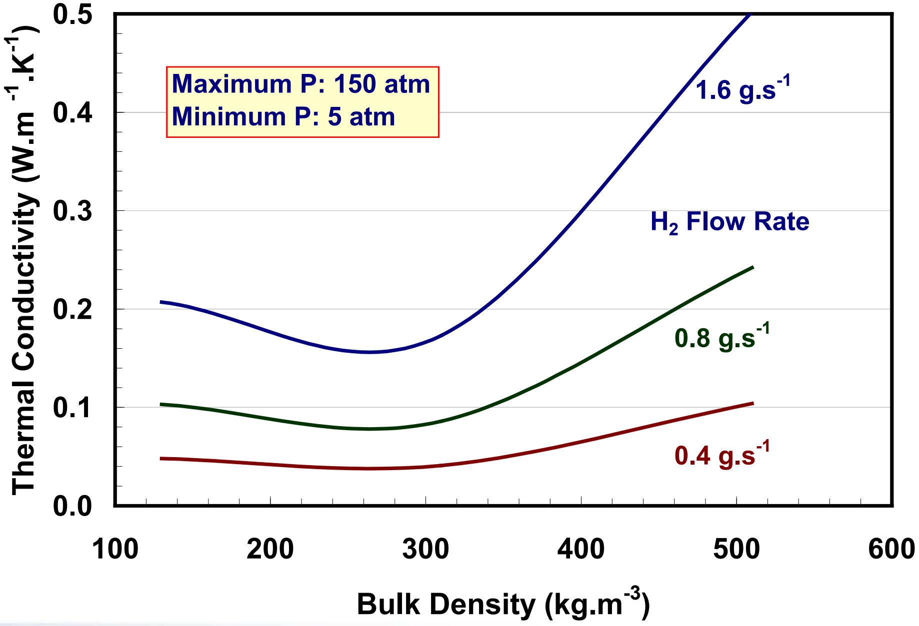


Discharge Dynamics: MOF-5 Powder and Pellets

All results for LH_2 refueling

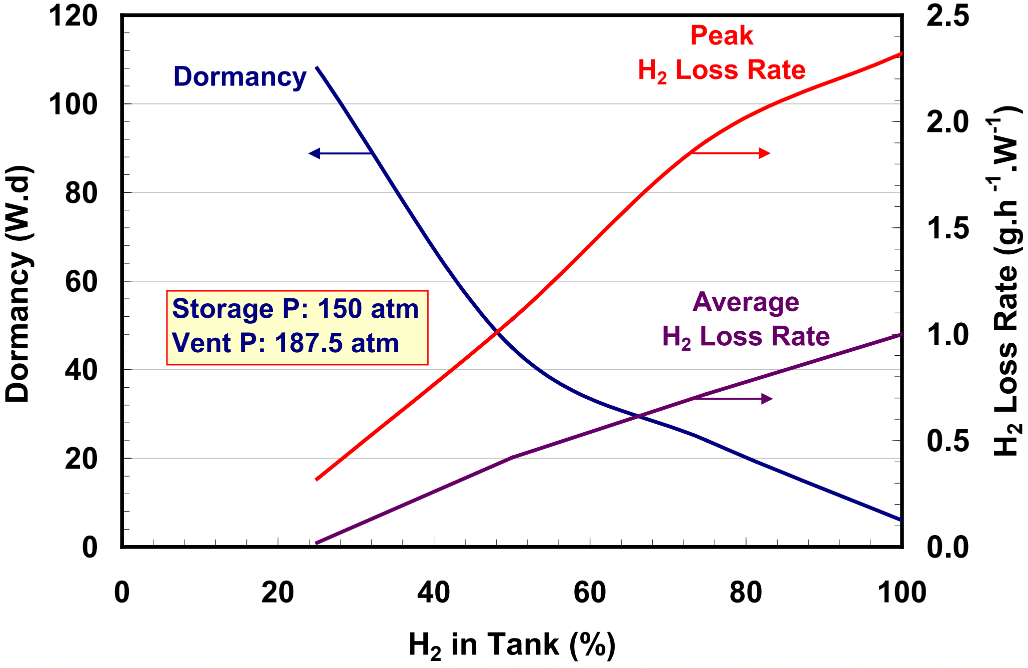
- Required bed permeability for 1 psi in-bed pressure drop and 20 charge and discharge tubes: 10^{-14} – 10^{-13} m^2
  - Initial measurement: 5.4×10^{-13} m^2 for 360 $kg.m^{-3}$ density pellet
- Required conductivity for 10 U tubes: 0.04 – 0.5 $W.m^{-1}.K^{-1}$
  - Measured conductivity for powder and pellets: 0.088 $W.m^{-1}K^{-1}$
  - Measured conductivity for 500 $kg.m^{-3}$ pellets with 10 wt% graphite flakes: ~0.6 $W.m^{-1}K^{-1}$





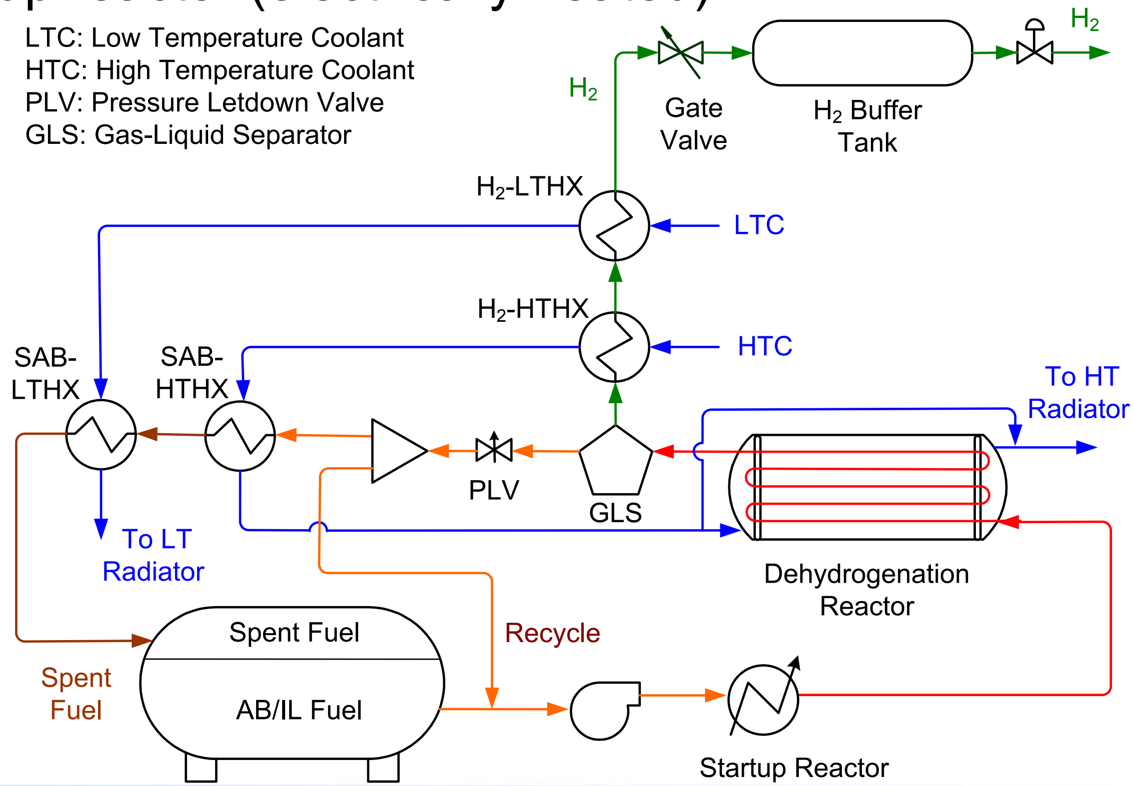
Dormancy and H_2 Loss: MOF-5 Powder and Pellets

- Dormancy: Function of amount of H_2 stored and P/T at start of the event
  - Minimum dormancy is 6 W.d (1.2 days at 5 W in-leakage rate)
  - Peak H_2 vent rate is 0.3-1.9 $g.h^{-1}.kg^{-1}$ for 5 W in-leakage rate, 25-100% initially full tank
  - Average loss rate below the 0.05 $g.h^{-1}.kg^{-1}$ DOE target if the tank less than one-third full
  - No H_2 loss if tank is <15% full, or with minimal daily driving



H_2 Storage using Ammonia Borane in Ionic Liquids

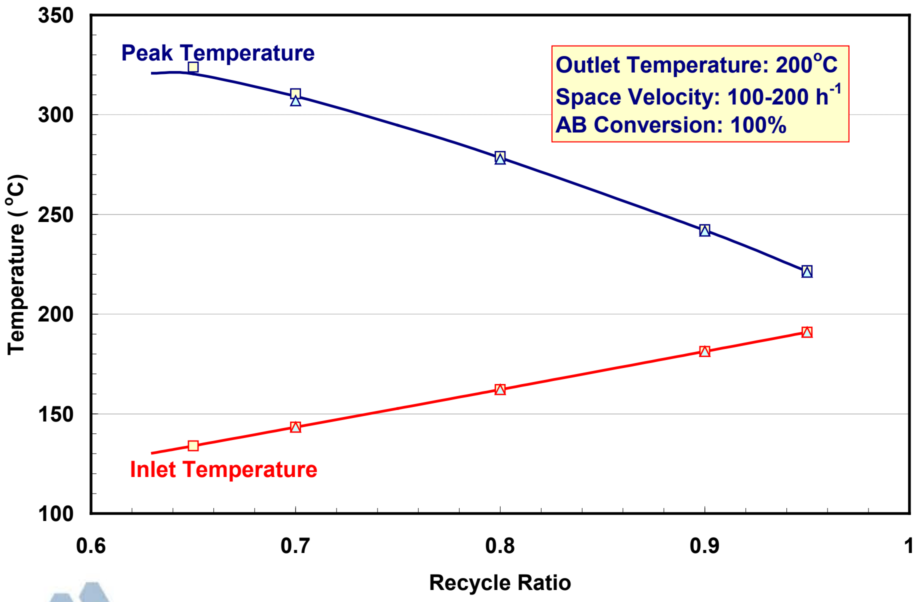
- Volume exchange tank design for storing fresh and spent fuel
- Adiabatic vs. non-adiabatic dehydrogenation reactor
- Buffer hydrogen tank
- Heat transfer system (FCS HT and LT coolants)
- Gas liquid separator (coalescing filter)
- Startup reactor (electrically heated)

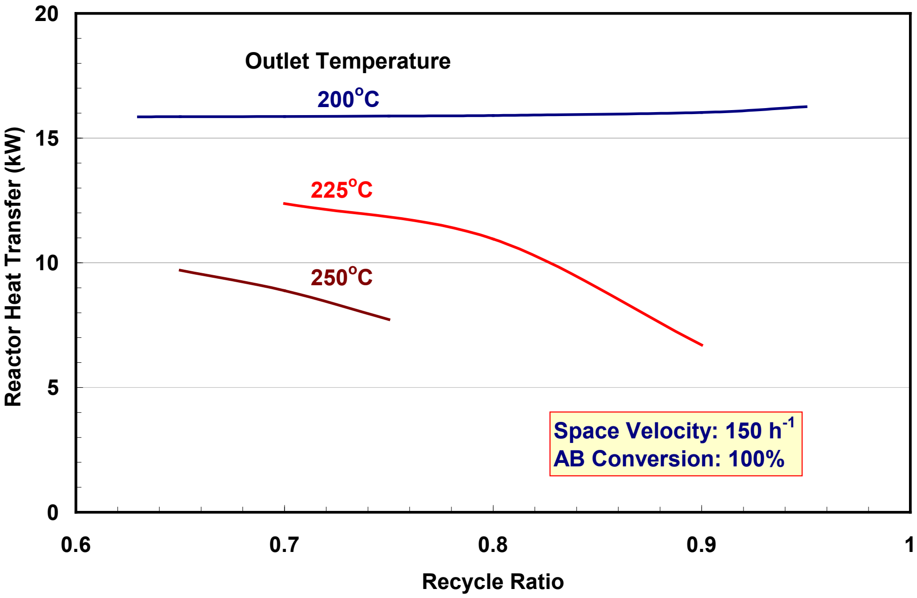


LTC: Low Temperature Coolant
HTC: High Temperature Coolant
PLV: Pressure Letdown Valve
GLS: Gas-Liquid Separator

Reactor Operating Temperatures

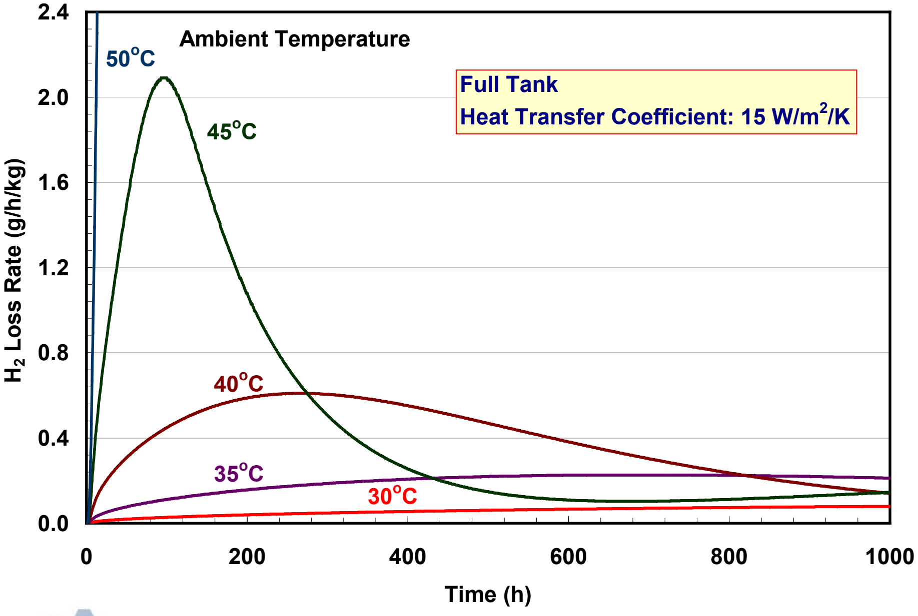
- All results for 100% conversion (2.35 H_2-equiv released)
- Increasing recycle leads to lower peak and higher reactor inlet T
  - Stability of ionic liquid related to peak T; inlet T affects choice of pump materials
- Reactor peak and inlet T are insensitive to LHSV and outlet T
- Low recycle ratio is preferred because pumping power increases nonlinearly with R
- Reactor heat transfer decreases as the outlet T is allowed to rise

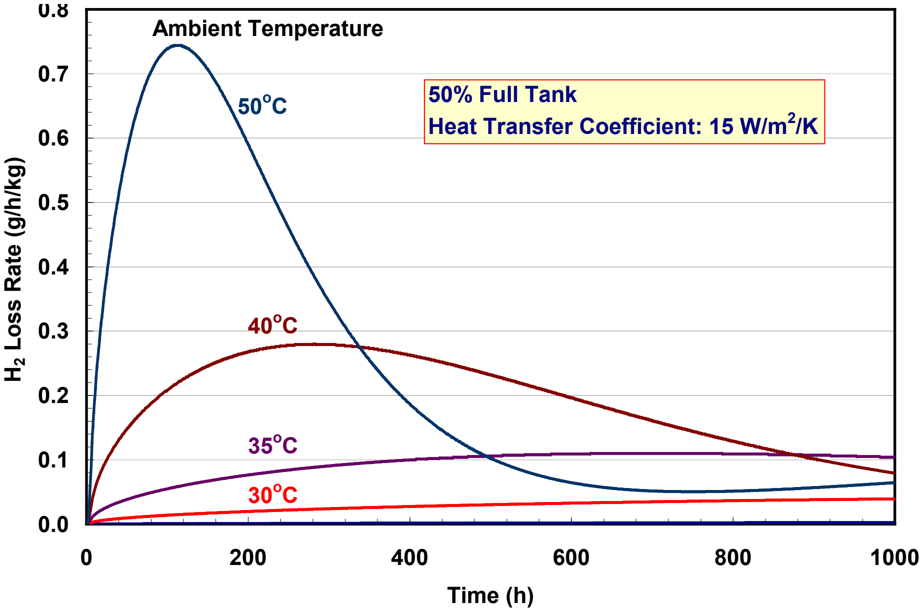




AB Stability

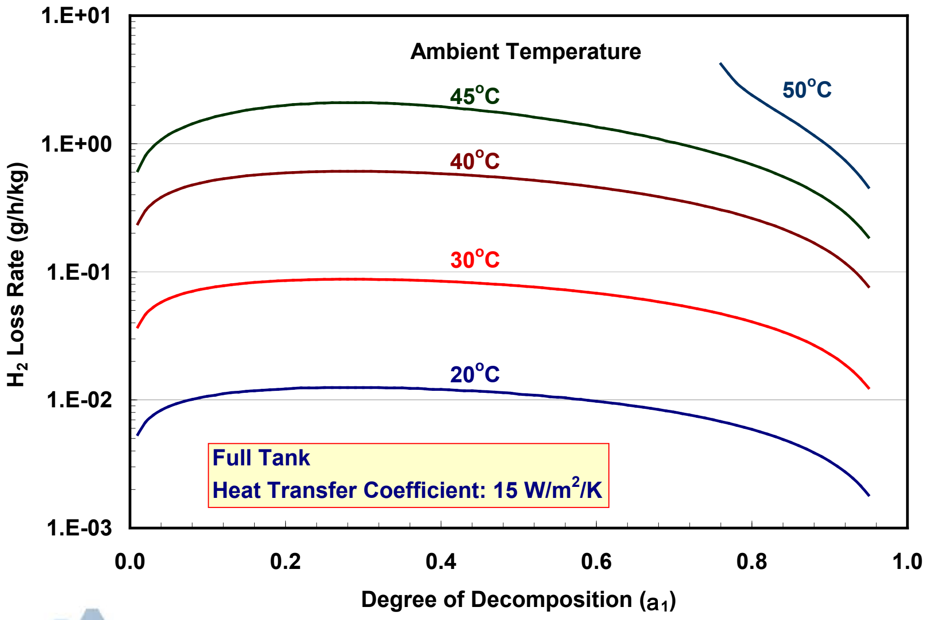
- All results obtained with kinetic constants derived using 75-110°C data
  - H_2 loss rate >> 0.05 g/h/kg at ≥50°C ambient temperature, 15 $W.m^{-2}.K^{-1}$ heat transfer coefficient for natural convection
  - Loss rate target met at <30°C ambient temperature (full tank)
  - Loss rate proportionately lower with partially full tank
  - Maximum cumulative loss limited to 1 H_2-equiv

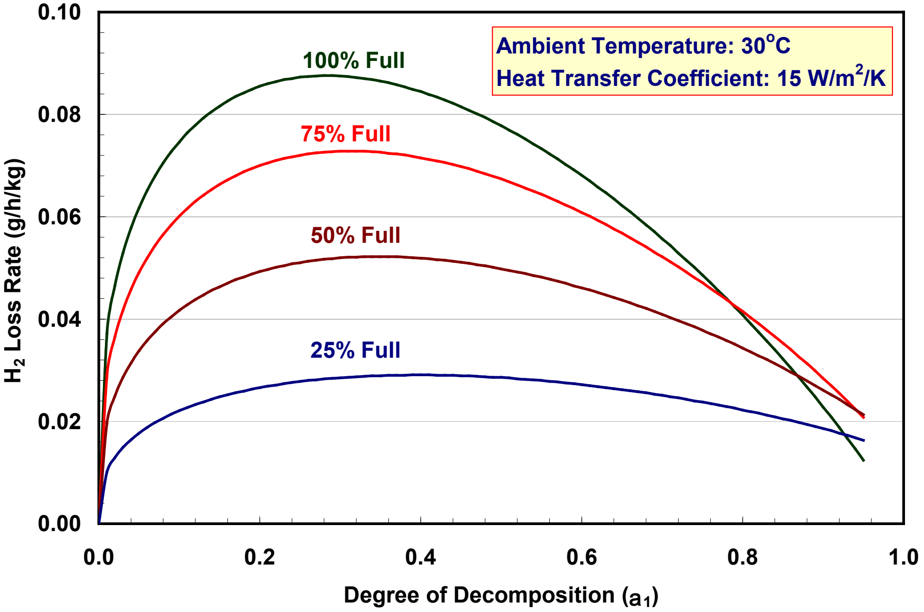




Stationary Loss Rates (AB)

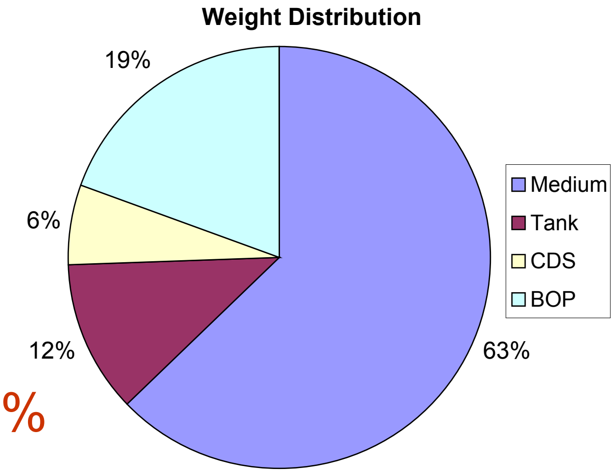
- Stationary rate defined as state at which rates of heat generation and heat loss to the ambient are equal
  - True steady state does not exist because α changes continuously
  - No stationary state at >50°C ambient temperature (full tank)
  - Results consistent with dynamic simulations
  - Desirable activation energy >142 kJ/mol for acceptable loss rates



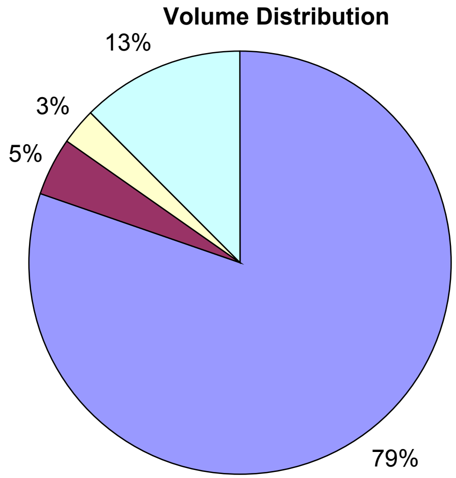


Preliminary Summary: AB System Analysis

- Product stream recycle is needed to control the reactor peak temperature and AB conversion
- Recycle between 0.6 and 0.95 for complete AB conversion
  - Very difficult to control the peak temperature with heat transfer
  - Lower peak temperatures with higher recycle, but pumping power increases non-linearly
- The reactor can also be operated adiabatically while controlling peak T and AB conversion
  - The reactor peak temperature can be lower if operated adiabatically but the recycle ratio is high



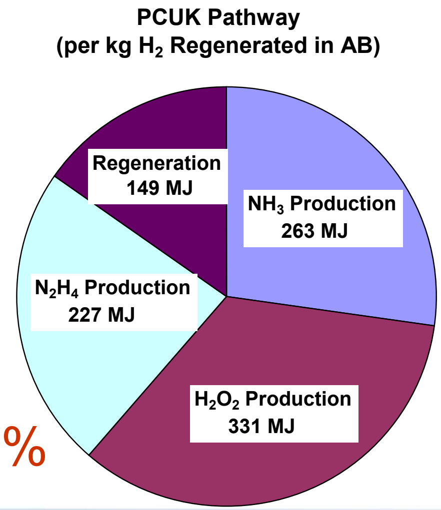
4.9 wt%



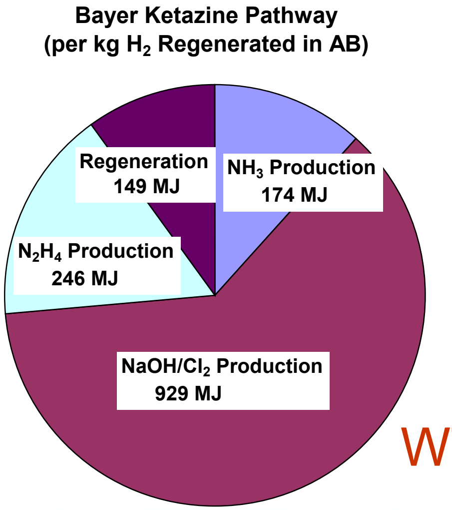
49.5 g.L^{-1}

AB Regeneration Using Hydrazine

- LANL has developed a one-pot process for regenerating spent AB using hydrazine (N_2H_4) as the limiting reagent in liquid ammonia
  - $BNH_2 + N_2H_4 \rightarrow BH_3NH_3 + N_2$
- Currently hydrazine is produced by the Bayer Ketazine or PCUK Peroxide process
  - Bayer Ketazine process feed materials: Cl_2, NaOH, and NH_3
  - PCUK process feed materials: H_2O_2 and NH_3
- FCHtool analysis: energy to produce N_2H_4 dominates the overall energy consumed in AB regeneration



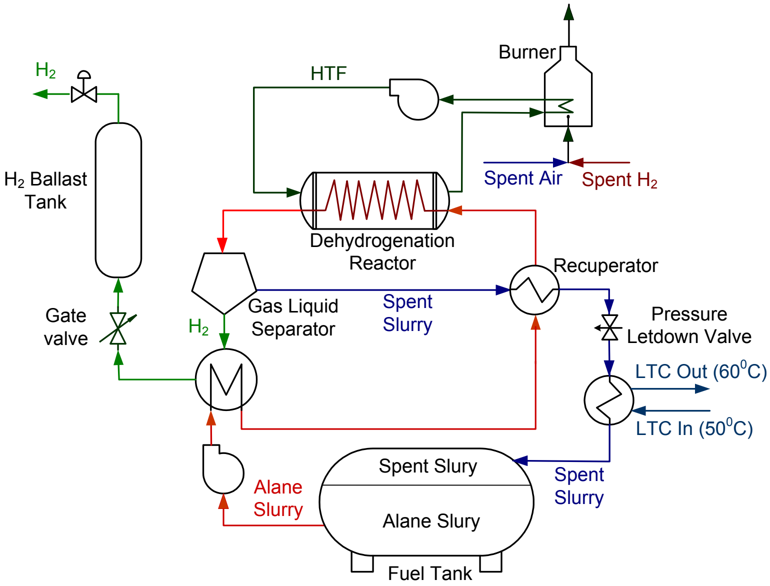
WTT Efficiency = 12%

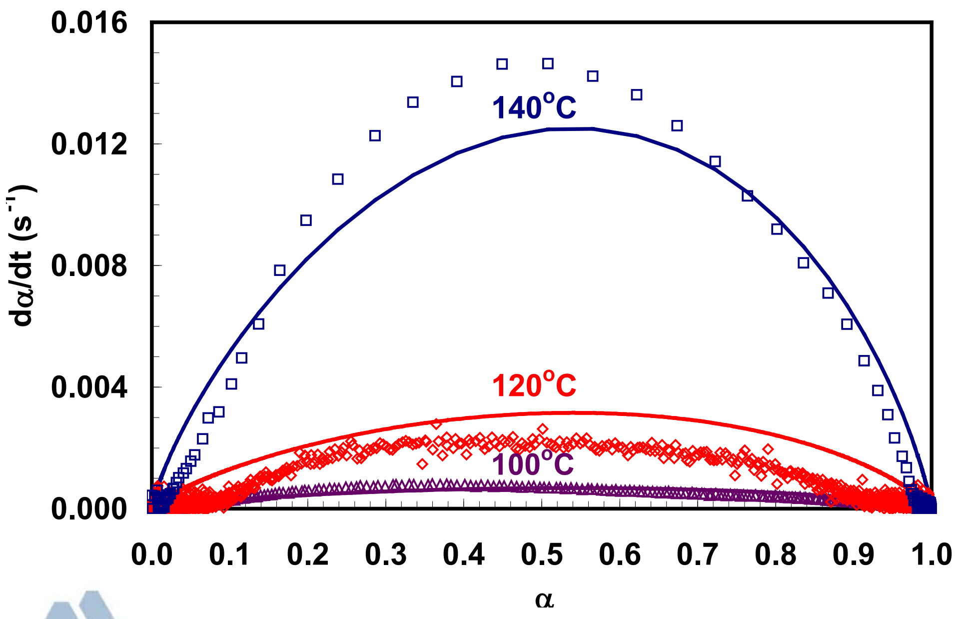


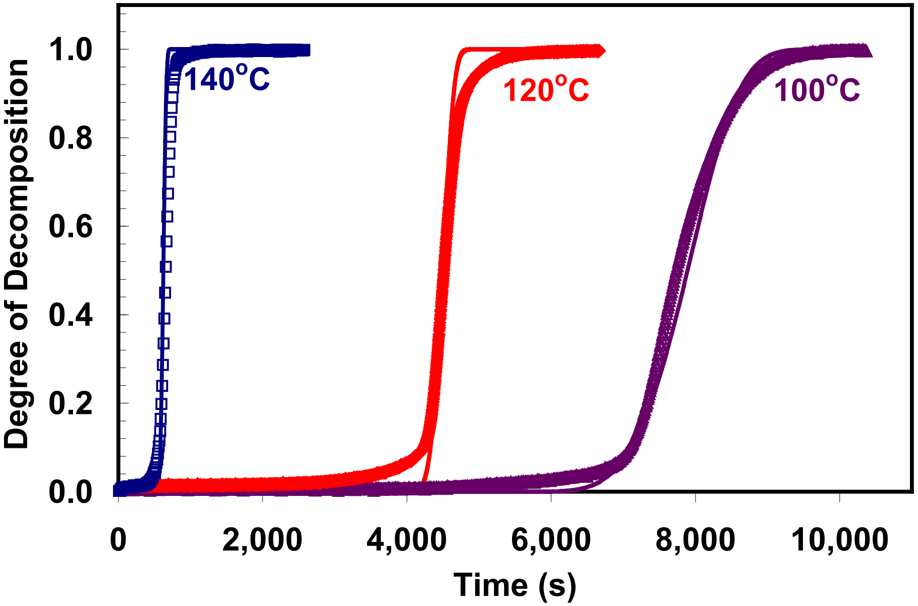
WTT Efficiency = 8%

H_2 Storage in Alane Slurry: Decomposition Kinetics

- Analyzing new BNL data for micron-sized particles in dibutyl ether (slurry with 60-wt% solids)
- Faster kinetics than previous nano-sized dry powder
- Fitted to Avrami-Erofevev equation with n = 4.5, E = 93.1 kJ/mol
- Induction time correlated with T





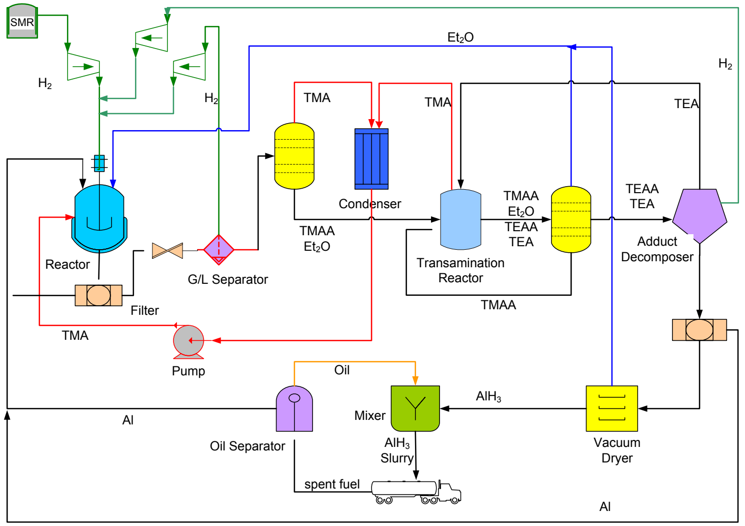


$$d\alpha / dt = nk(1-\alpha)[-\ln(1-\alpha)]^{(n-1)/n}$$

Regeneration of Alane

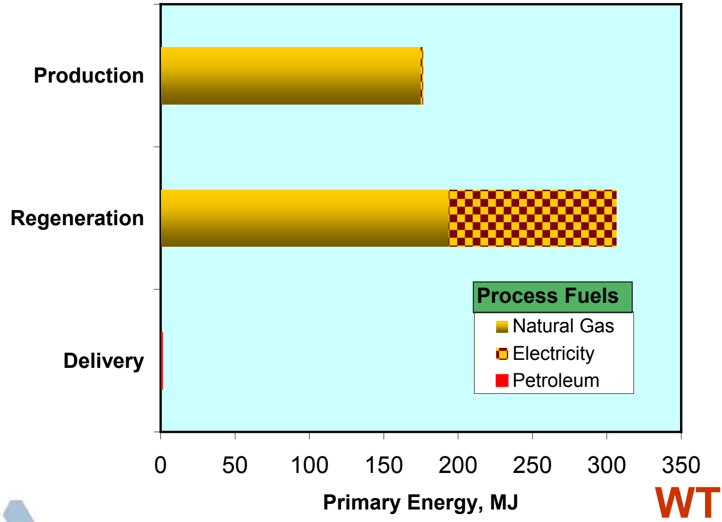
Three-step process

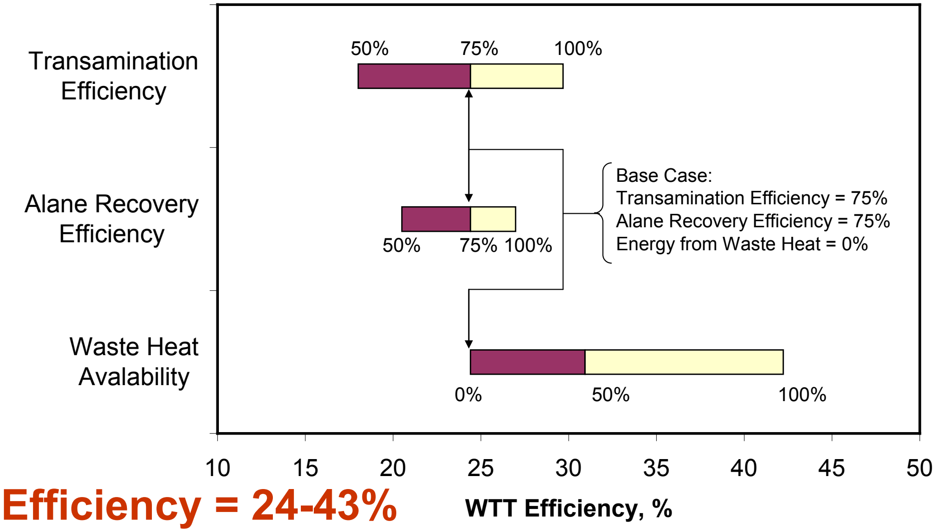
- Formation of a first tertiary amine alane adduct (TMAA or DMEAA)
- Transamination of TMAA or DMEAA to form triethylamine alane adduct (TEAA)
- Decompose TEAA to recover alane



FCHtool analysis: 85% thermal efficiency, 73% SMR efficiency

- Molar ratio: ether/Al = 4, TEA/DMEA = 4, TEA/TMAA = 4





WTT Efficiency = 24-43%

Summary and Status

- Results given as single data points, consult references for range, sensitivity and background
- Metrics cover all DOE targets for on-board and off-board storage
- Some results vetted, others for developmental materials and processes
- Completed analyses of multi-tank systems, MOF-5, and AB systems
  - AlH_3 slurry ongoing
  - Reversible metal hydride: $2LiNH_2/MgH_2$ and $LiNH_2/MgH_2$
  - Physical storage systems: CcH_2 storage issues

Performance and Cost Metric	Units	cH2 350-T4	cH2 700-T4	LH2	CcH2	MOF-5	AB	2010 Targets	2015 Targets	Ultimate Targets
Comment		1-Tank	1-Tank			Powder				
Usable Storage Capacity (Nominal)	kg-H_2	5.6	5.6	5.6	5.6	5.6	5.6			
Usable Storage Capacity (Maximum)	kg-H_2	5.6	5.6	5.6	6.6	5.6	5.6			
System Gravimetric Capacity	wt%	5.5	5.2	5.6	5.5-9.2	6.5	4.9	4.5	5.5	7.5
System Volumetric Capacity	kg-H_2/m^3	17.6	26.3	23.5	41.8-44.7	34.9	49.5	28	40	70
Storage System Cost	$/kWh	15.5	18.9	TBD	12	TBD	TBD	4	TBD	TBD
Fuel Cost	$/gge	4.2	4.3	TBD	4.80	4.6	TBD	3-7	2-6	2-3
Cycle Life (1/4 tank to Full)	Cycles	NA	NA	NA	5500	5500	NA	1000	1500	1500
Minimum Delivery Pressure, FC/ICE	bar(abs)	4	4	4	3-4	5	5	5/35	5/35	3/35
System Fill Rate	kg-H_2/min	1.5-2	1.5-2	1.5-2	1.5-2	1.5-2	1.5-2	1.2	1.5	2.0
Minimum Dormancy (Full Tank)	W-d	NA	NA	2	4-30	6	6			
H_2 Loss Rate (Maximum)	g/h/kg-H_2	NA	NA	8	0.2-1.6	1.9	0.75	0.1	0.05	0.05
WTE Efficiency	%	56.5	54.2	22.3	41.1	41.1	12.0	60	60	60
GHG Emissions (CO_2 eq)	kg/kg-H_2	14.0	14.8	TBD	19.7	19.7	62.9			
Ownership Cost	$/mile	0.13	0.14	TBD	0.12	TBD	TBD			

Future Work

As lead for Storage System Analysis Working Group, continue to work with DOE contractors to model, validate, and analyze various developmental hydrogen storage systems.

Physical Storage

- Multi-tank compressed H_2 tank systems representative of current designs
- Supercritical cryo-compressed storage concepts

Metal Hydrides

- Update of alane slurry storage system analysis (BNL collaboration)
- Regeneration of alane/other off-board regenerable metal hydrides
- Reversible metal-hydride storage system

Sorbent Storage

- Analysis of generic sorbent system with arbitrary heat of adsorption

Chemical Hydrogen

- On-board system for AB/IL class of materials (LANL collaboration)
- Fuel cycle efficiency of AB regeneration (LANL collaboration)

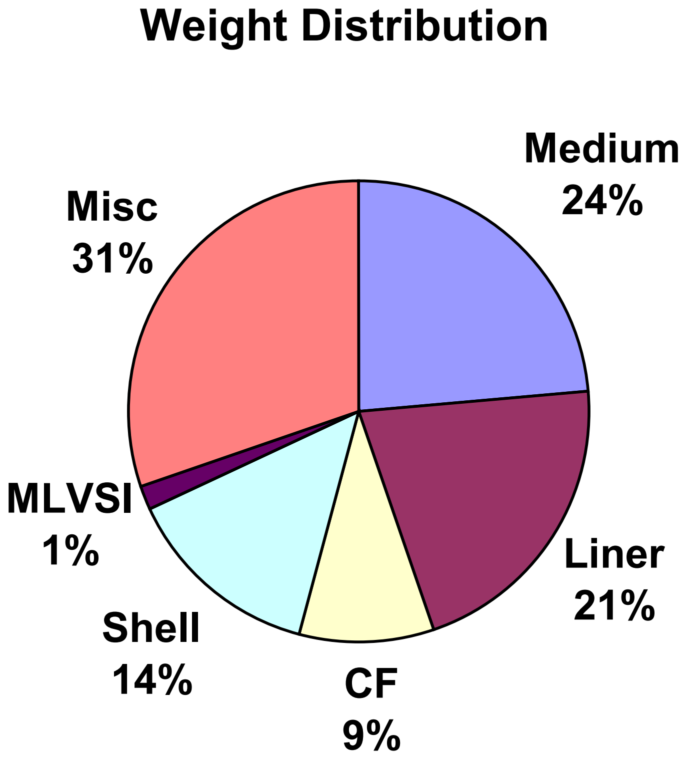
Supplemental Slides

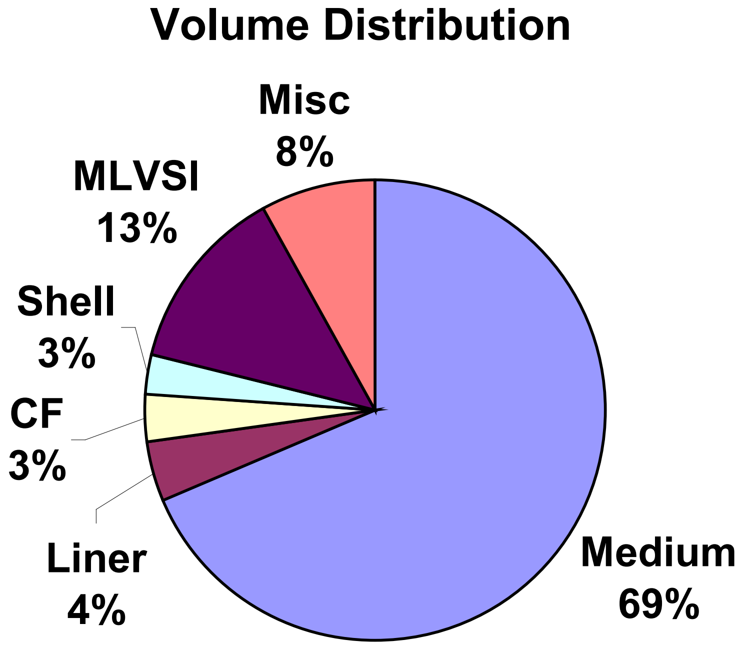
MOF-5 On-Board Performance: Key Assumptions

	Parameter	Reference Values
Sorbent	**MOF-5 (Basolite Z100-H)**	Sudik, AIChE Meeting, 2010
	Skeletal density	2030 $kg.m^{-3}$
	Crystallographic density	610 $kg.m^{-3}$
	Bulk density	130 $kg.m^{-3}$ (powder), 310-790 $kg.m^{-3}$ (pellets)
	Thermal conductivity	0.088 $W.m^{-1}.K^{-1}$
Insulation	**Multi-Layer Vac. Super Insulation**	Aluminized Mylar sheets, Dacron spacer
	Layer density	28 cm^{-1}
	Density	59.3 $kg.m^{-3}$
	Pressure	10^{-5} torr
	Effective conductivity	5.2×10^{-4} $W.m^{-1}.K^{-1}$
Tank	**T700S Carbon Fiber**	Toray Carbon Fiber
	Tensile strength	2550 MPa
	Density	1600 $kg.m^{-3}$
	L/D	3
	Liner	Al 6061-T6 alloy, 5500 PT cycles, 125% NWP
	Shell	3.2-mm thick Al 6061-T6 alloy alloy
Refueling	**Adiabatic Refueling with LH_2**	
	LH_2 pump efficiency	60-70%
	Storage temperature	Function of storage pressure
	Temperature swing	Function of storage pressure and temperature
Discharge	**H_2 Recirculation**	
	Temperature	273 K
	Recirculation rate	TBD
Balance of System	Miscellaneous weight	16 kg
	Miscellaneous volume	10 L

Weight and Volume Distribution

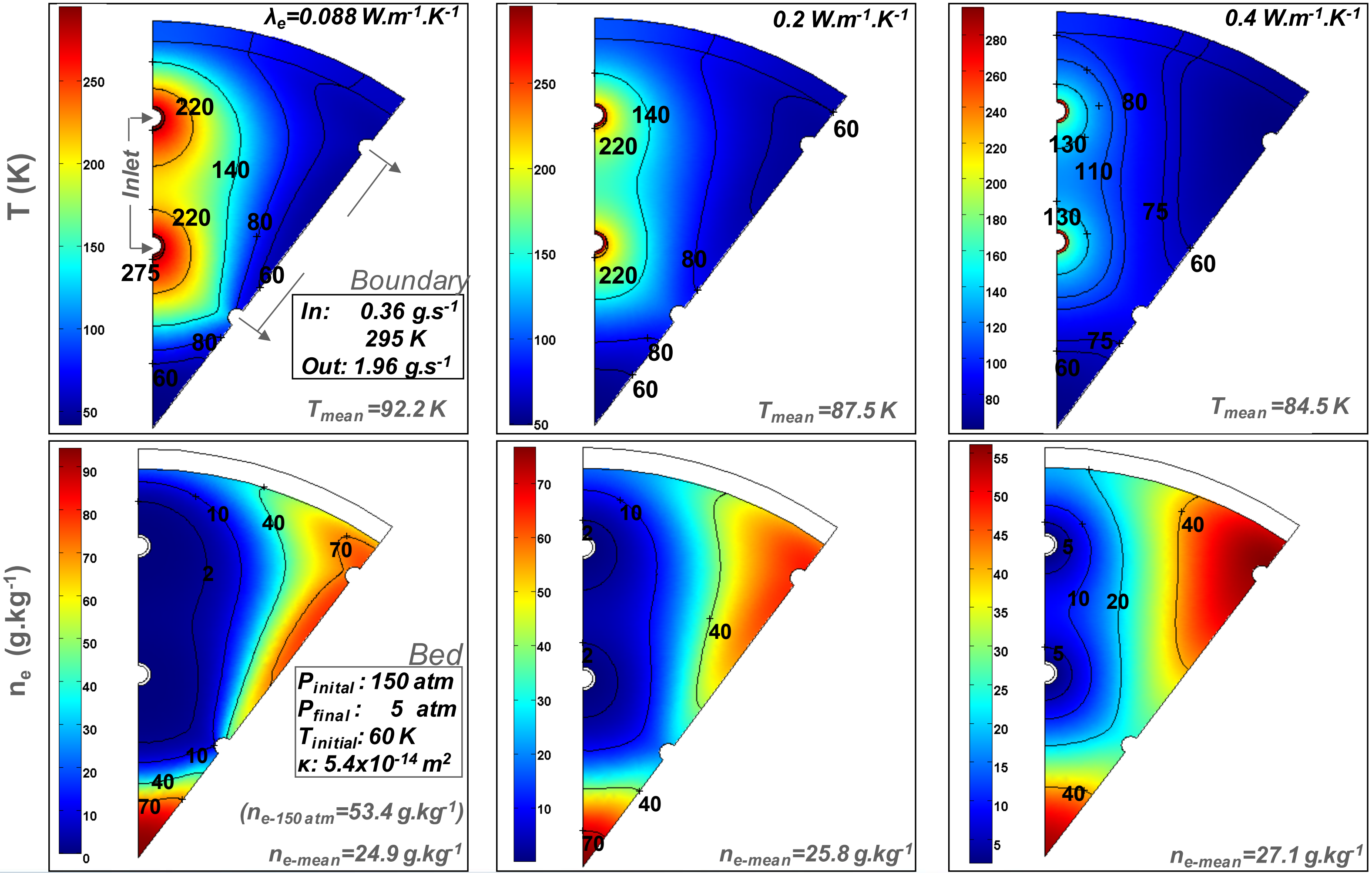
- 6.5-wt% gravimetric and 34.9 kg.m^{-3} volumetric capacities with MOF-5 powder at 60-K storage T and 150-atm storage P
  - Medium and liner account for ~50% of the overall weight
  - 69% volumetric efficiency





Discharge Dynamics: Temperature and Sorption Fields

- Effect of bed thermal conductivity on temperature and sorption fields after discharge at full flow rate (1.6 $g.s^{-1}$)
  - MOF-5 powder, storage P: 150 atm, storage T: 60 K



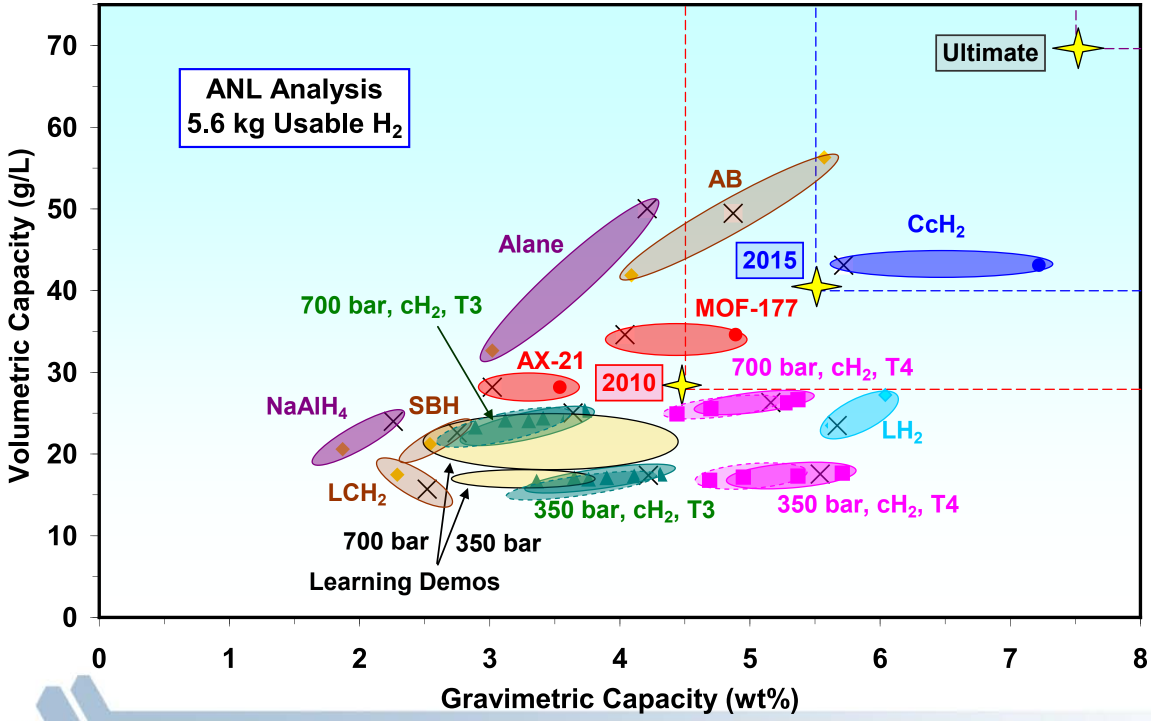
AB/bmimCl as H_2 Carrier

- Work at UPenn has shown that 1.1 H_2-equiv are released in 5 min and 2.2 H_2-equiv in 20 min from 50:50 wt% AB/bmimCl at 110°C

	Unit	Value	Comments/Source
AB			
Molecular weight		30.9	
H_2 content	wt.%	19.6	
Melting point	°C	110 - 114	E. Mayer, Inorg. Chem., 12, 1954–1955, 1973
Density	kg/m^3	780	
Thermal stability and decomposition	°C	90 -110 150°C >450°C	1st H_2-equiv released, >1 h induction period for release at 85°C 2nd H_2-equiv released 3rd H_2-equiv released
ΔH	kJ/mol-H_2	21	Exothermic reaction
Solvent: 1-butyl-3-methylimadazolium chloride (bmimCl)			
Molecular weight		174.7	
Melting point	°C	70	BASF
Flash point	°C	192	BASF
Density	kg/m^3	1050	at 80°C, BASF
Viscosity	Pa-s	0.147	at 80°C, BASF
Specific heat	kJ/kg-K	1.81	at 80°C, BASF
Thermal stability	°C	?	
50:50 wt% AB/bmimCl			
H_2 content	wt.%	9.9	Himmelberger et al, Inorg. Chem., 48, 9883-9889, 2009
Melting point	°C	NA	Liquid at room temperature
Density	kg/m^3	NA	
Viscosity	Pa-s	NA	Stirrable liquid at room temperature
Specific heat	kJ/kg-K	NA	
Thermal stability and decomposition	°C	NA	Foams once H_2 is released; foam begins to convert to white solid after releasing 1 H_2-equiv; entire mixture becoms solid after releasing 2 H_2-equiv; no induction period for H_2 release.
ΔH	kJ/mol-H_2	33	Exothermic reaction

Storage Capacity

- Of all the systems built, Gen3 CcH_2 has the highest demonstrated gravimetric and volumetric capacity
- Alane slurry shows high volumetric capacity but stable 70-wt% slurry not formulated, volume-exchange tank not developed
- On-going studies to find AB/IL formulations that remain liquid under all conditions, volume-exchange tank not developed
- cH_2 model capacities in agreement with Tech Val data



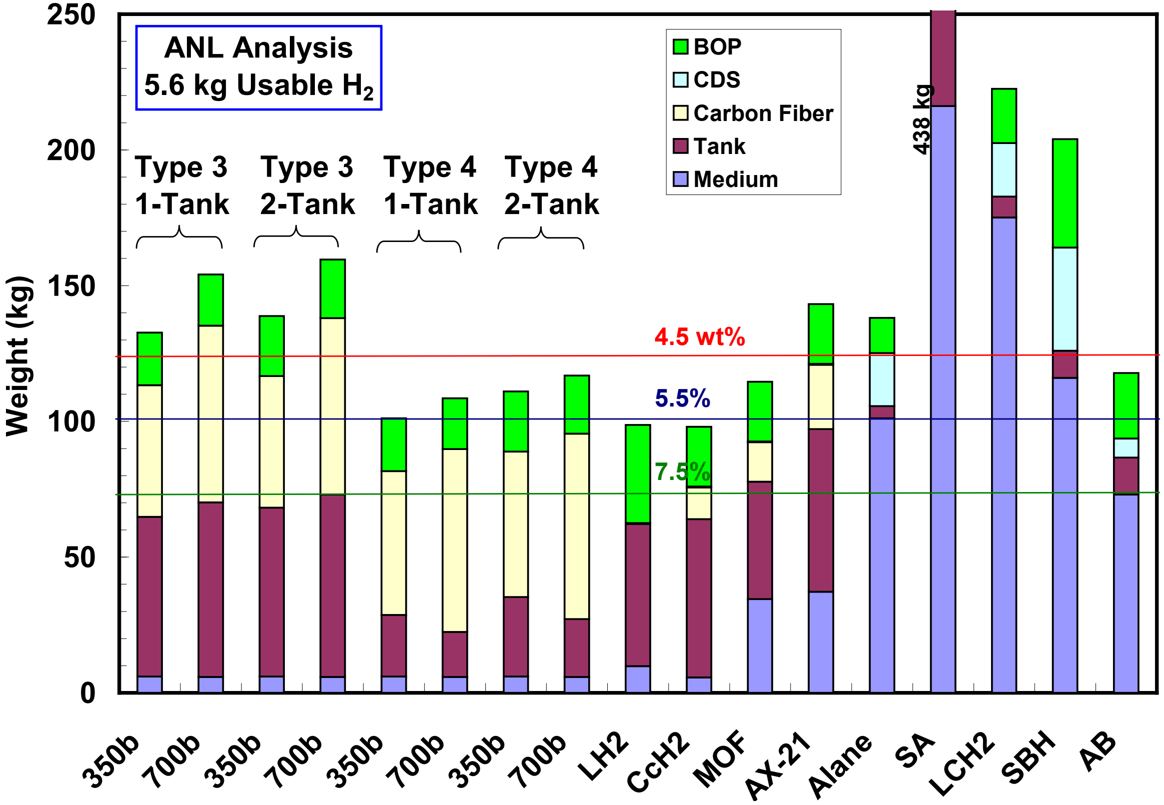
- Diagram to be regarded as a snapshot in time
- Different systems not analyzed to same level of sophistication
- Advanced materials not ready for deployment
- Some component concepts require further development

Consult ANL reports for complete details, assumptions and background

Weight Distribution

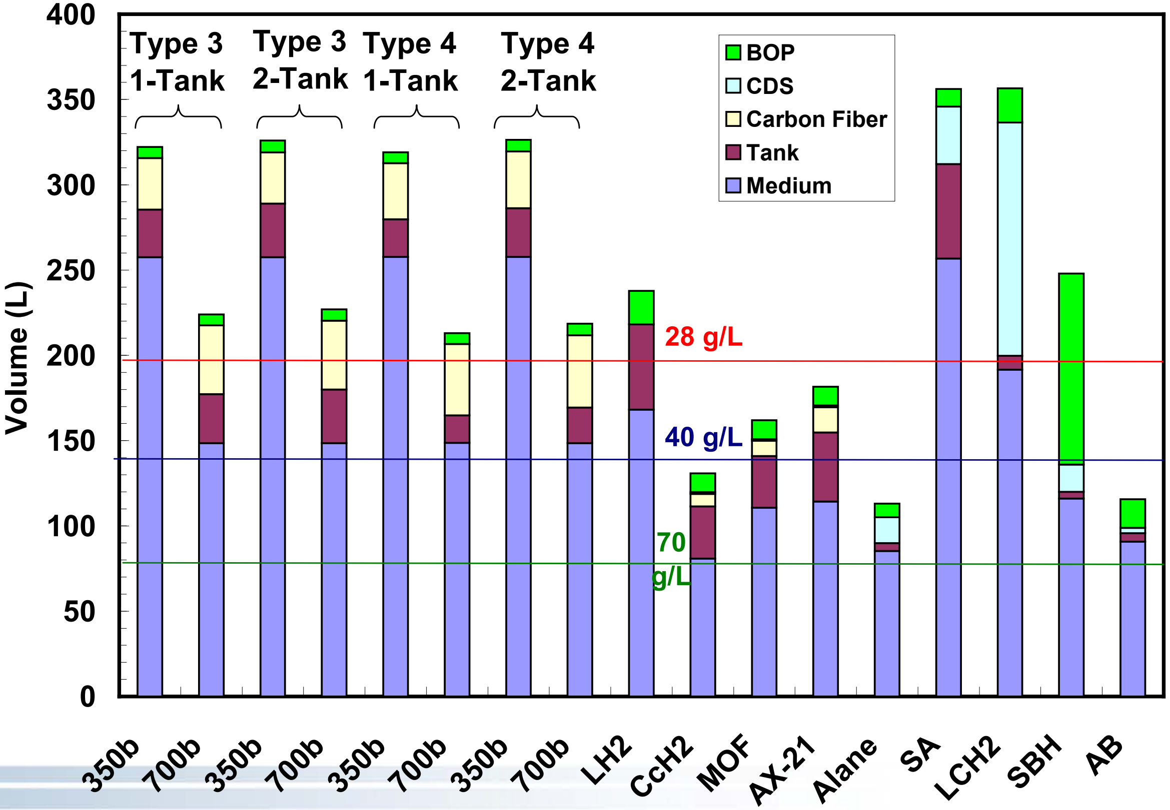
- 350-bar cH_2, LH_2 & CcH_2 systems may meet 2015 gravimetric target
- CcH2 system with Al shell approaches the ultimate gravimetric target
- CF is the main contributor to the overall weight in cH_2 systems
- Metal liner is a heavy component in all Type-3 pressure vessels
- Medium weight dominates in metal hydride and chemical H_2 systems

cH_2: Compressed H_2
350b: 350 bar
700b: 700 bar
LH_2: Liquid H_2
CcH2: Cryo-compressed H_2
MOF: MOF-177
SA: $TiCl_3$ catalyzed $NaAlH_4$
LCH2: Organic liquid carrier
SBH: Alkaline $NaBH_4$ solution
AB: Ammonia borane



Volume Distribution

- CcH_2 system meets 2015 volumetric target but not ultimate target
- Medium volume significant in all options and, by itself, exceeds the 2015 system target in cH_2 systems
- Insulation volume important in cryogenic systems
- CDS in LCH2 is bulky because of highly endothermic reaction
- BOP in SBH (adiabatic reactor, exothermic release) is bulky because of condensers

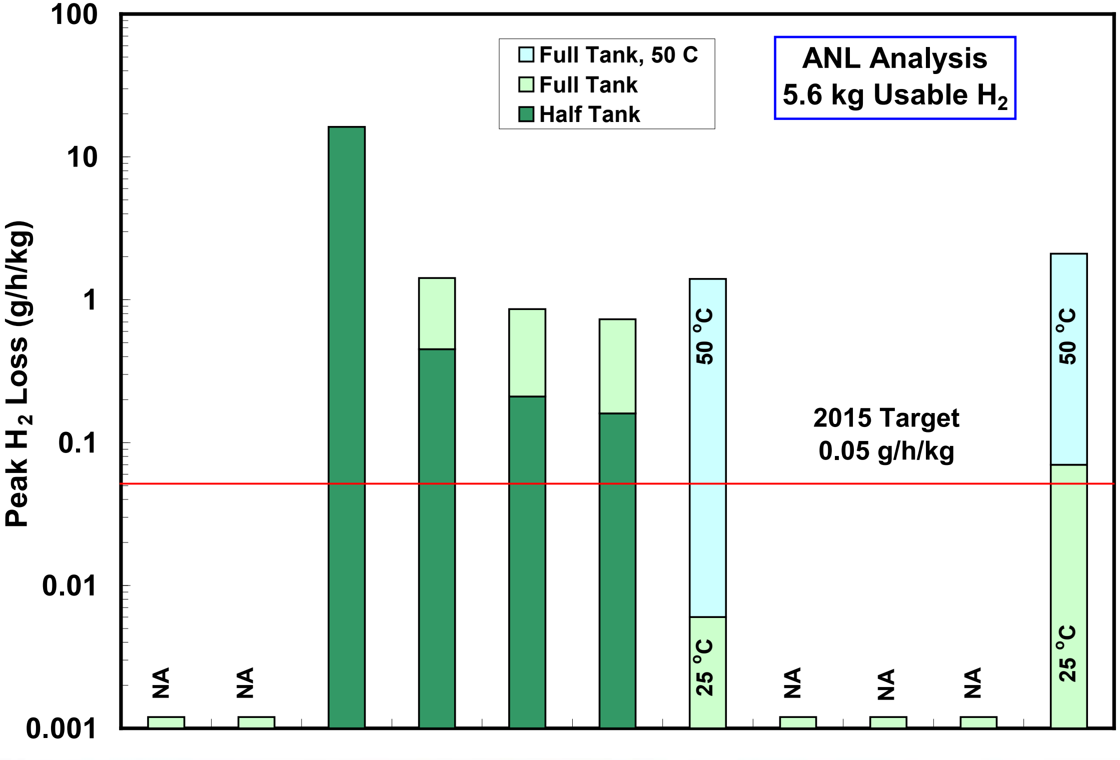


BOP: Balance of Plant

CDS: Charge-Discharge System

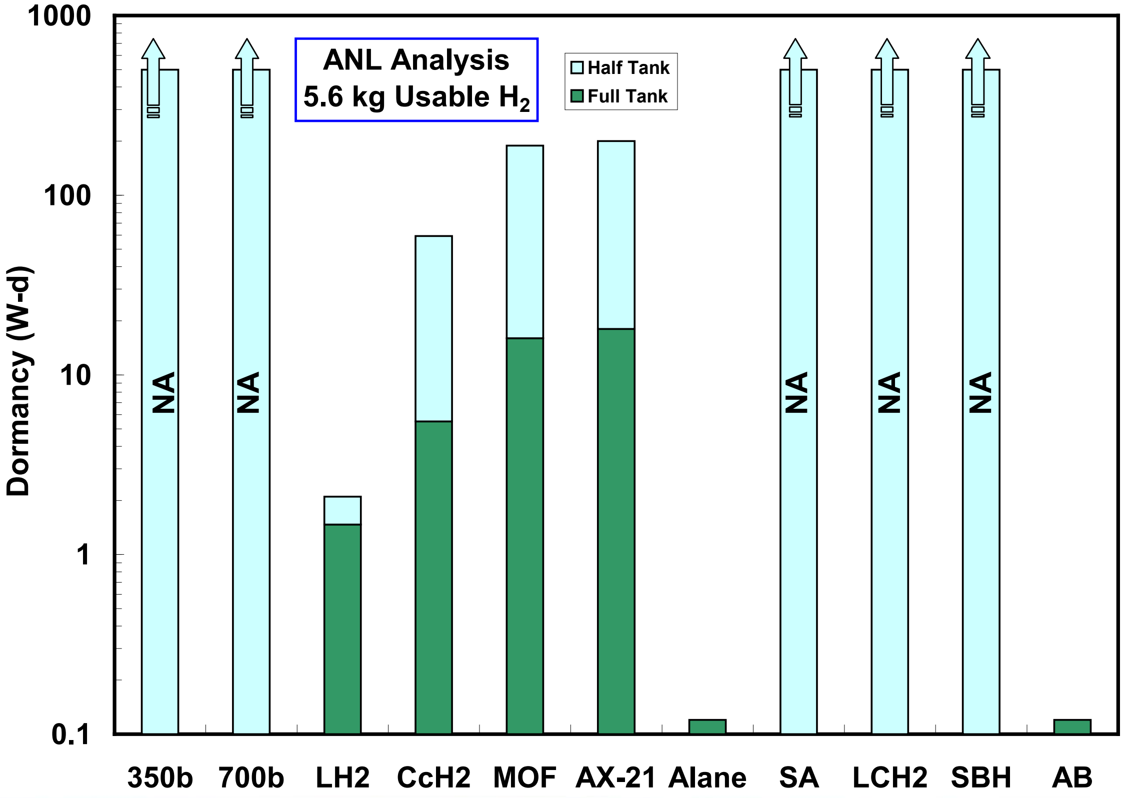
Hydrogen Loss During Extended Parking

- 40% of H_2 stored in LH_2 tank vented to ambient in a typical use cycle
- Negligible H_2 loss from insulated cryogenic pressure vessels with some daily driving
- H_2 loss from alane determined by kinetics and ambient temperature, not by heat transfer
- H_2 loss from AB/IL determined by kinetics, ambient temperature, and heat transfer coefficient



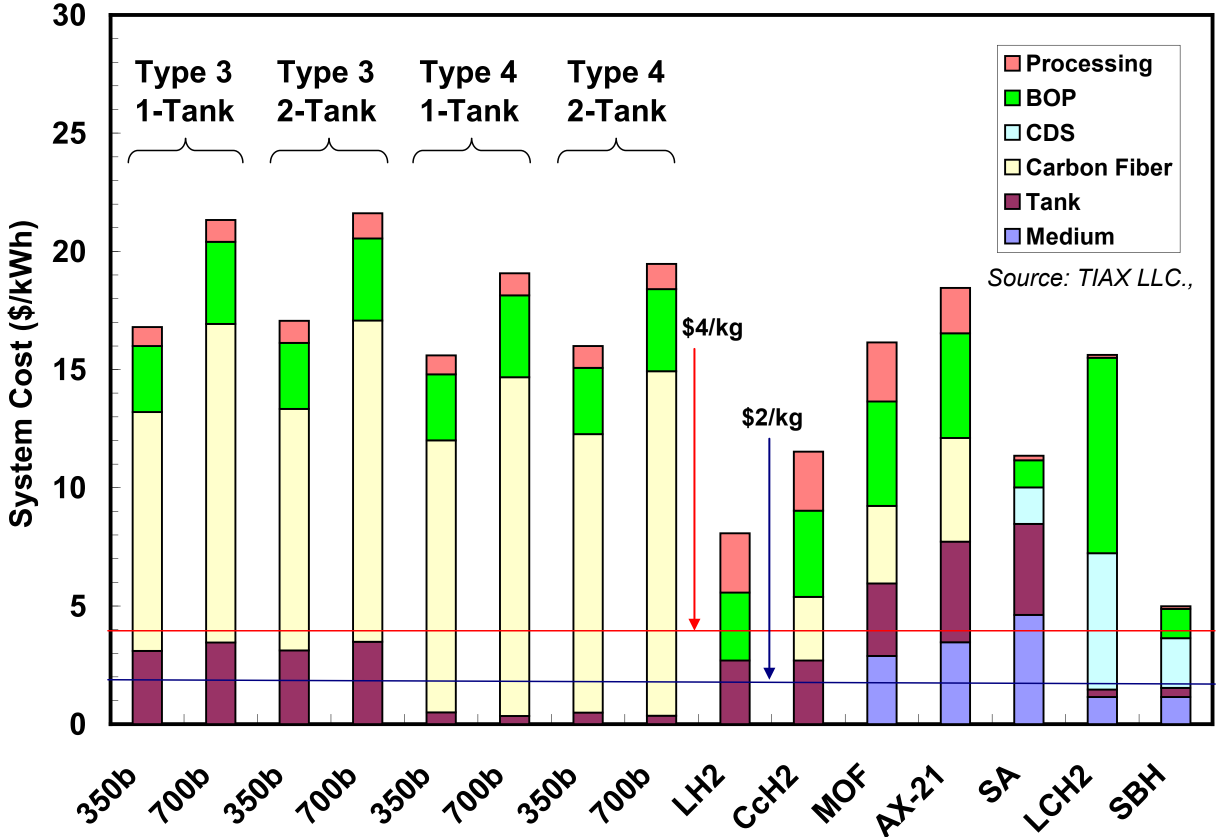
Dormancy

- Shorter dormancy in LH_2 system if the fuel tank is partially full
- Longer dormancy in CcH_2 system with partially-full tank, no stranded driver syndrome
- Longer dormancy in cryogenic sorbent systems than CcH_2 because of heat of desorption
- Dormancy definition not meaningful for alane and AB storage



Cost of On-Board Systems at High-Volume Manufacturing

- Cost data from TIAX studies with ANL inputs, 500,000 units/year
- Fiber cost dominates in cH_2 systems, less expensive in cryogenic sorption systems
- Material cost important in sorption systems and in SA system
- Dehydrogenation catalyst cost important in LCH2 system

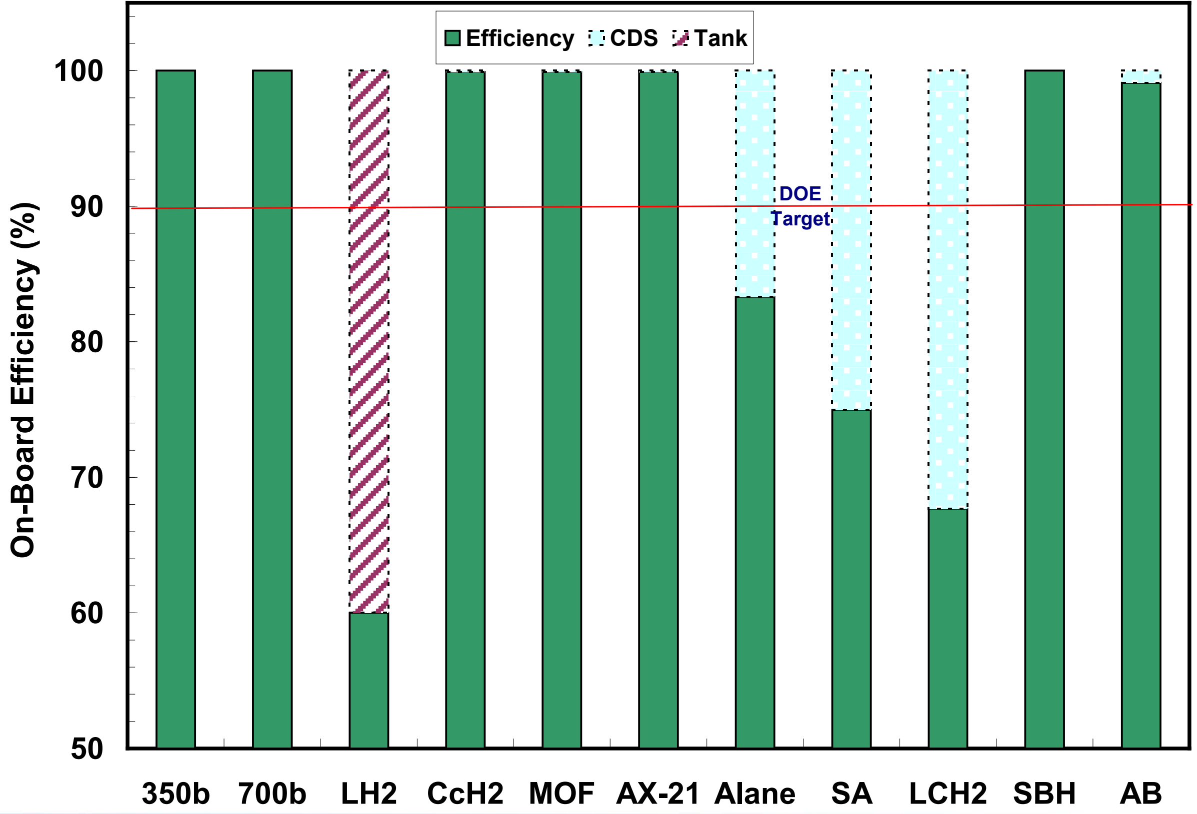


Source: TIAX LLC.,

Consult TIAX reports for complete details, assumptions and background

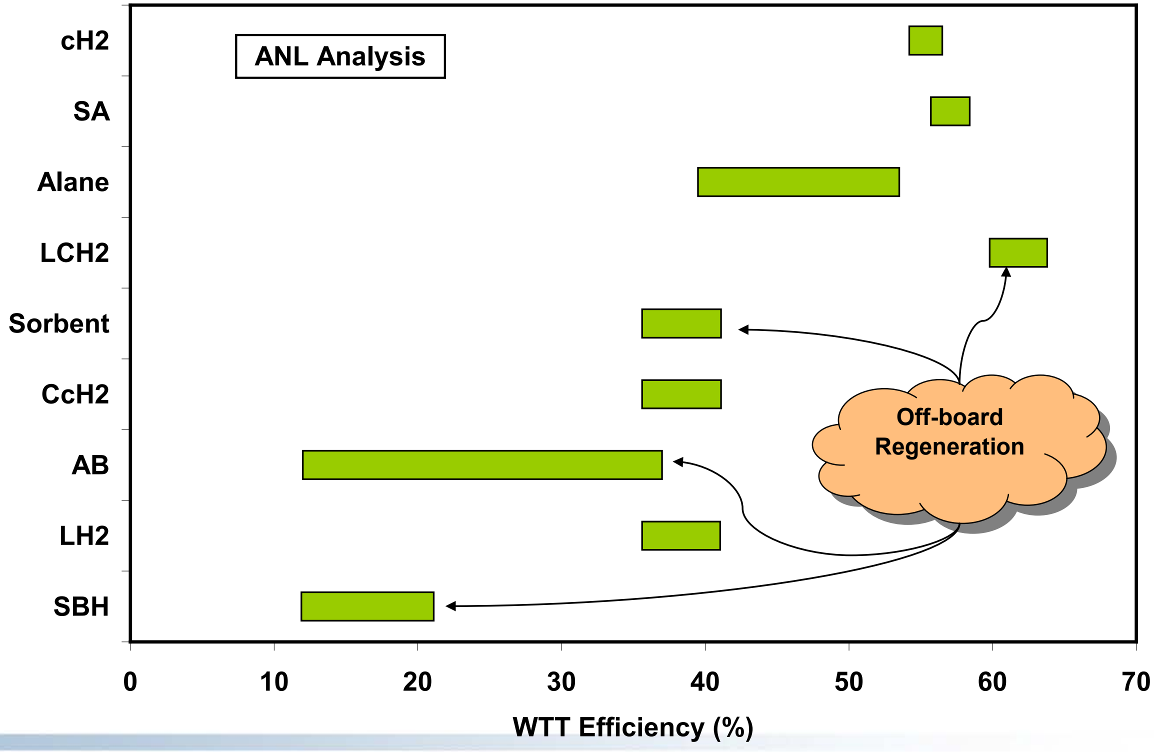
Efficiency of On-Board Systems

- Venting loss accounts for inefficiency of LH_2 system
- 10-30% H_2 consumed in alane, SA and LCH2 systems to sustain high-temperature endothermic reactions
- ~1% loss in AB system efficiency because of fuel pump, additional FCS coolant and radiator fan power
- DOE target for on-board system efficiency is 90%



Well-to-Tank Efficiency

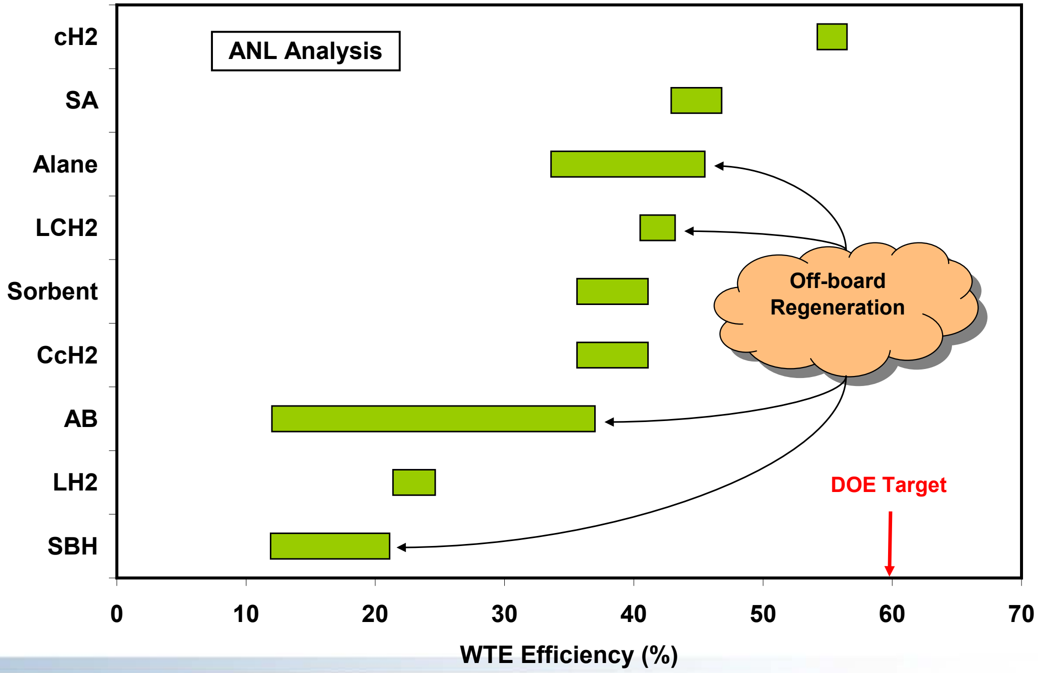
- 350- and 700-bar cH_2 options have <60% WTT efficiency
- Reversible metal hydrides may have higher WTT efficiency than cH_2
- LCH2 regeneration is exothermic and can reach 60% efficiency
- High uncertainty in alane regeneration efficiency because of vacuum distillation steps and low-grade waste heat requirement
- Options involving cryogenic H_2 have < 41% WTT efficiencies
- Low efficiencies for AB and SBH regeneration



Note: No-go decision was made on hydrolysis of SBH for on-board applications

Well-to-Engine Efficiency

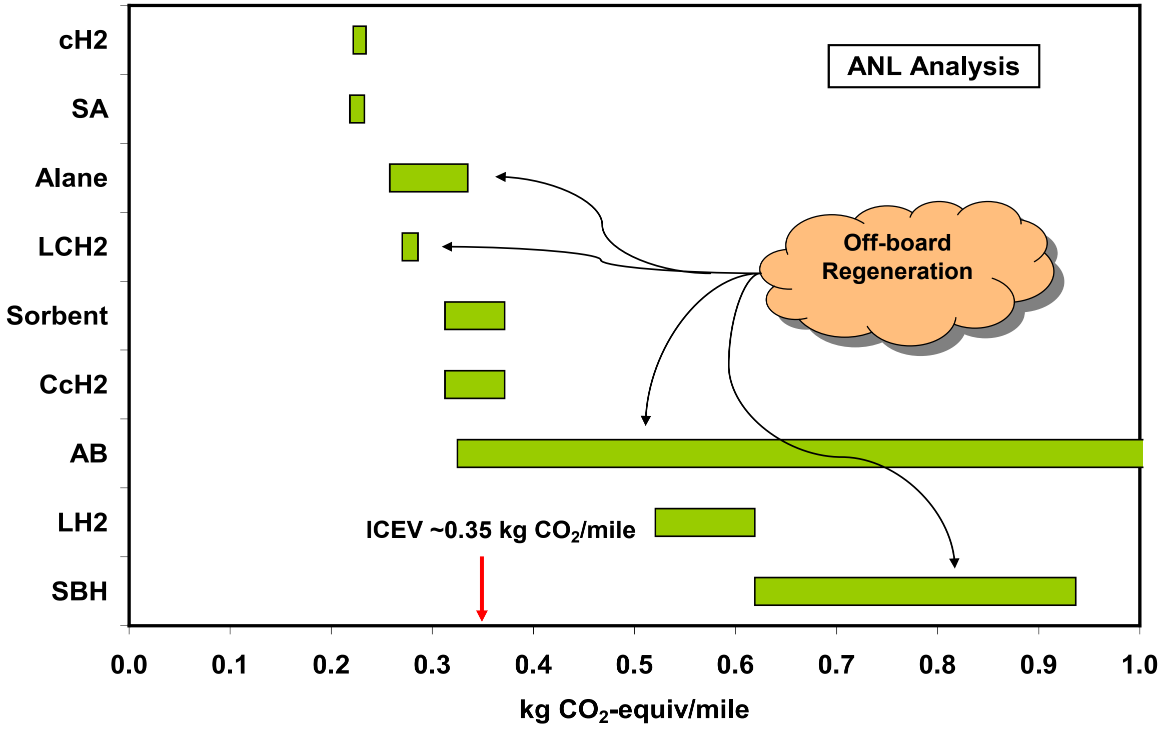
- Only cH_2 and CcH_2 have same WTT and WTE efficiencies
- Sorbent systems have nearly same WTT and WTE efficiencies
- Low WTE efficiencies for exothermic AB and SBH options because of off-board losses in regeneration
- Low WTE efficiencies for cryogenic options because of off-board losses in liquefaction
- WTE efficiencies <50% for endothermic SA and LCH2 options because of on-board losses



Note: No-go decision was made on hydrolysis of SBH for on-board applications

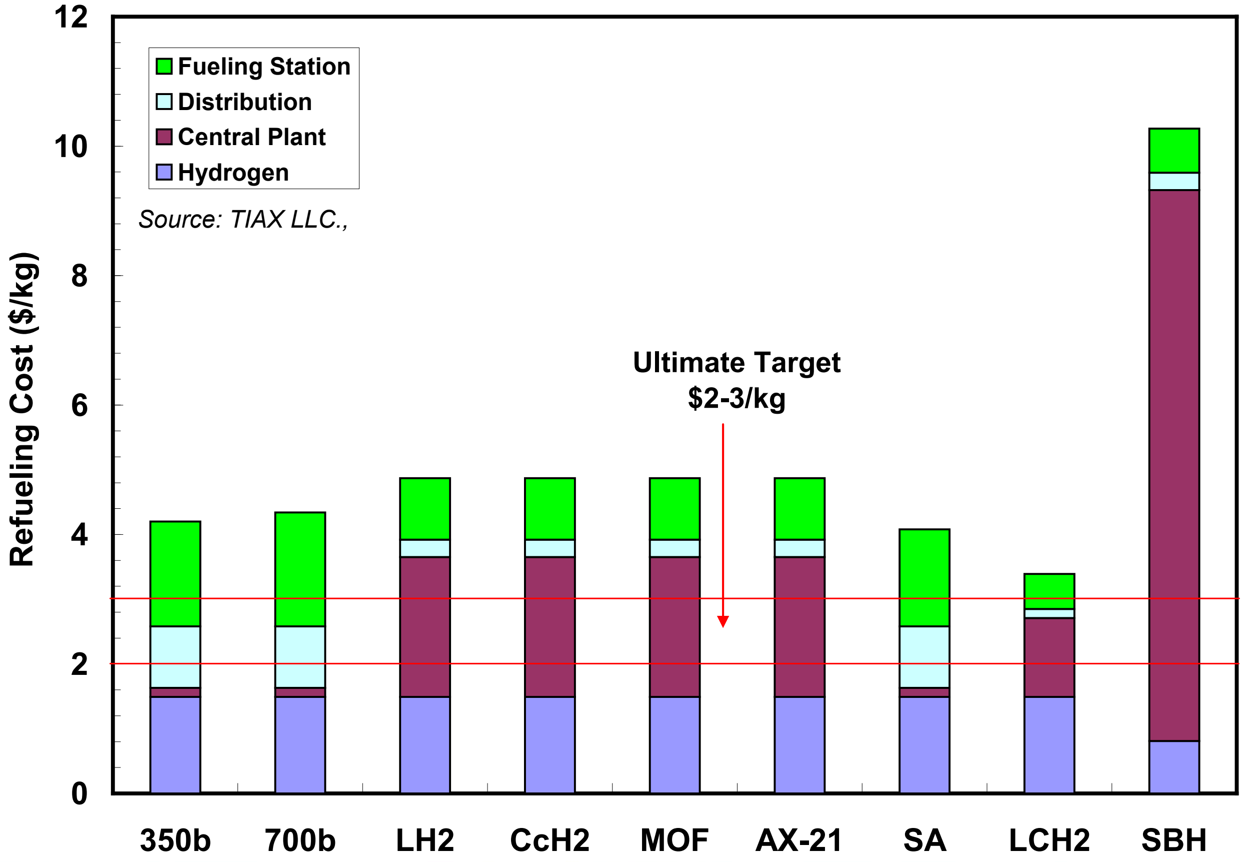
Greenhouse Gas Emissions

- Values given in kg of CO_2 equivalent per kg of H_2 delivered to the vehicle or per mile driven
  - 63.4 mpgge assumed fuel economy for 2015 advanced FC vehicle
- As reference, GHG emissions for 2015 mid-size ICE vehicle with 31 mpgge fuel economy is 0.35 kg-CO_2/mile



Refueling Cost

- H2A data for cost of unit operations, natural gas at \$0.22/Nm^3
- Liquefaction contributes significantly to the fuel cost in options requiring LH$_2$
- Regeneration is the main component of fuel cost in SBH option
- No storage option can meet the \$2-3/kg cost target (untaxed)



Source: TIAX LLC.,

Consult ANL and TIAX reports for complete details, assumptions and background