# System Level Analysis of Hydrogen Storage Options

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# Overview

## Timeline

- Project start date:  Oct 2009
- Project end date:   Sep 2014
- Percent complete:  20%

## Budget

- FY10:  $700 K
- FY09:  $960 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:  System Life-Cycle Assessments

## Partners/Interactions

- FreedomCAR and Fuel Partnership
- Storage Systems Analysis Working Group, MH COE, CH COE
- BMW, Caltech, Ford, GM, LANL, LLNL, TIAX, Lincoln Composites, SCI, UTC, and other industry

# Objectives and Relevance

- Perform independent systems analysis for DOE
  - Provide input for go/no-go decisions
- Provide results to CoEs for assessment of performance targets and goals
  - Address all aspects of on-board and off-board storage targets including capacity, charge/discharge rates, GHG emissions, safety, and cost
- 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 physical, complex metal hydride, sorbent, and chemical hydrogen storage systems
  - Select rigor of analysis to resolve system-level issues, conduct trade-off analysis and provide fundamental understanding of system/material behavior
- Calibrate, validate and evaluate models
- Work closely with the DOE Contractors, CoEs, Storage Tech Team, other developers, and Storage Systems Analysis Working Group (SSAWG)
- Assess improvements needed in materials properties and system configurations to achieve $H_2$ storage targets
- Organize monthly SSAWG calls and communicate results and discuss work plans

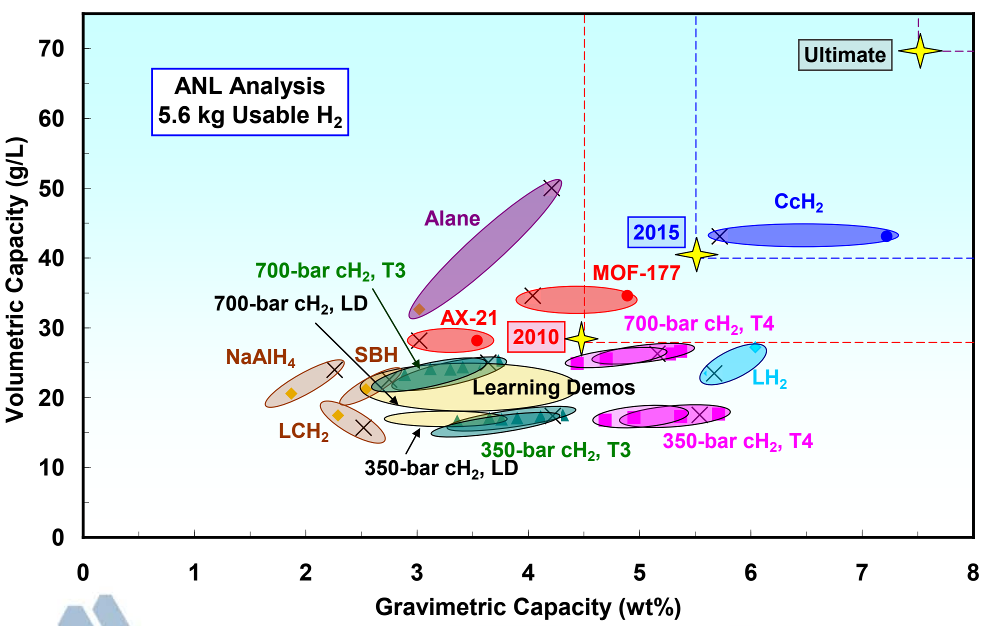
# Collaborations

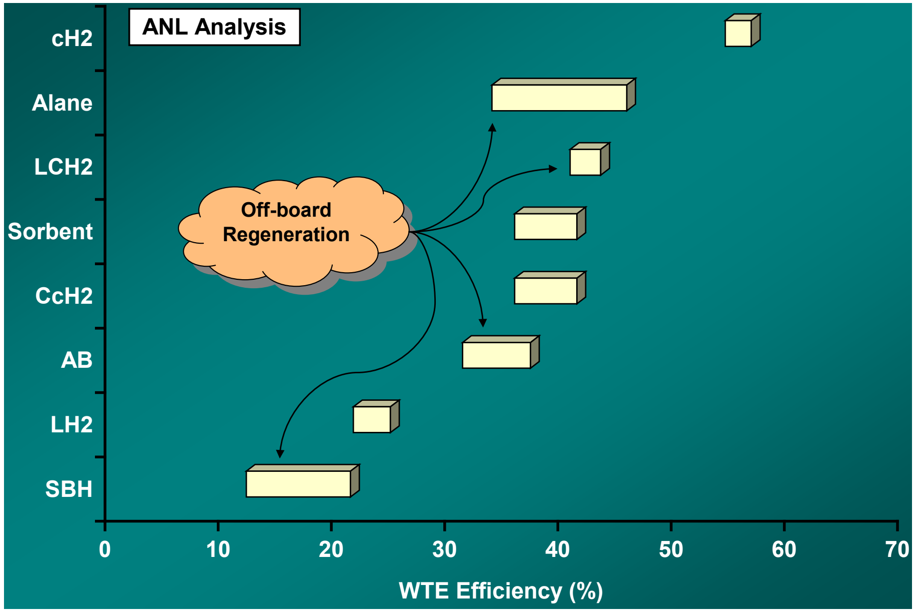
| | |
|---|---|
| cH2 | Lincoln Composites, Quantum, SCI |
| CcH2 | BMW, LLNL, SCI |
| Metal Hydrides | BNL, UH/UB, UTC |
| Chemical Hydrides | APCI, CHCoE (LANL/UPenn) |
| Sorbents | HSCoE (NREL), SWRI® |
| GHG Emissions | ANL (GREET) |
| Off-Board Regeneration | MHCoE (BNL, SRNL), CHCoE (LANL, PNNL) |
| Off-Board Cost | ANL (H2A Group), ANL (HDSAM) |
| On-Board Cost | TIAX |
| SSAWG | CHCoE, HSCoE, HSECoE, MHCoE, DOE, OEMs, Tank Manufactures,TIAX |

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

# Technical Accomplishments

- Systems analyzed or updated in FY2010
  - Physical storage: cH2, CcH2, LH2
  - Sorption storage: MOF-177, AC
  - Chemical storage: AB/IL
- Systems are at different stages of development and have been analyzed to different levels of sophistication
  - Results are constantly updated



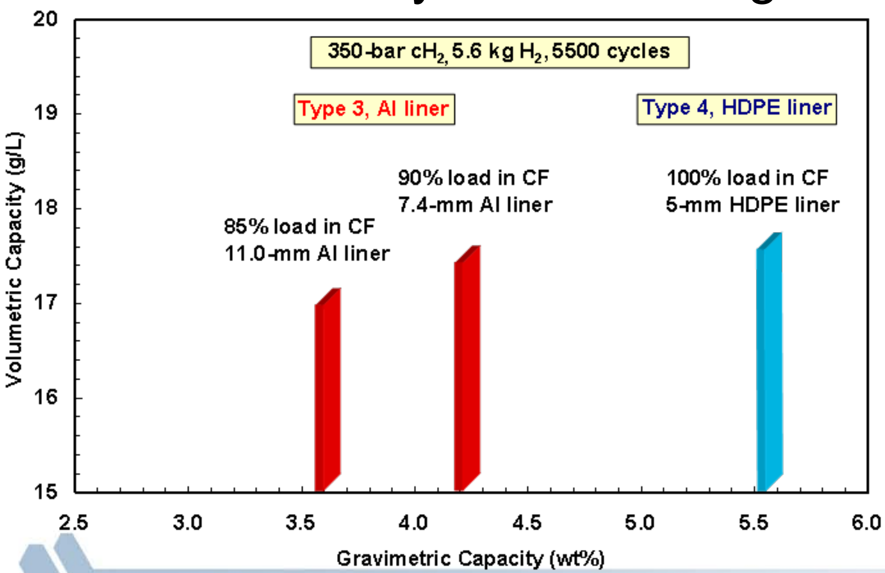



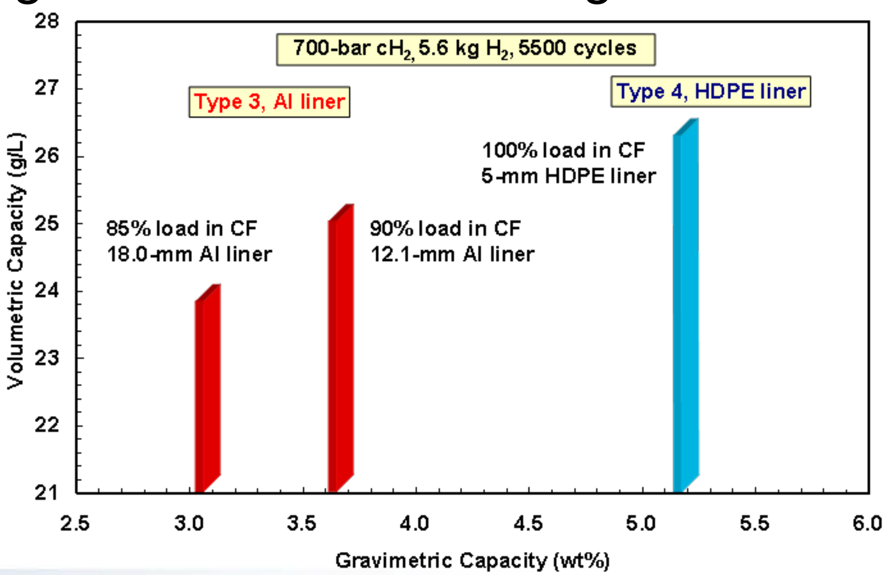
# System Analysis of Physical Storage Systems

- Benedict-Webb-Rubin equation of State: REFPROP coupled to GCtool
- Carbon Fiber Netting Analysis
  - Algorithm for optimal dome shape with geodesic winding pattern (i.e., along iso-tensoids)
  - Algorithm for geodesic and hoop windings in cylindrical section
- Fatigue Analysis of Type 3 Tanks
  - Algorithm for residual compressive stresses introduced by auto-frettage, pre- and post-proof load distribution between liner and CF
  - Unloading of residual stresses under cryogenic conditions
  - S/N curves for Al 6061-T6 alloy, non-zero mean stresses
  - 5500 pressure cycles at 1.25 NWP (SAE J2579)
- Dynamic models for gaseous/liquid refueling, discharge, dormancy
- Models for off-board analysis
  - FCHtool and GREET for greenhouse gas emissions
  - H2A for pathway analysis
  - HDSAM for scenario analysis

# Compressed $H_2$ Storage in Type 3 and Type 4 Tanks

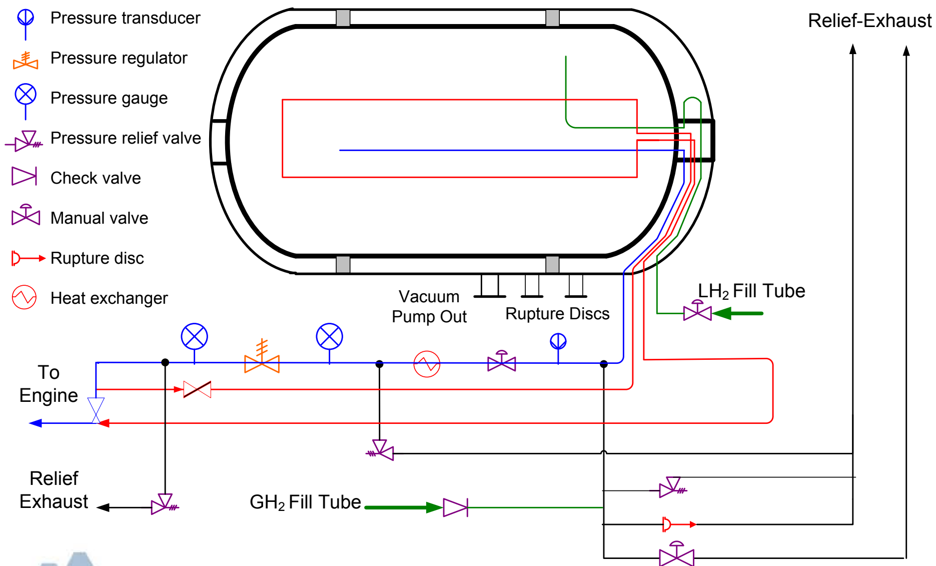
- Type 3 Tanks
  - For cost and weight reasons, shift the load to carbon fiber
  - Maximum load share in CF limited to 90% because of liner fatigue life and constraint on proof pressure
  - Type 3 tank may not be appropriate for service at 700 bar
- Type 4 Tanks (Single-tank design)
  - Higher volumetric but lower gravimetric capacity at 700 bar
  - CF requirement function of translation efficiency, safety factor and variability of fiber strength at high volume manufacturing

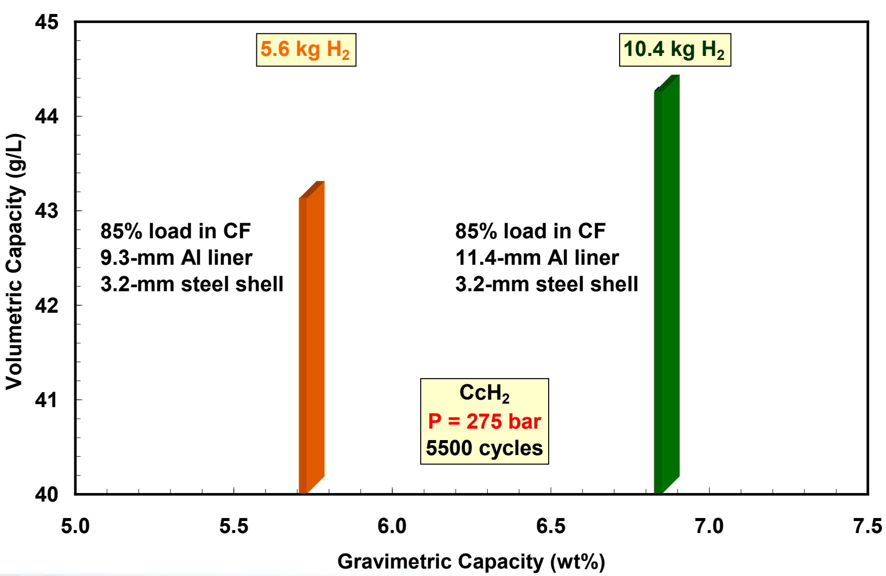


# Cryo-Compressed $H_2$ Storage

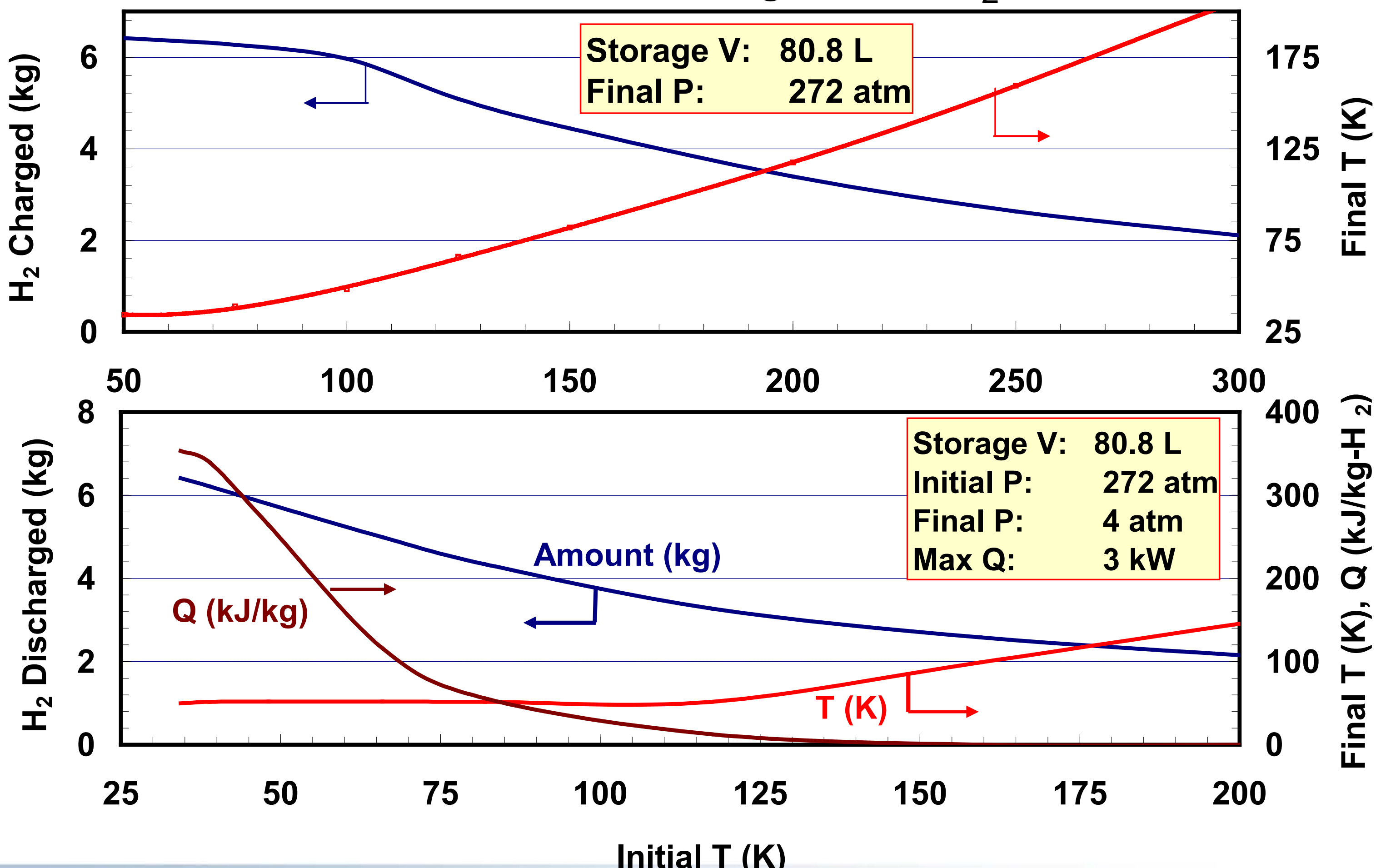
- LLNL Gen-3 System Configuration
  - Reduced insulation, Better packaging, Vacuum valve box eliminated
  - In-tank heat exchanger, 4000-psi pressure vessel rating
- Projected capacity of the scaled 5.6-kg system meets 2015 targets
  - Single vs. double flow nozzle, liquid $H_2$ pump
  - Gravimetric capacity > 9% with aluminum shell but higher cost
  - Maximum CF load share limited to 85% at cryogenic T, 276 bar



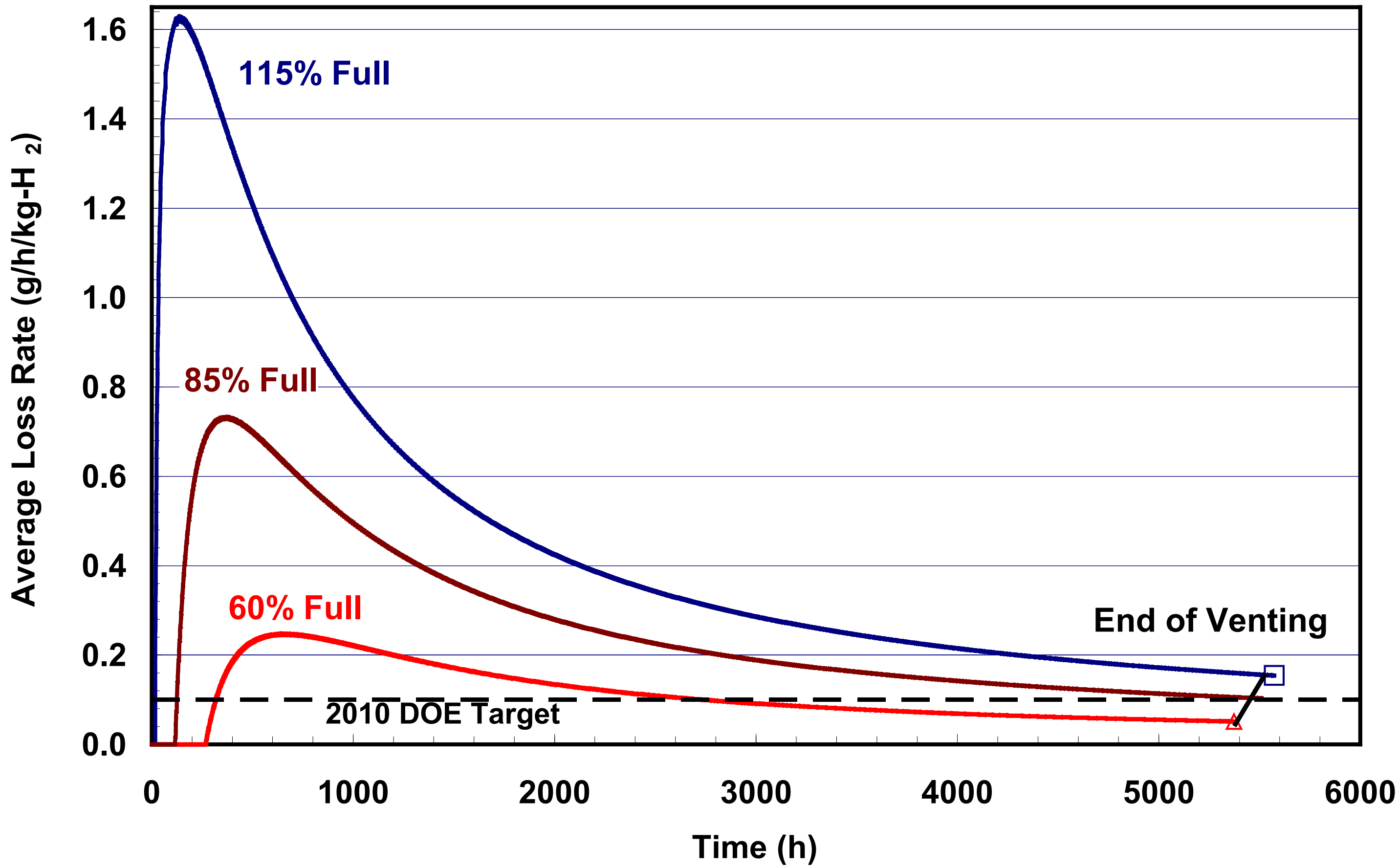
# Charge and Discharge Behavior

- Storage capacity is a function of initial temperature
  - Can store 6.4 kg usable $H_2$ (80.8 g/L) starting from 50 K, 4 atm
- Heat supplied during discharge to maintain 4-atm minimum P
  - 2.3 MJ for 34.3 K initial T, 6.4 kg stored $H_2$

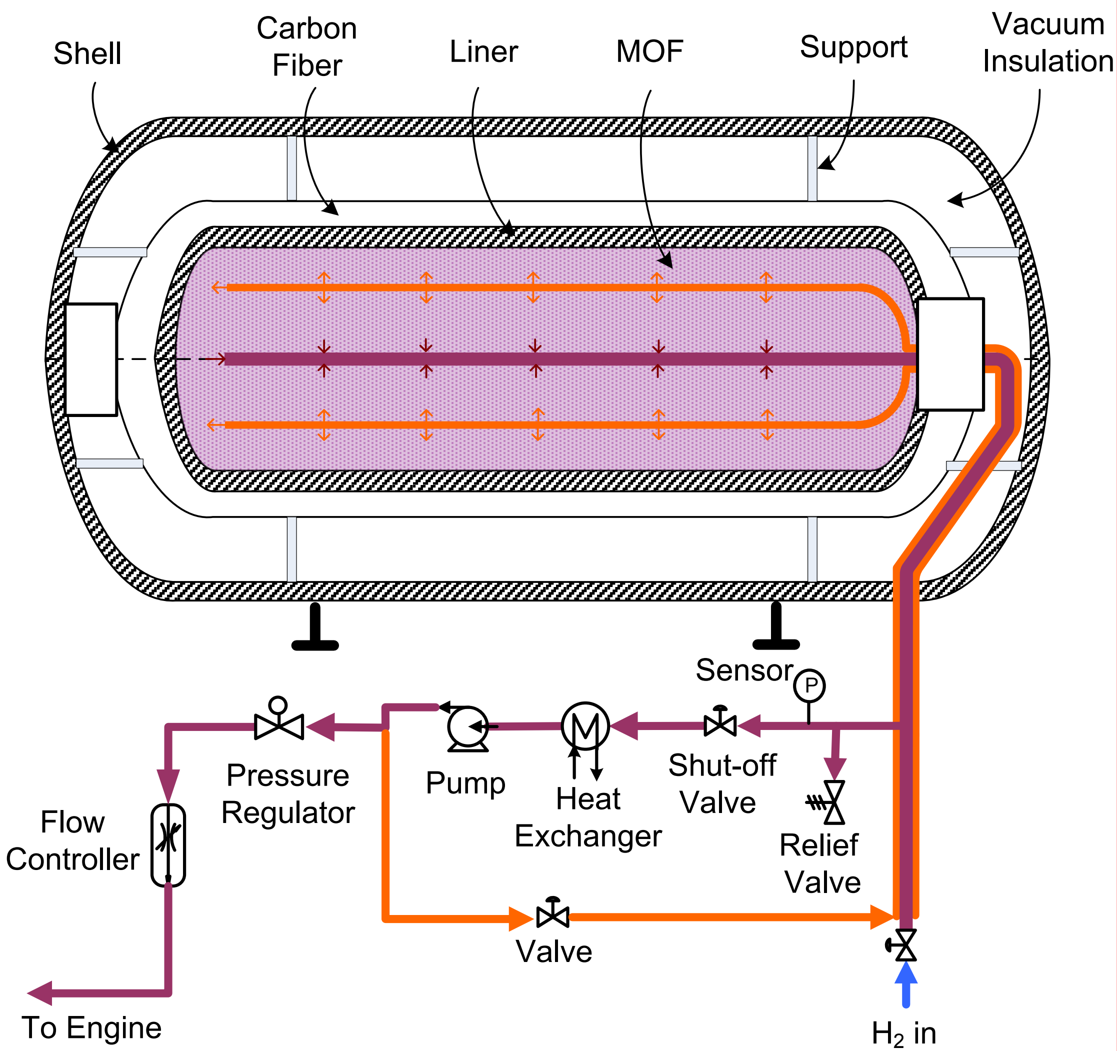


# Dormancy and Hydrogen Loss Rate

- No loss of hydrogen after tank reaches 323 K, tank 30% full
- Difficult to always meet the targets of 0.1/0.05 g/h/kg-$H_2$ with 5 W reference heat in-leakage rate
- No $H_2$ loss with minimal daily driving (LLNL work)



# Hydrogen Storage in Metal Organic Frameworks
# Adiabatic Liquid $H_2$ Refueling




## Key System Requirements

**Storage Medium**

- 5.6 kg recoverable $H_2$
- 4-bar minimum delivery P
- MOF-177, 0.6 packing fraction

**Type-3 Containment Vessel**

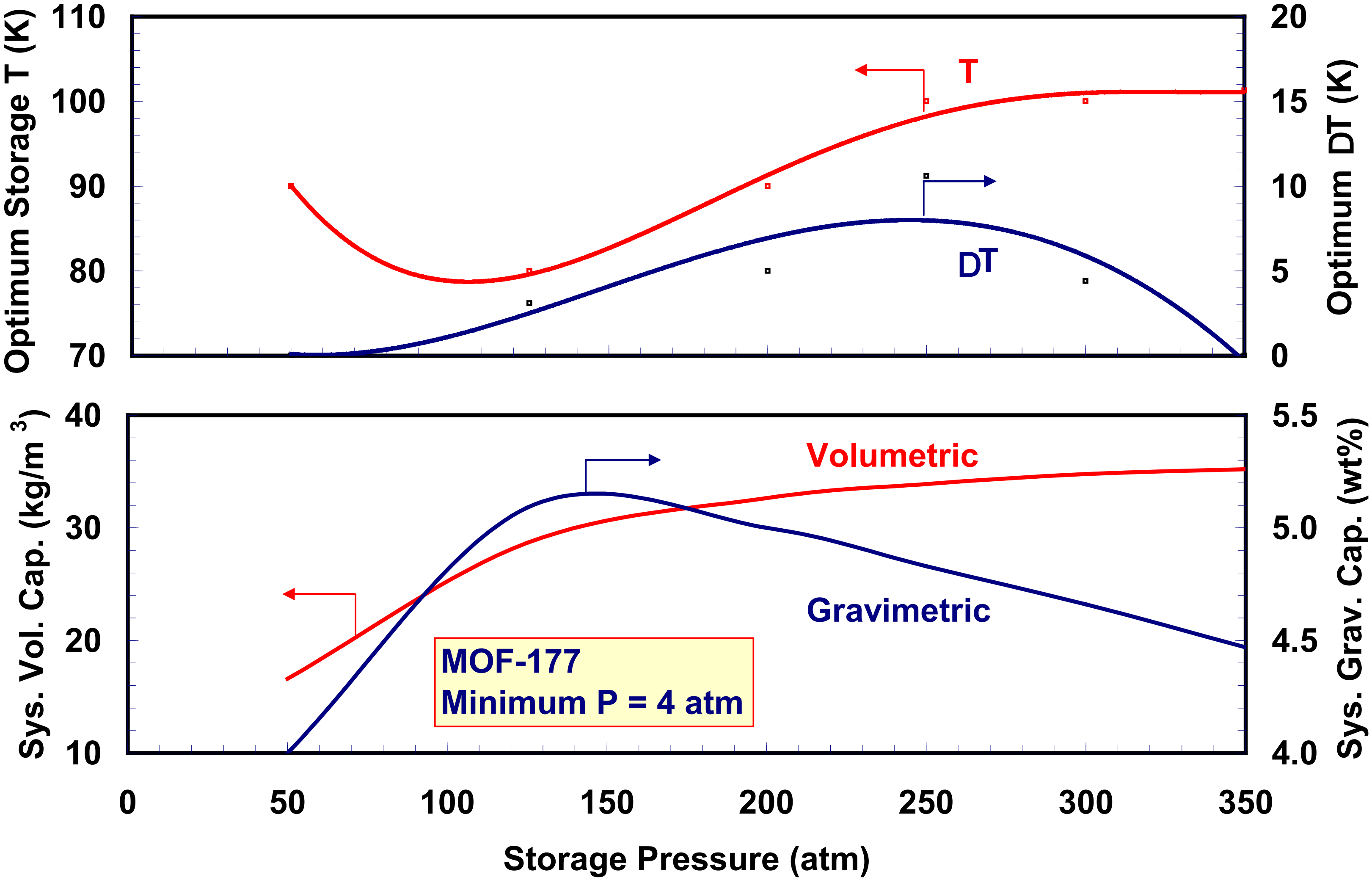
- 2.25 safety factor
- 5,500 P and T cycles
- Toray 2550 MPa CF
- Al 6061-T6 alloy liner

**Heat Transfer System**

- 1.5 kg/min $H_2$ refueling rate
- 1.6 g/s $H_2$ min flow rate
- 1.3 W radiative in-leakage

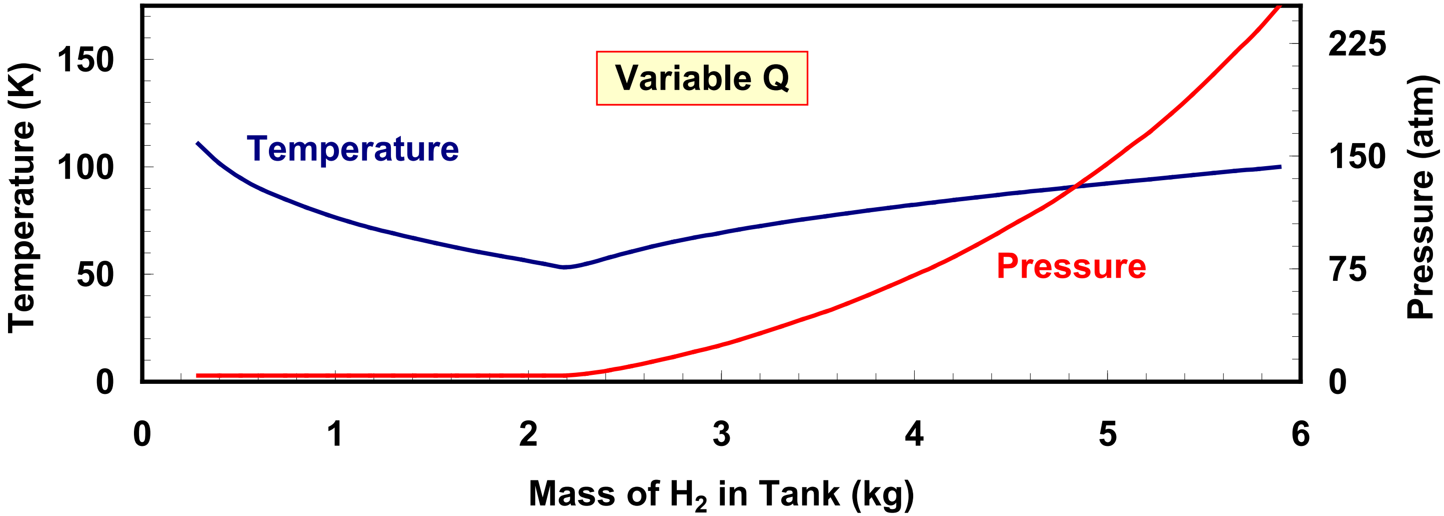
# System Storage Capacity – Optimum P & T

- System gravimetric capacity peaks at ~150 atm but the volumetric capacity increases slowly with storage pressure



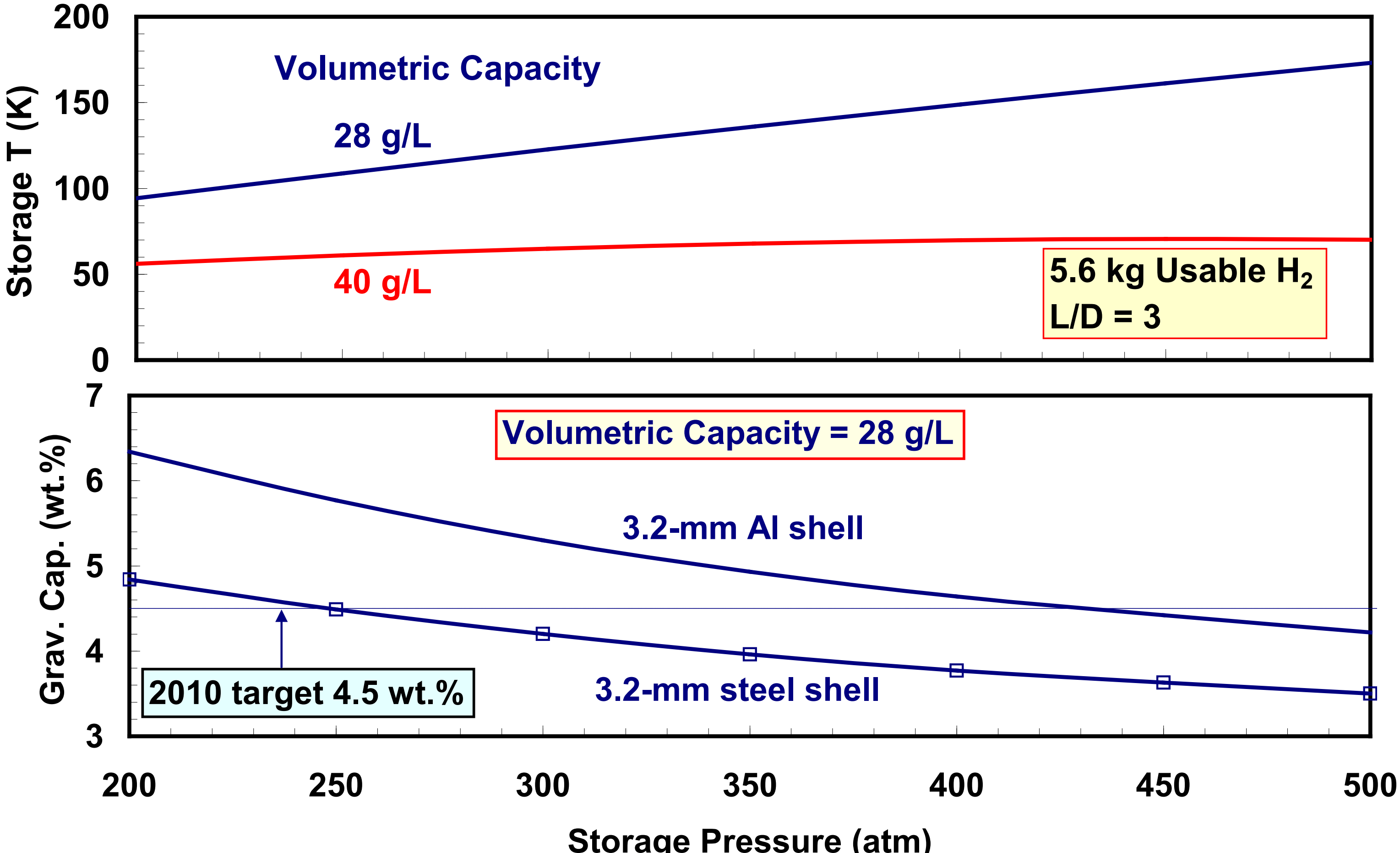
# Refueling/Discharge Dynamics and Dormancy

- Refueling: 7.1 MJ evaporative cooling load
  - 62% for $\Delta$H, 38% for sensible cooling and PV work
- Discharge options
  - Constant Q (1.2 kJ/g of $H_2$ discharged), 1.9 kW
  - Variable Q, heat supplied only if tank P < 4 atm, 6.3-kW peak Q
- Dormancy: Function of amount of $H_2$ stored and P/T at start of the event
  - Minimum dormancy is 16 W.d (2.8 days at 5 W in-leakage rate)
  - Peak $H_2$ vent rate is 1 g/h/W (4.8 g/h at 5 W in-leakage rate)



# Cold Gas Storage

- Gravimetric capacity suffers at high pressures and low temperatures
- At low pressures, liquid $H_2$ may be needed to reach the storage temperatures required for target volumetric capacity
- Difficult to match 2015 targets without liquid $H_2$ infrastructure



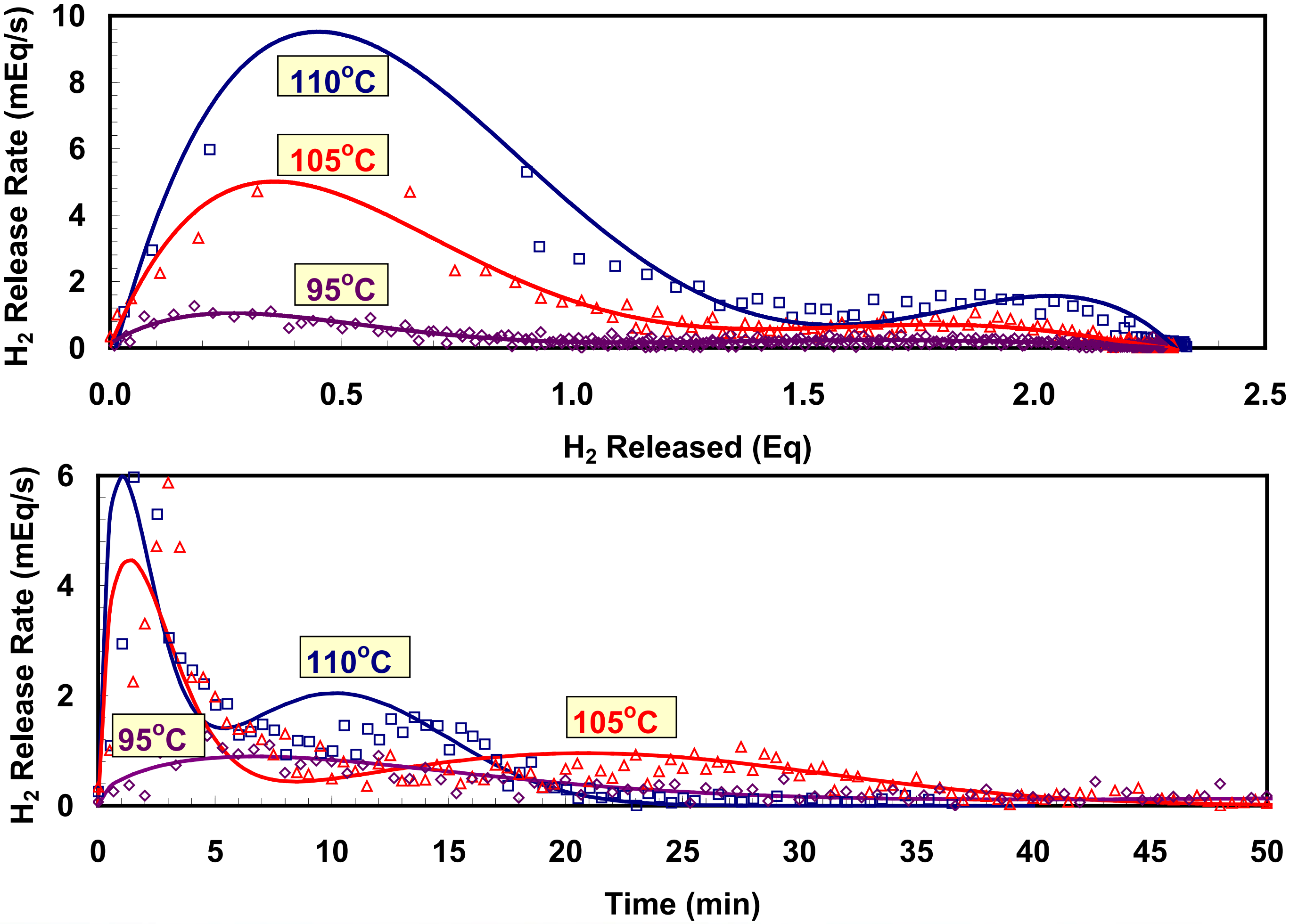
# Hydrogen Storage using Ammonia Borane in Ionic Liquids – Preliminary Results

- 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<br>150°C<br>>450°C | 1st $H_2$-equiv released, >1 h induction period for release at 85°C<br>2nd $H_2$-equiv released<br>3rd $H_2$-equiv released |
| DH | 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. |
| DH | kJ/mol-$H_2$ | 33 | Exothermic reaction |

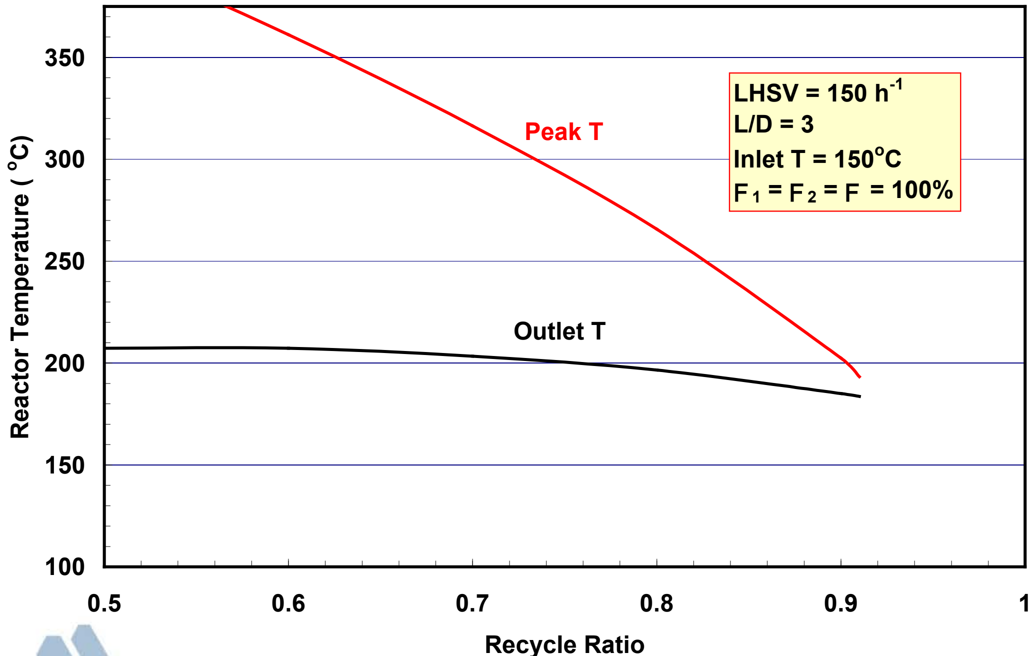
# Dehydrogenation Kinetics: 50:50-wt% AB in bmimCl

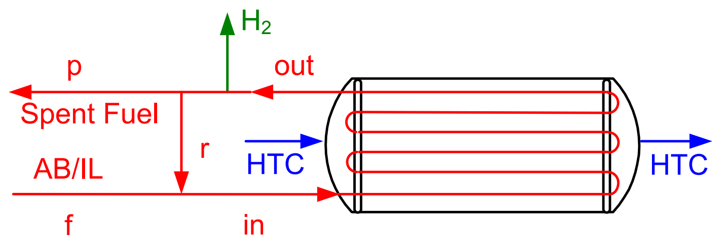
- Avrami-Erofeyev fits to rates derived from UPenn cumulative release data
- Need T > 150°C for 67 mEq/s average release rate if 2 $H_2$-equiv are to be released in 30 s, 120 $h^{-1}$ liquid hourly space velocity (LHSV)



# Dehydrogenation Reactor Performance

- Main challenge: control peak T and AB conversion using heat transfer and product recycle (R: recycle ratio)
  - Adiabatic T rise in excess of 500°C ($\Delta T_{ad} = 295 N_{H2}$)
- Difficult to control the peak temperature by heat transfer
- Inverse relationship between peak temperature and inlet temperature
- R < 0.95 for 100% conversion (2.2 $H_2$-Eq) at 150°C T,150 $h^{-1}$ LHSV
- R > 0.8 to limit maximum temperature to 250°C

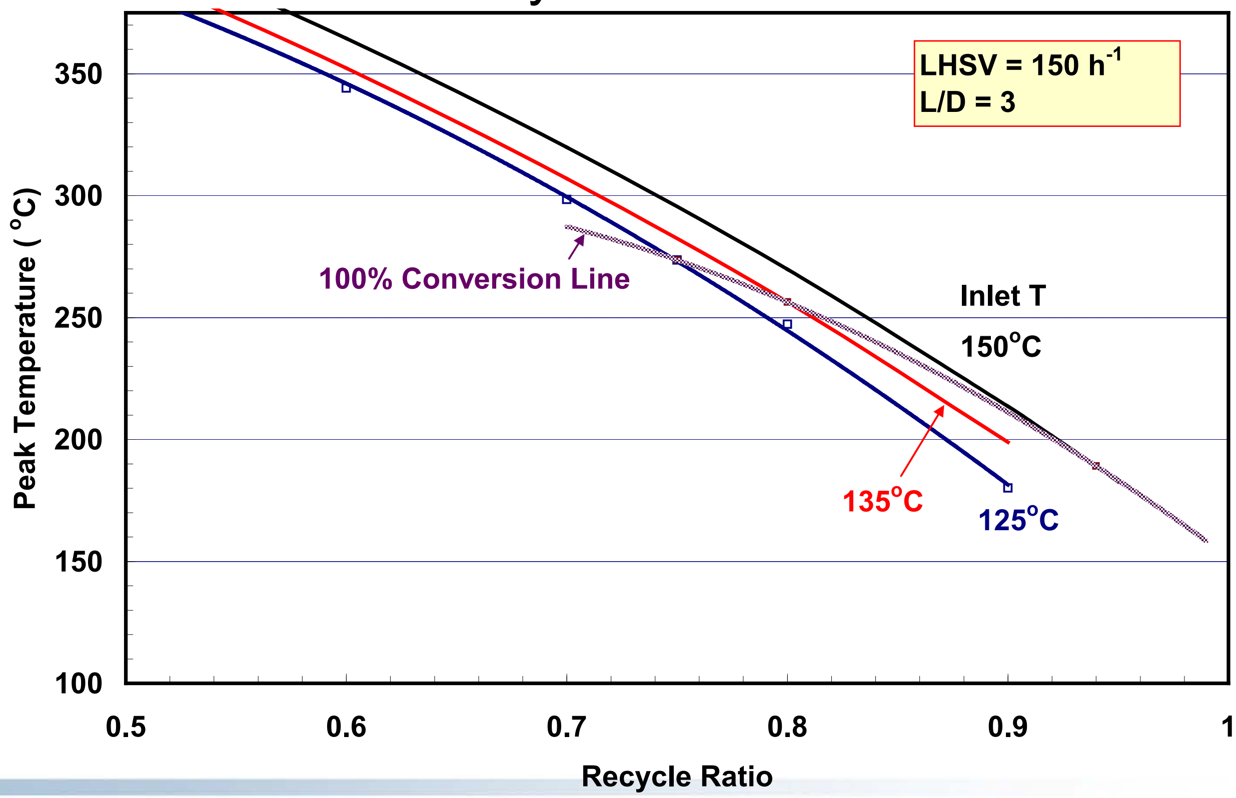



- AB flow rate adjusted for 1.6 g/s of $H_2$ at 100% conversion
- Coolant (ethylene glycol) flow rate adjusted for 10°C $\Delta T$ with 26.4 kW heat transfer

# Adiabatic Operation of Reactor

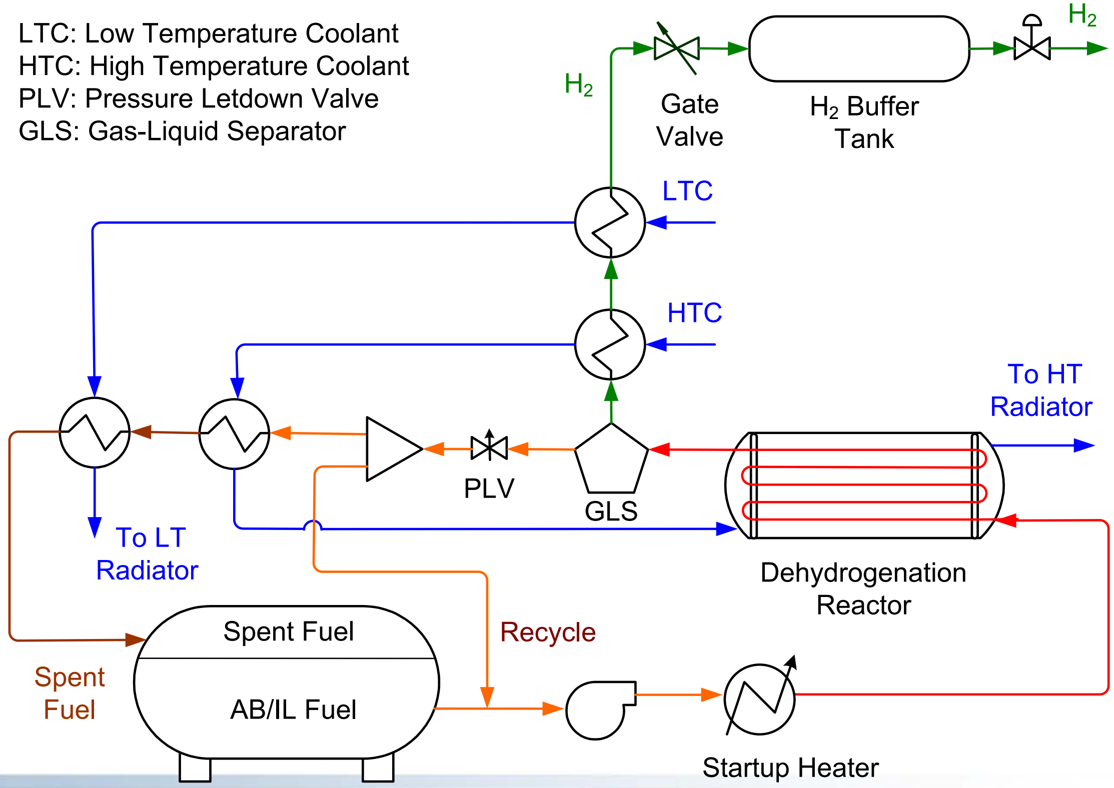
- The 100% conversion line determines the maximum recycle ratio as a function of the inlet temperature
- Lower peak temperature if the reactor is operated adiabatically: 275°C vs. >320°C with cooling (125°C inlet T)
- Simpler reactor design but 100% of the heat of reaction has to be removed elsewhere in the system



# On-board System Configuration

- 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 heater (electrical)

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



# 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
- Providing quantitative results for kinetics and thermodynamics of sorption & desorption and hydrogenation & dehydrogenation, usable & recoverable $H_2$, cyclic material behavior, on-board & off-board heat transfer, GHG emissions, regeneration pathways and efficiencies, and fuel and ownership cost

| Performance and Cost Metric | Units | cH2 350-bar | cH2 700-bar | LH2 | CcH2 | MOF-177 | 2010 Targets | 2015 Targets | Ultimate Targets |
|---|---|---|---|---|---|---|---|---|---|
| Usable Storage Capacity (Nominal) | kg-$H_2$ | 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 | | | |
| System Gravimetric Capacity | wt% | 5.5 | 5.2 | 5.6 | 5.5-9.2 | 4.0 | 4.5 | 5.5 | 7.5 |
| System Volumetric Capacity | kg-$H_2$/$m^3$ | 17.6 | 26.3 | 23.5 | 41.8-44.7 | 34.6 | 28 | 40 | 70 |
| Storage System Cost | $/kWh | 13.4 | 20 | TBD | 12 | 18 | 4 | 2 | TBD |
| Fuel Cost | $/gge | 4.2 | 4.3 | TBD | 4.80 | 4.6 | 2-3 | 2-3 | 2-3 |
| Cycle Life (1/4 tank to Full) | Cycles | NA | NA | NA | 5500 | 5500 | 1000 | 1500 | 1500 |
| Minimum Delivery Pressure, FC/ICE | atm | 4 | 4 | 4 | 3-4 | 4 | 4/35 | 3/35 | 3/35 |
| System Fill Rate | kg-$H_2$/min | 1.5-2 | 1.5-2 | 1.5-2 | 1.5-2 | 1.5-2 | 1.2 | 1.5 | 2.0 |
| Minimum Dormancy (Full Tank) | W-d | NA | NA | 2 | 4-30 | 2.8 | | | |
| $H_2$ Loss Rate (Maximum) | g/h/kg-$H_2$ | NA | NA | 8 | 0.2-1.6 | 0.9 | 0.1 | 0.05 | 0.05 |
| WTT Efficiency | % | 56.5 | 54.2 | 22.3 | 41.1 | 41.1 | 60 | 60 | 60 |
| GHG Emissions ($CO_2$ eq) | kg/kg-$H_2$ | 14.0 | 14.8 | TBD | 19.7 | 19.7 | | | |
| Ownership Cost | $/mile | 0.12 | 0.15 | TBD | 0.12 | 0.15 | | | |

# Future Work

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

Physical Storage

- Multi-tank compressed $H_2$ tank system
- Advanced cryo-compressed storage concepts

Metal Hydrides

- Update of alane slurry storage system analysis
- 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 (PNNL/LANL collaboration)
- Advanced reactor concepts for organic liquid carriers

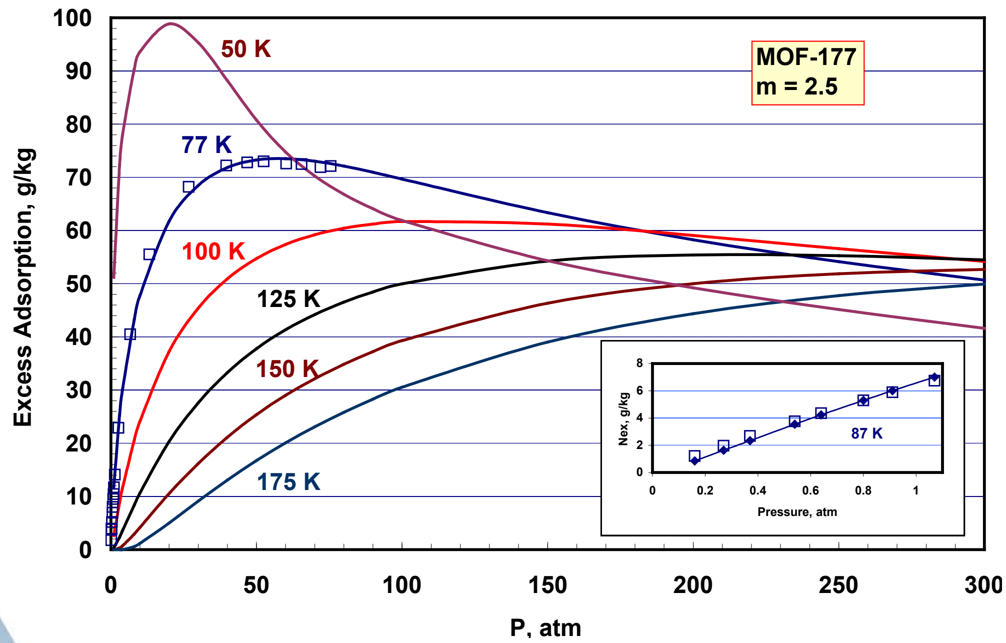
# Supplemental Slides

# On-Board Performance: Key Assumptions

| | Parameter | Reference Values |
|---|---|---|
| **Sorbent** | **MOF-177** | J. Mater. Chem., 2007, 17, 3197-3204 |
| | Skeletal density | 1534 kg/$m^3$ |
| | Crystallographic density | 427 kg/$m^3$ (1.56 $cm^3$/g pore volume) |
| | Bulk density | 256 kg/$m^3$ (0.6 packing fraction) |
| | Thermal conductivity | 0.3 W/m.K |
| **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 | $5.2\times10^{-4}$ W/m.K |
| **Tank** | **T700S Carbon Fiber** | Toray Carbon Fiber |
| | Tensile strength | 2550 MPa |
| | Density | 1600 kg/$m^3$ |
| | L/D | 2 |
| | Liner | Al 6061-T6 alloy, 5500 PT cycles, 125% NWP |
| | Shell | 3.2-mm thick Al 6061-T6 alloy |
| **Refueling** | **Adiabatic Refueling with $LH_2$** | |
| | Storage temperature | Function of storage pressure |
| | Temperature swing | Function of storage temperature |
| **Discharge** | **$H_2$ Recirculation** | |
| | Temperature rise | 150 K |
| | Recirculation rate | TBD |
| **System** | Miscellaneous weight | 16 kg |
| | Miscellaneous volume | 10 L |

# Modeled Hydrogen Adsorption Isotherms

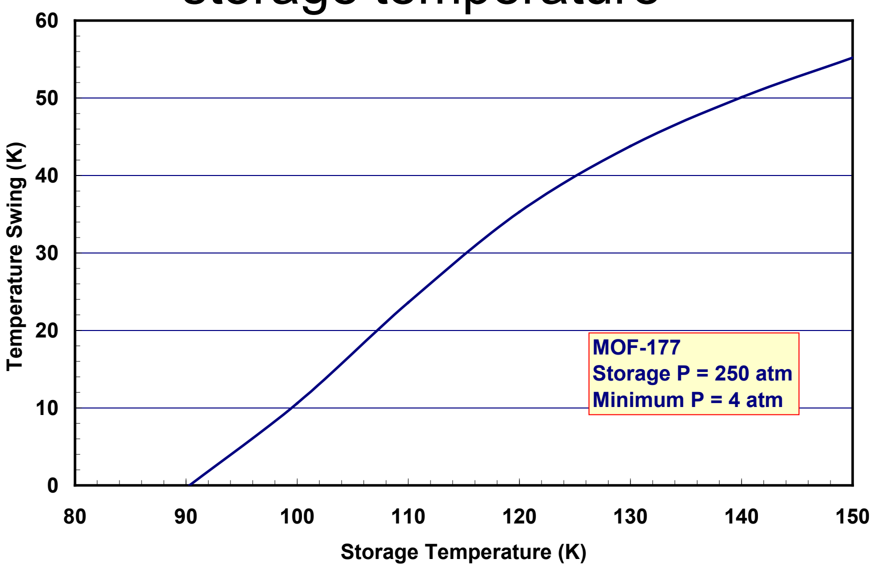
- H Furukawa, M Miller, M Yaghi (J. Mater. Chem. 2007, 3197 – 3204)
  - MOF-177, $Zn_4O$(1,3,5-benzenetribenzoate) crystals
  - Peak 75 g-$H_2$/kg surface excess at 77 K, 70 atm;110 g/kg absolute
- Low-T data fitted to Dubinin-Astakhov (D-A) isotherm with m=2.5
  - Derived $\Delta H_a$: 5.3 kJ/mol at $N_a/N_{a,max}$<<0.1, 2 kJ/mol at $N_a/N_{a,max}$=0.5
- Need temperature swing to release $H_2$ sorbed in MOF
  - At 4 atm, $N_{ex}/N_{ex,max}$=79% (50 K), 41% (77 K), 19% (100 K)

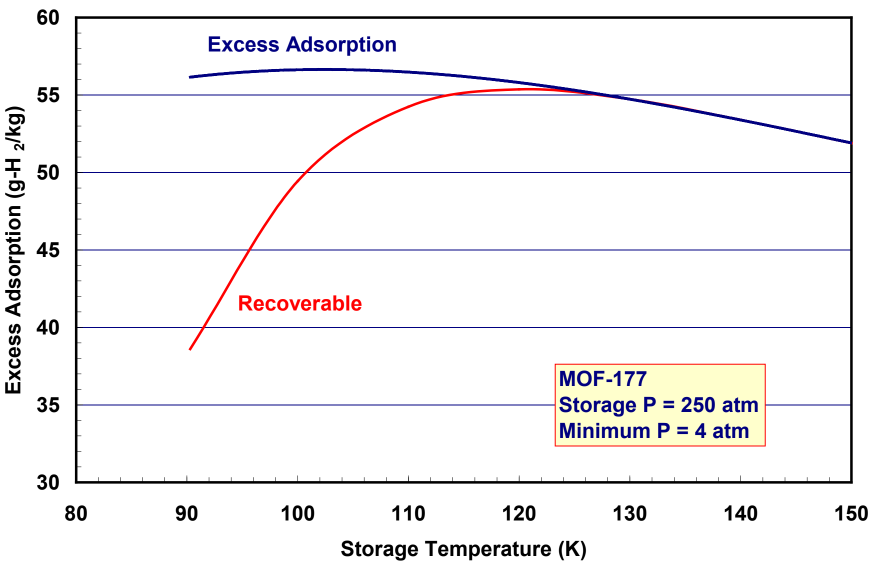



Modeled Uptake at 100 K
- 62 g-$H_2$/kg peak excess adsorption at 100 atm
- 101 g-$H_2$/kg peak absolute adsorption at 100 atm

# Adiabatic Refueling Option

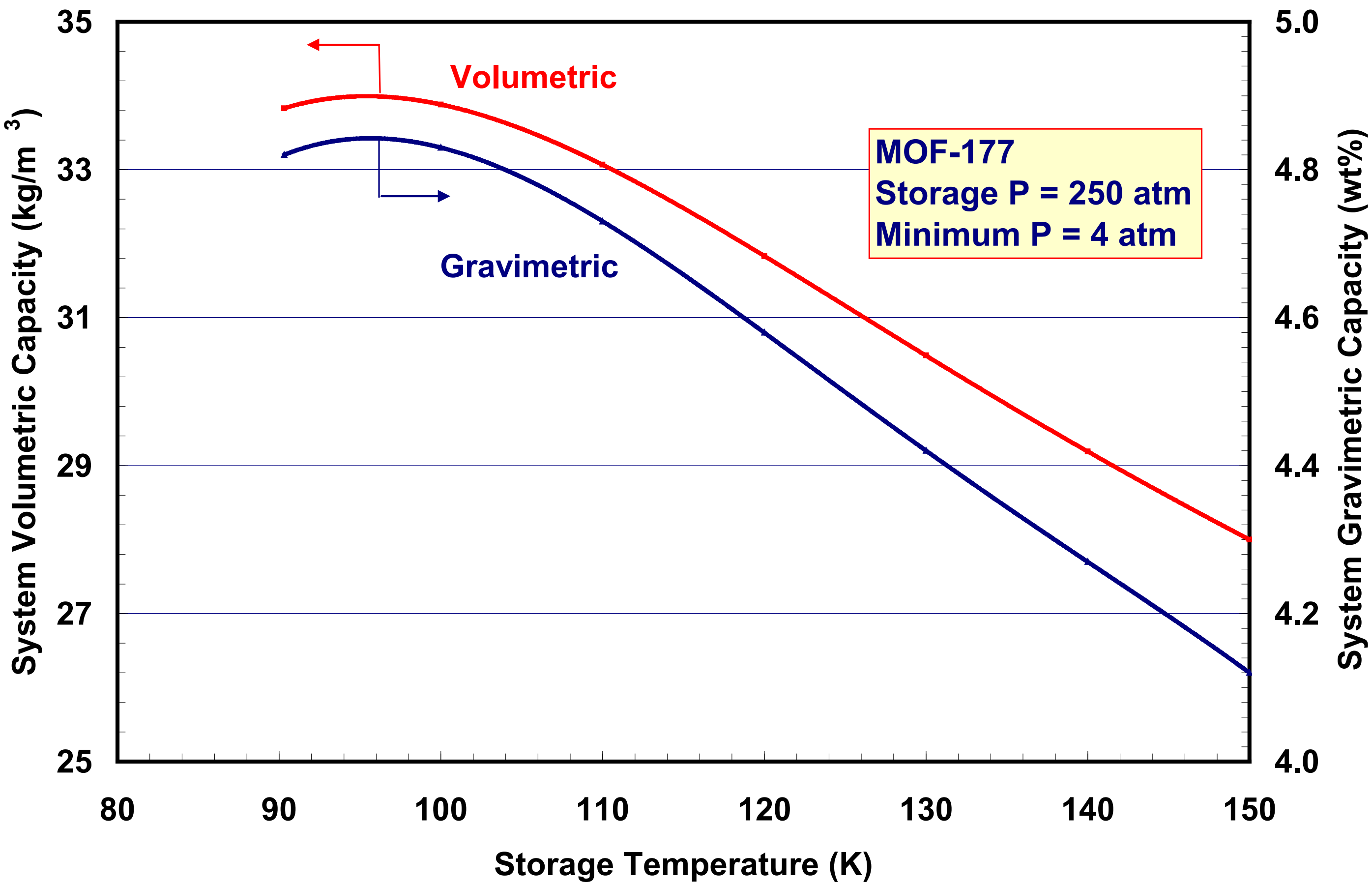
- Adiabatic refueling with $LH_2$
  - Hydrogen recirculated during discharge to provide the heat of desorption & $\Delta T$
- Optimum storage temperature (120 K) for maximum recoverable excess adsorption capacity
  - Allowable temperature swing increases with increase in storage temperature, $\Delta T = 0$ at 90 K
  - Excess adsorption capacity generally decreases with increase in storage temperature



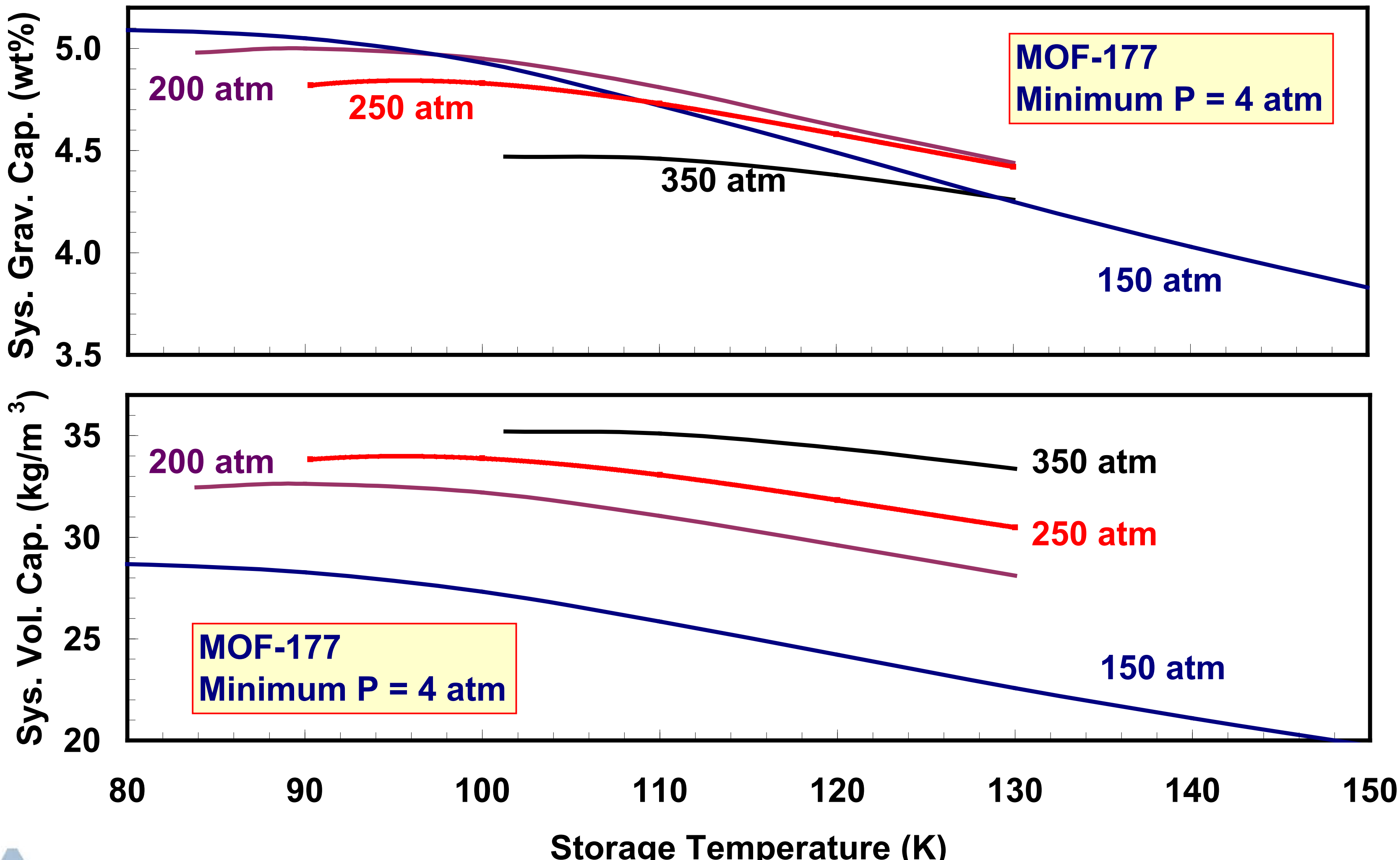
# System Storage Capacity - Optimum Temperature

- Optimum storage T (95 K) for maximum system capacity is lower than the T at which recoverable excess capacity is maximum
  - 4.8 wt% maximum system gravimetric capacity
  - 33.9 kg-$H_2$/$m^3$ maximum system volumetric capacity



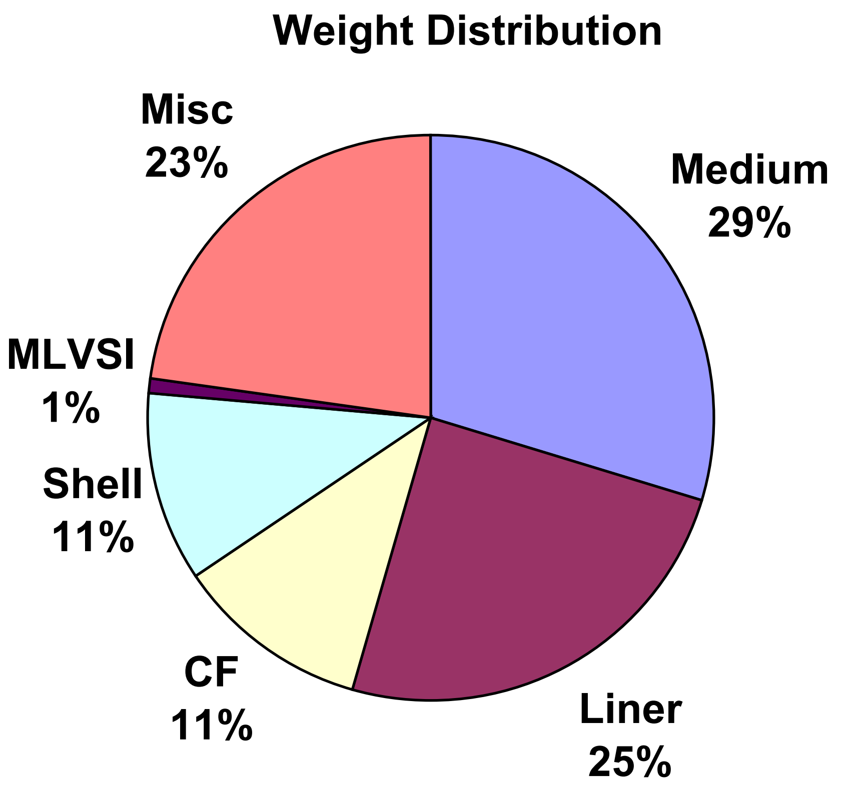
# System Storage Capacity – Optimum Pressure

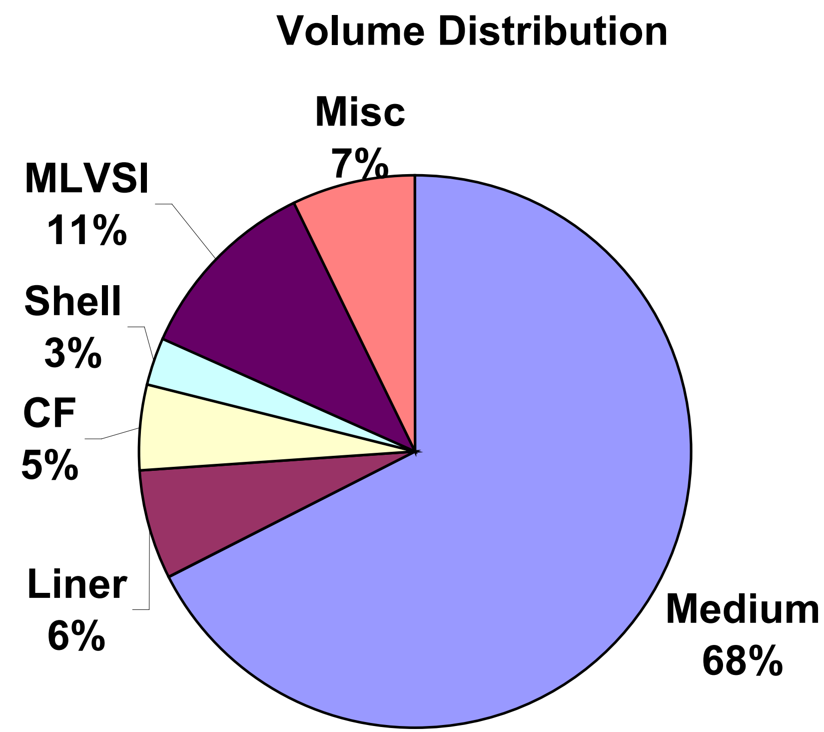
- Optimum storage temperature is a function of storage pressure
- Gravimetric capacity peaks at about 150 atm storage pressure



# Weight and Volume Distribution

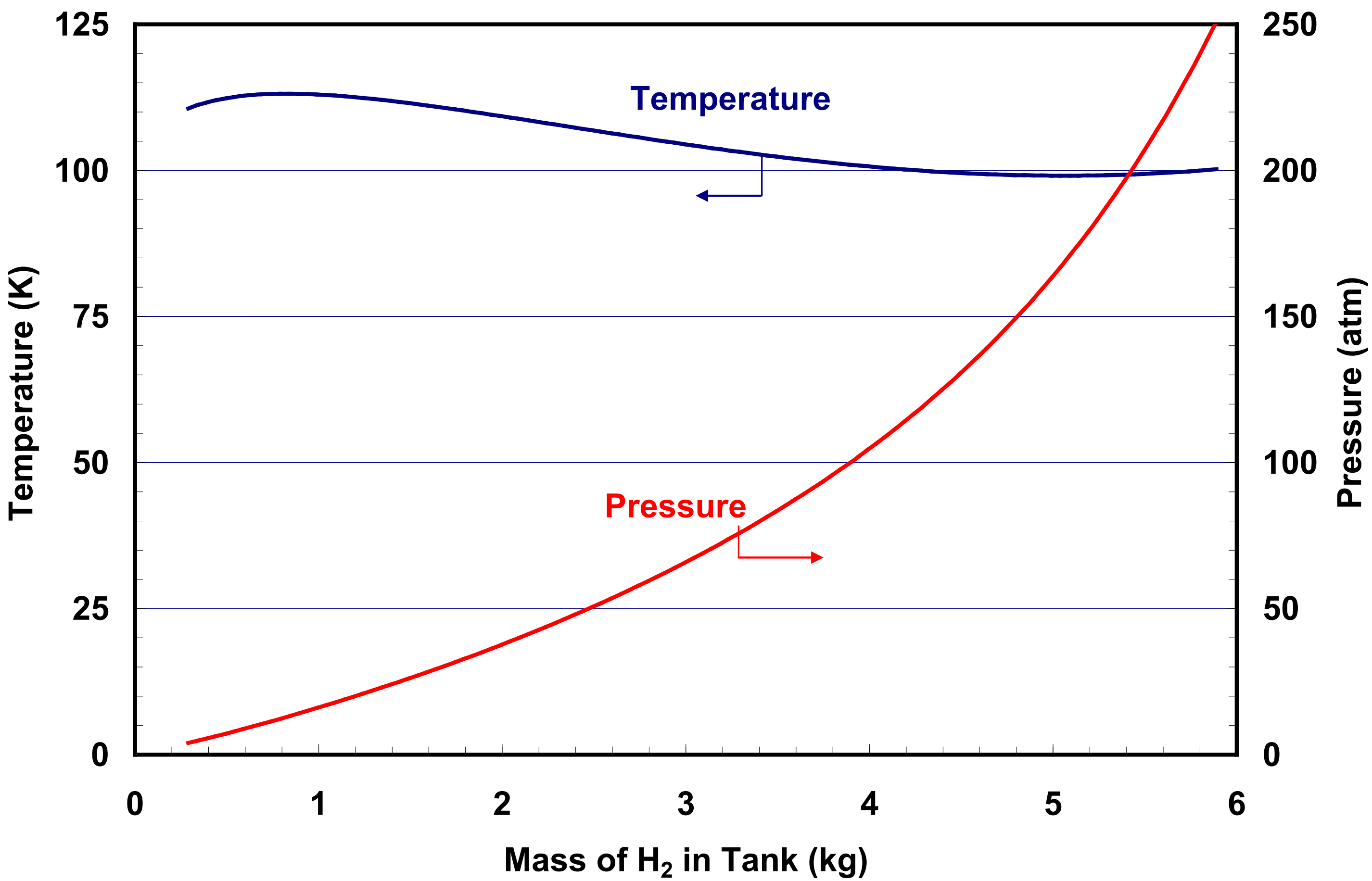
- 4.8-wt% gravimetric and 33.9 kg/m$^3$ volumetric capacity at 250 atm
  - Medium and liner account for >50% the overall weight
  - 68% volumetric efficiency



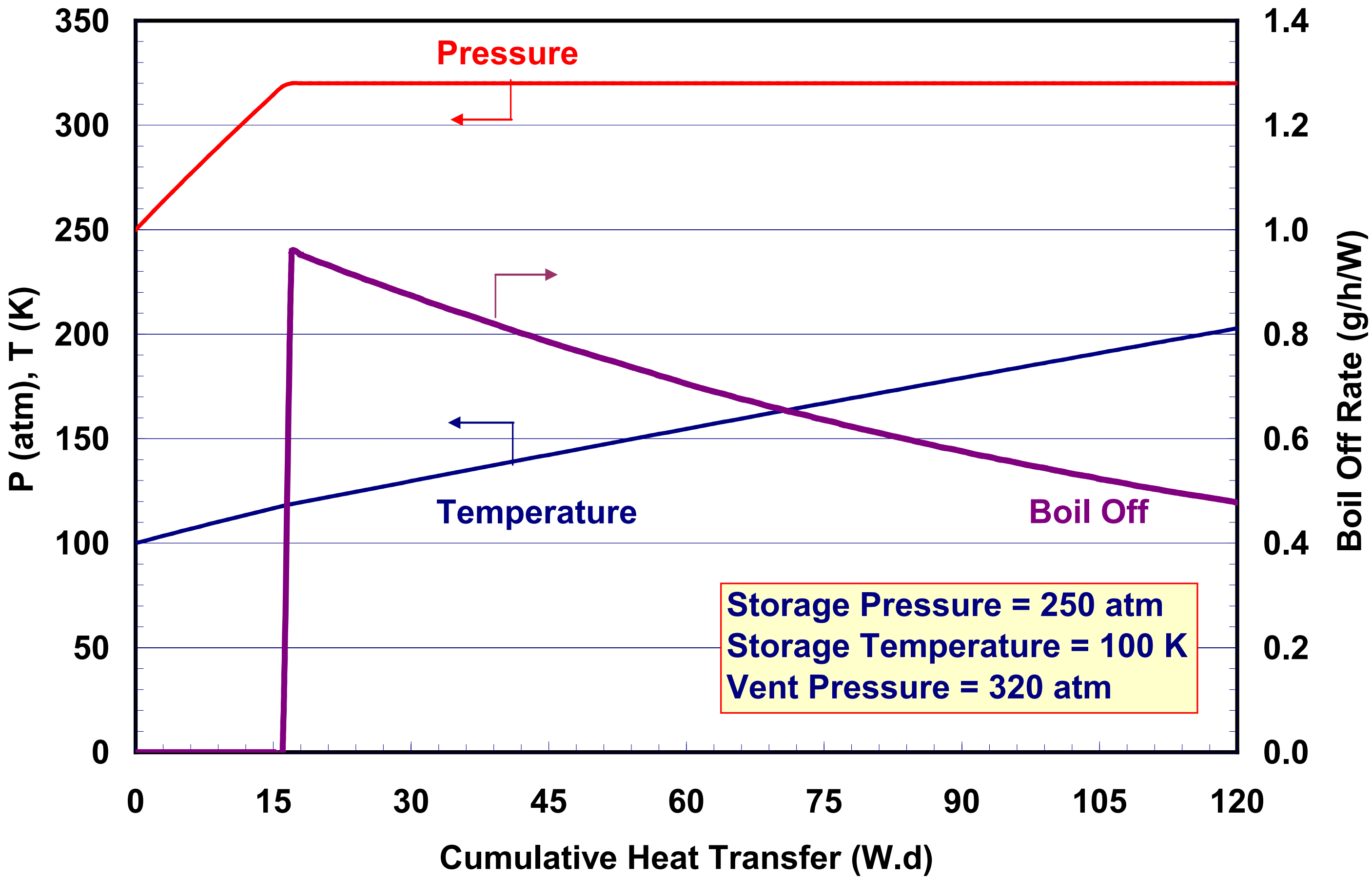
# Refueling Dynamics

- Evaporative cooling (7.1 MJ cooling load)
  - 62% of the cooling duty is due to heat of adsorption
  - 38% is due to sensible cooling of active thermal mass and PV work



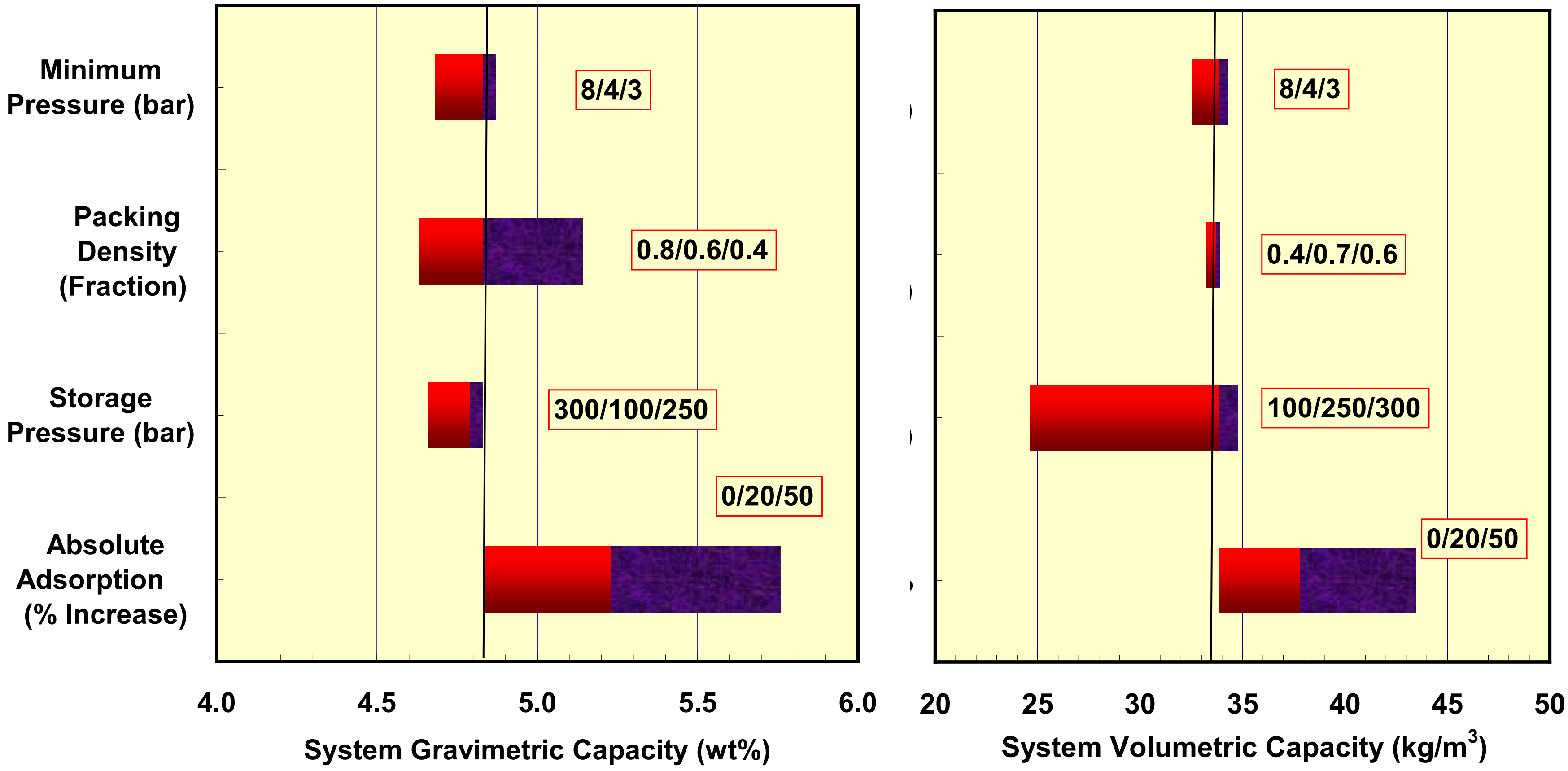
# Dormancy

- Dormancy: Function of amount of $H_2$ stored and P/T at start of the event
  - Minimum dormancy is 16 W.d (2.8 days at 5 W in-leakage rate)
  - Peak $H_2$ vent rate is 1 g/h/W (4.8 g/h at 5 W in-leakage rate)



# Sensitivity Analysis

- Baseline conditions: 250 bar, 100 K, 0.6 packing fraction
- Allowable DT depends on operating conditions and decreases with increase in adsorption



# Off-Board Performance

- Two pathways: SMR/U.S grid mix and electrolysis/renewable
- Three market penetrations: 2/15/40% (Sacramento, CA)

| Process | Nominal Value | Source/Comment |
|---|---|---|
| **Production** | | |
| SMR central plant capacity | 341,448 kg $H_2$/d | H2A, turnkey from Krupp-Uhde |
| SMR efficiency | 73% | H2A |
| Central electrolysis, electrolyzer capacity | 1046 kg $H_2$/d | H2A |
| Electrolysis efficiency | 74.7% | H2A |
| Electricity production efficiency | 32.2% | EIA projected U.S. grid for 2015, inclusive of 8% transmission loss from power plant to user site |
| Cost of natural gas | $0.22/Nm3 | H2A |
| Cost of electricity | $0.05-0.06/kWh | H2A |
| **Delivery** | | |
| $H_2$ Liquefaction | 8.2 kWh/kg | HDSAM, 150 tons/day liquefier |
| Truck capacity | 4300 kg | HDSAM |
| Station capacity | 400-1000 kg/d | 2-40% market penetration, HDSAM |
| Boil-off losses | 9.5% | HDSAM: liquefaction 0.5%, storage 0.25%/day, loading 0.5 %, unloading 2%, cryopump 3% |
| **On-board** | | |
| Manufacturer/dealer markup | 1.72 | DOE 2008 |
| Discount rate | 15% | DOE 2008 |
| Vehicle fuel economy | 63.0 mpgge | PSAT |
| Annual mileage | 12,000 miles | DOE 2008 |
| **Regulated pollutant and GHG emissions** | range | GREET |

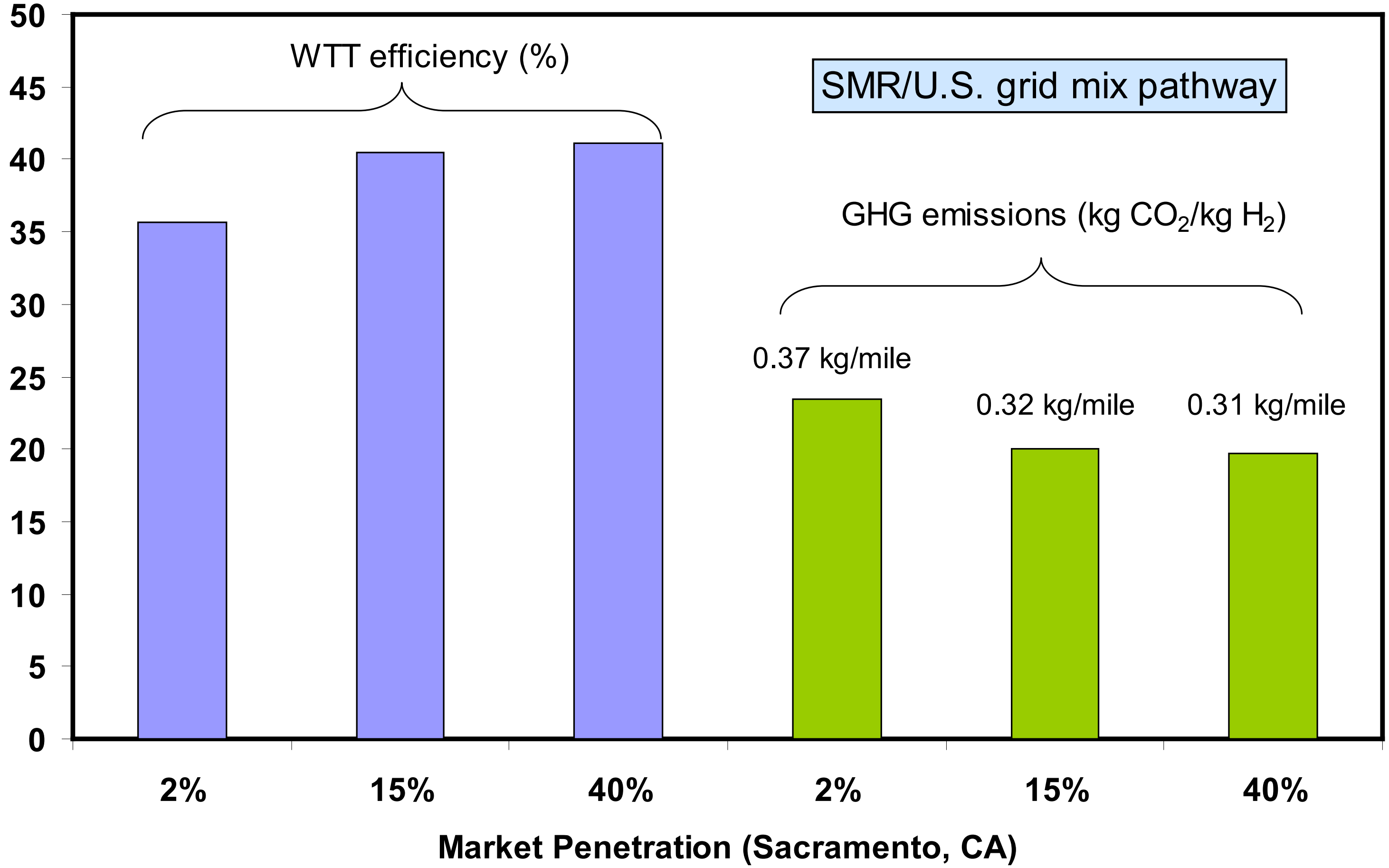
# Regulated Pollutant and GHG Emissions

- Total GHG emissions = 19.7 kg/kg-$H_2$ ($CO_2$ equivalent)
  - Production: 62% (inclusive of 9.5% $H_2$ loss during on-site storage and distribution)
  - Storage: 37% (central liquefaction)
  - Distribution: <1% (truck delivery)
- g/kg-$H_2$ delivered to vehicle

| Process | VOC | CO | $NO_x$ | $PM_{10}$ | $SO_x$ | $CH_4$ | $N_2O$ | $CO_2$ | GHG |
|---|---|---|---|---|---|---|---|---|---|
| $H_2$ Production | - | - | - | - | - | 0.02 | 0.00 | 11,613 | 12,180 |
| Liquefaction | 0.64 | 1.66 | 10.92 | 9.52 | 24.20 | 9.16 | 0.10 | 6,987 | 7,227 |
| Refueling Station | 0.02 | 0.05 | 0.30 | 0.26 | 0.67 | 0.26 | 0.00 | 195 | 201 |
| Truck Delivery | 0.04 | 0.12 | 0.45 | 0.02 | 0.03 | 0.10 | 0.00 | 86 | 89 |
| Total: | 0.70 | 1.83 | 11.67 | 9.80 | 24.90 | 9.54 | 0.10 | 18,881 | 19,697 |

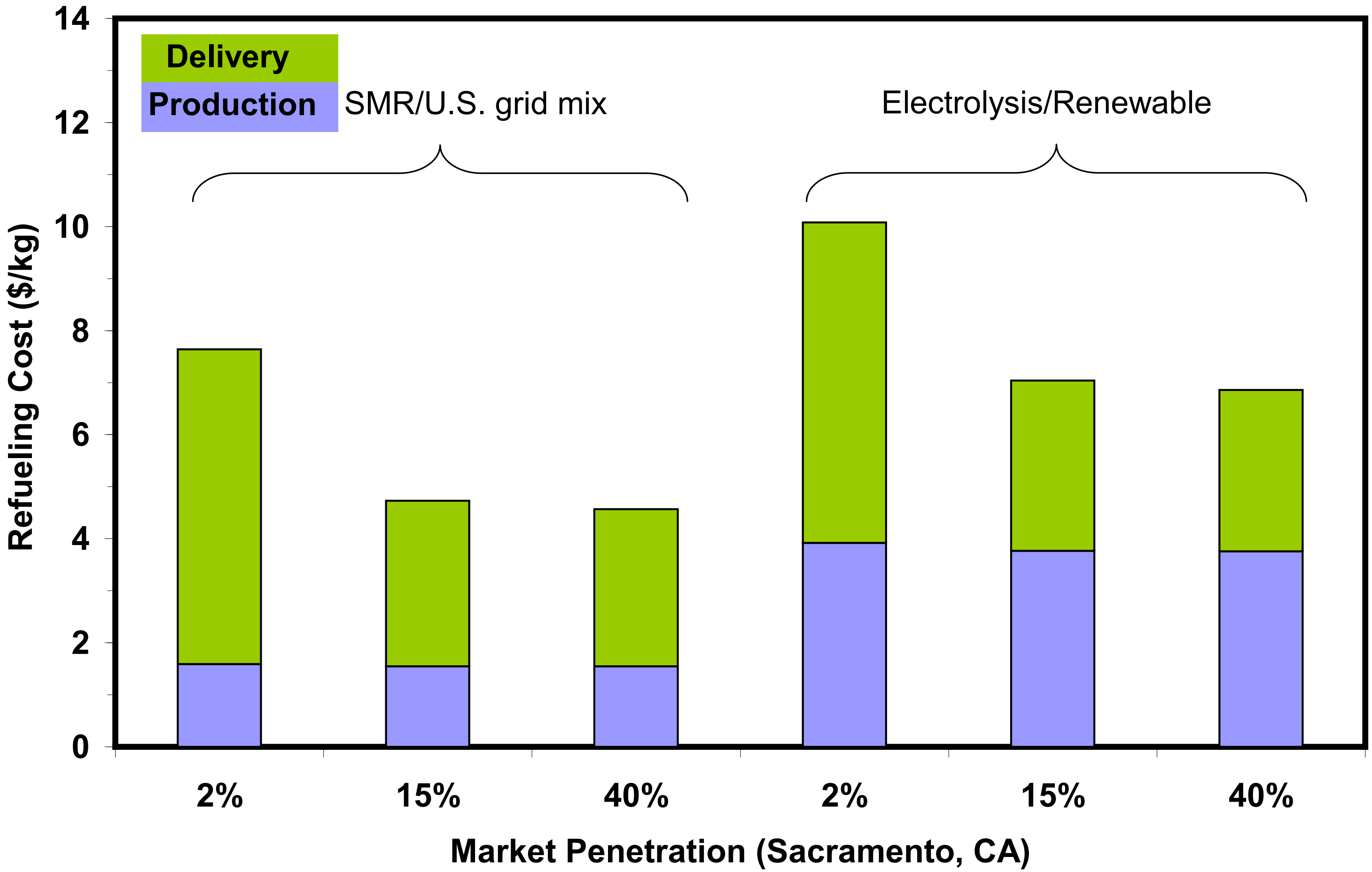
# WTT Efficiency and GHG Emissions

- 35.6-41.1% WTT efficiency, below 60% DOE target for physical storage
- GHG emissions are comparable to conventional gasoline ICEV (~0.35 kg $CO_2$/mile, 30 mpg)



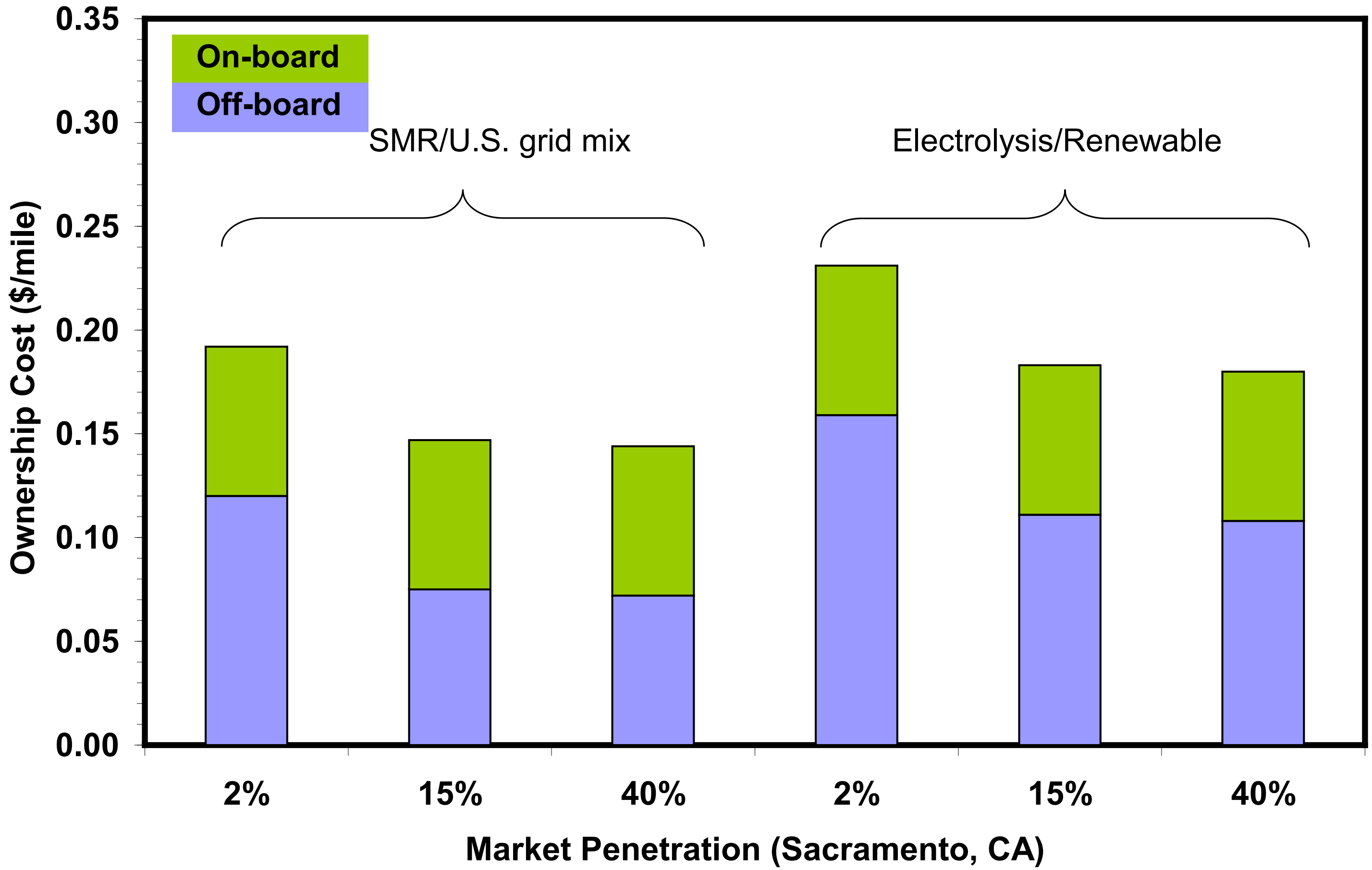
# Refueling Cost

- Fuel cost dominates production cost (SMR: 77% fuel, 14% capital
- Capital cost dominates delivery cost (55% capital, 18% fuel)
- Delivery cost dominates refueling cost in SMR pathway (67%)



# Ownership Cost

- On-board system accounts for 50% of ownership cost in SMR pathway ( $18/kWh preliminary TIAX cost estimate)
- Ownership cost >50% higher than for conventional gasoline ICEV (~$0.1/mile, 30 mpg and $3/gal untaxed)



# On-Board and Off-Board Performance of Hydrogen Storage in Metal Organic Frameworks

On-Board Performance

- System with adiabatic liquid $H_2$ refueling
- Adsorption isotherms
- Gravimetric and volumetric storage capacity
- Refueling and discharge dynamics
- Dormancy and $H_2$ loss rate
- Sensitivity analyses

Off-Board Performance

- Regulated pollutant and GHG emissions
- WTT efficiency
- Refueling cost
- Ownership cost

# Hydrogen Storage using Ammonia Borane in Ionic Liquids – Preliminary Results

AB/IL on-board storage system

- Physical properties of ionic liquid solvent and AB solution
- Dehydrogenation kinetics
- Dehydrogenation reactor
  - Control of AB conversion and peak temperature
  - Adiabatic operation
- System configuration
- Future work
  - Reactor startup and shutdown
  - Shelf life
  - System gravimetric and volumetric capacities
  - Off-board regeneration and fuel cycle efficiency

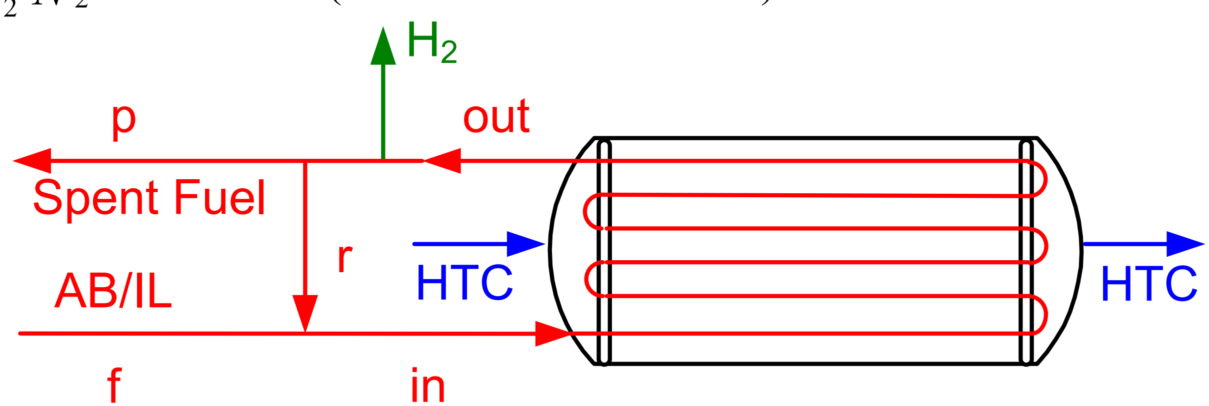
# Dehydrogenation Reactor Model

- Main challenge is to control the peak temperature (bmimCL stability, undesirable side products) and AB conversion (regenerability) by using heat transfer and/or product recycle
  - Adiabatic temperature rise in excess of 500$^{o}$C ($\Delta T_{ad} = 295 N_{H2}$)
- AB conversion ($\Phi$, $\Phi_1$, $\Phi_2$)
- Recycle ratio ($R$)
- Liquid hourly space velocity ($LHSV$) defined on the basis of volumetric flow rate of fuel (AB/IL)

$$\Phi = 1 - \frac{(\beta_1 + \beta_2)\dot{N}_1^{p} + \beta_2 \dot{N}_2^{p}}{(\beta_1 + \beta_2)\dot{N}_1^{f} + \beta_2 \dot{N}_2^{f}} \qquad R = 1 - \frac{(\dot{N}_1^{r} + \dot{N}_2^{r} + \dot{N}_3^{r} + \dot{N}_s^{r})}{(\dot{N}_1^{out} + \dot{N}_2^{out} + \dot{N}_3^{out} + \dot{N}_s^{out})} \qquad LHSV = \frac{\dot{V}_f}{V_t}$$

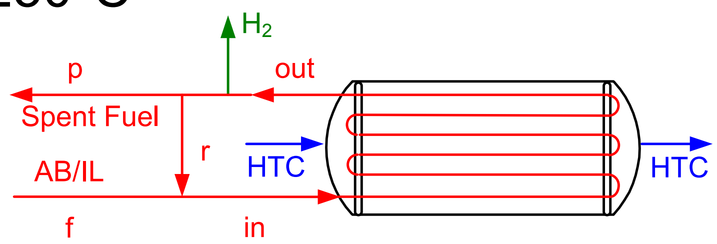
$$\Phi_1 = 1 - \frac{\dot{N}_1^{out}}{\dot{N}_1^{in}}$$

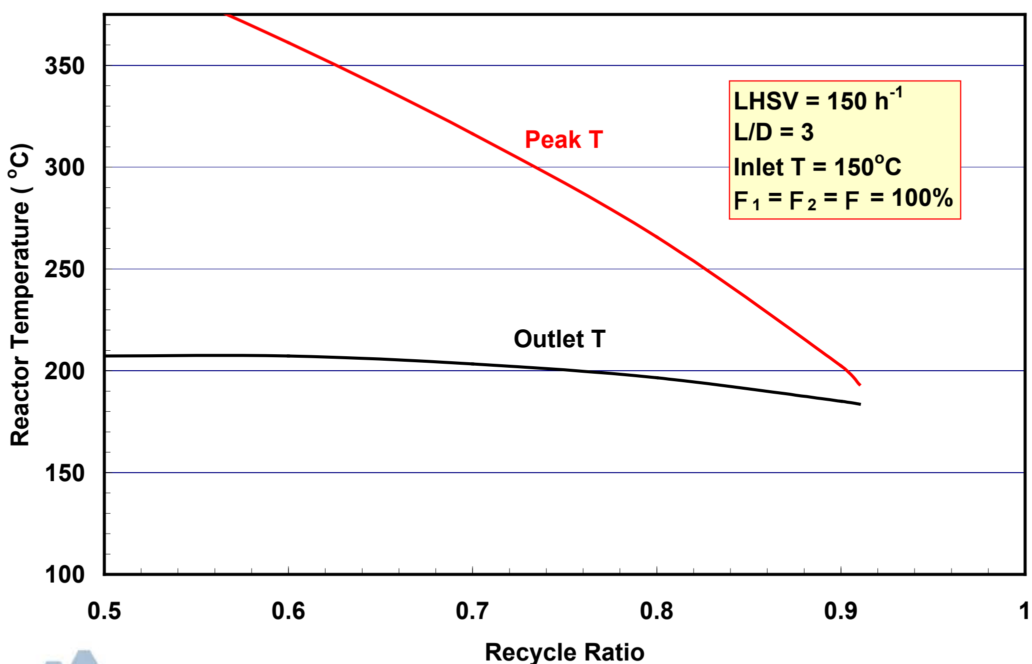
$$\Phi_2 = 1 - \frac{\dot{N}_2^{out}}{(\dot{N}_2^{in} + \Phi_1 \dot{N}_1^{in})}$$



# Dehydrogenation Reactor Performance

- Main challenge: control peak T and AB conversion using heat transfer and product recycle
  - Adiabatic T rise in excess of 500$^o$C ($\Delta T_{ad} = 295 N_{H2}$)
- R < 0.95 for 100% AB conversion at 150$^o$C inlet T and 150 $h^{-1}$ LHSV
- R >0.8 to limit maximum temperature to 250$^o$C

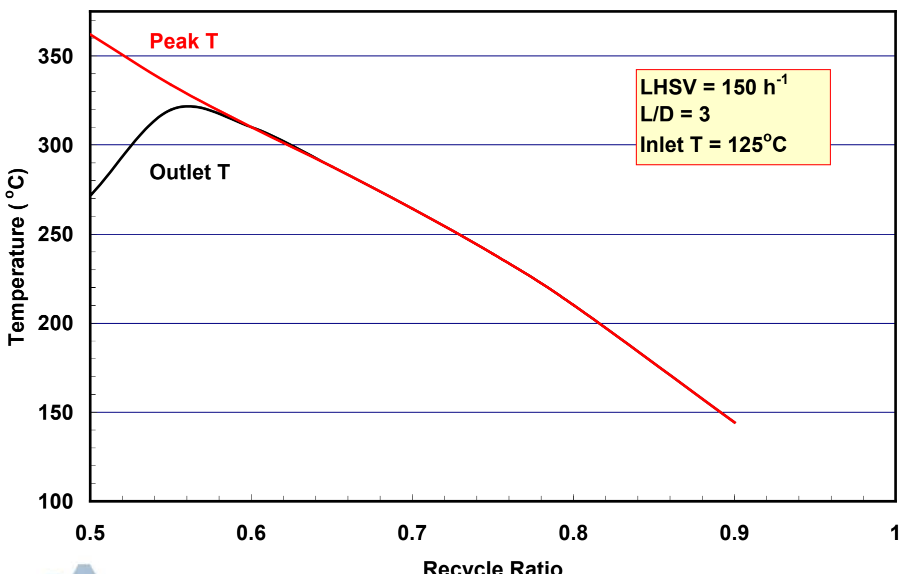


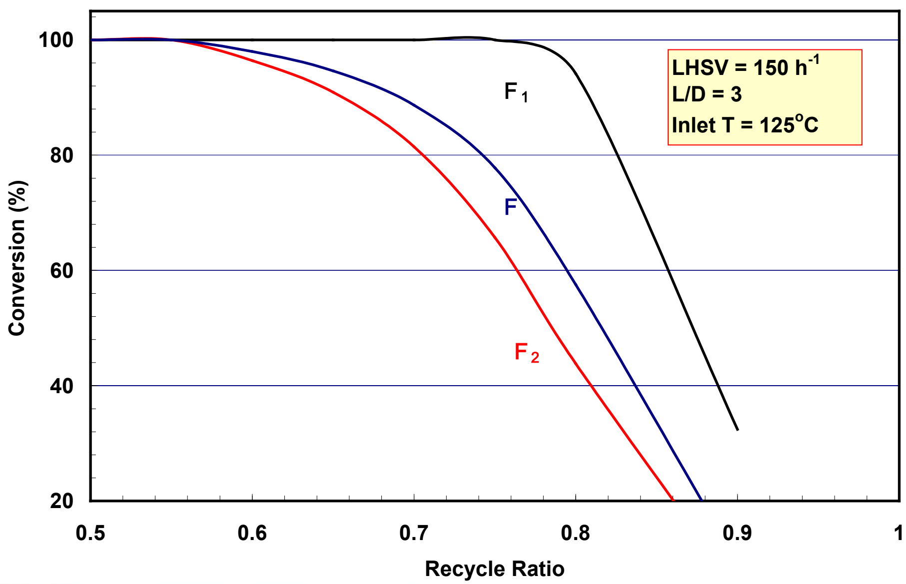




- AB flow rate determined to yield 1.6 g/s of $H_2$ at 100% conversion
- Coolant (ethylene glycol) flow rate determined to limit $\Delta T$ to 10$^o$C while absorbing 26.4 kW of heat

# Reactor Temperature and Conversion

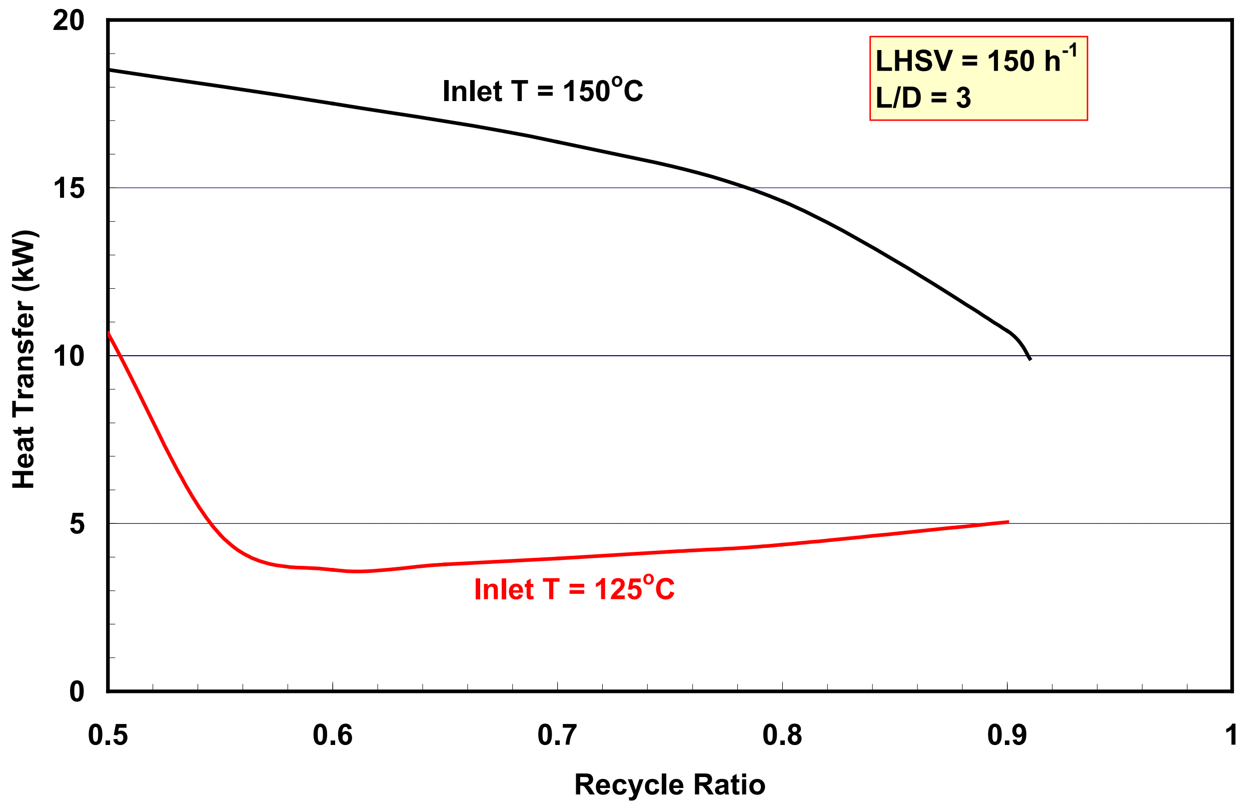
- Peak temperature is a function of inlet temperature and R (conversion)
  - R <0.55 for 100% conversion at 125$^{o}$C inlet T and 150 $h^{-1}$ LHSV
  - Peak T > 315$^{o}$C for R < 0.55
  - For specified conversion, not possible to control the peak temperature by reducing the inlet temperature
  - The coolant removes only a fraction of the heat released
  - Difficult to limit the peak temperature by controlling heat transfer



# Reactor Heat Transfer

- Heat transfer depends on the LHSV and R
- Depending on the inlet T and recycle ratio (given LHSV) the coolant removes only a fraction of the heat released by the exothermic reaction (26.4 kW at 100% conversion)
- Difficult to limit the peak temperature by controlling heat transfer



# Summary and Interim Conclusions

Product stream recycle needed to control the reactor peak temperature and AB conversion

- Depending on the inlet temperature, R may be > 0.9 to limit the peak temperature to <200$^{o}$C
  - Very difficult to control the peak temperature with heat transfer
  - Lower inlet temperature does not necessarily lead to lower peak temperature
- The reactor can be operated adiabatically while controlling peak T and AB conversion
  - The reactor peak temperature can be lower if operated adiabatically

Remaining challenges

- Reactor startup and shutdown
- Heat rejection