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System Level Analysis of Hydrogen Storage Options

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Project ID: ST31

U.S. Department of Energy

UChicago Argonne LLC

A U.S. Department of Energy laboratory managed by UChicago Argonne, LLC

Overview

Timeline

- Project start date: Oct 2004
- Project end date: Sep 2009
- Percent complete: 50%

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

- FY06: $400 K
- FY07: $400 K

Interactions

- FreedomCAR and Fuel Partnership
- Storage Systems Analysis Working Group, MH COE, CH COE
- TIAX, LLNL, SNL, MCEL, APCI, H2A, and other industry

Objectives

- Perform independent systems analysis for DOE
  - Provide input for go/no-go decisions
- Model and analyze various developmental hydrogen storage systems
- Analyze hybrid systems that combine features of more than one concept
- Develop models that can be used to “reverse-engineer” particular technologies
  - Provide guidance to meet targets
- 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 (Assessment: October 2006)

- Determined the storage capacity of LLNL Gen-2 system, and the dynamics of LH2 refueling, discharge and dormancy

Carbon Storage (Joule Milestone: December 2006)

- Status report on the storage capacity of systems with activated carbons at low T & high P

Metal Hydrides (Joule Milestone: March 2007)

- Joint ANL-UTRC status report on gravimetric and volumetric capacities of metal-hydride storage systems and intrinsic capacities needed to meet 2010 and 2015 system targets

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

- Evaluated energy consumed in regenerating SBH using MCEL flow sheet and the overall fuel cycle efficiency

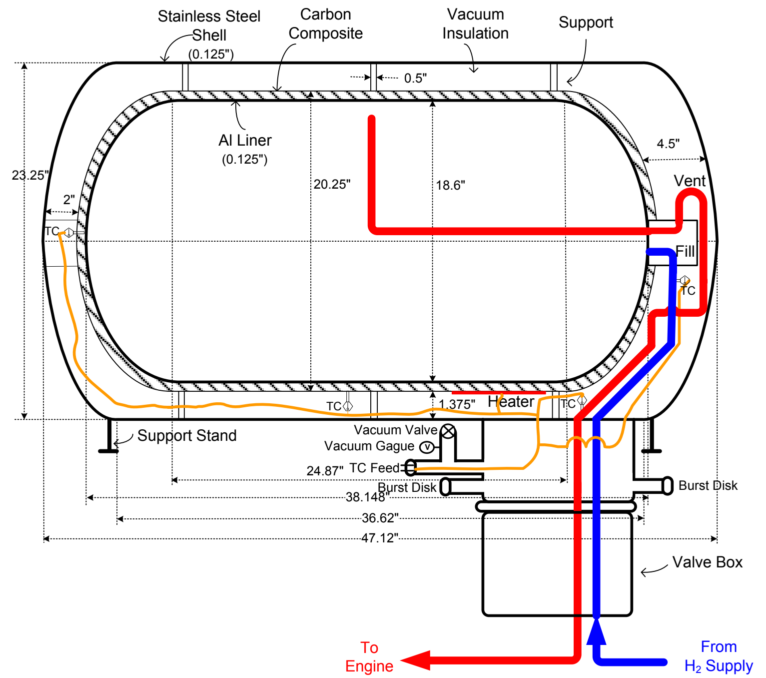
Hydrogen Storage in Liquid Carriers (FY 2007-2008)

- System analysis to determine the intrinsic capacities, thermodynamics and kinetics needed to satisfy targets

Cryo-Compressed Storage

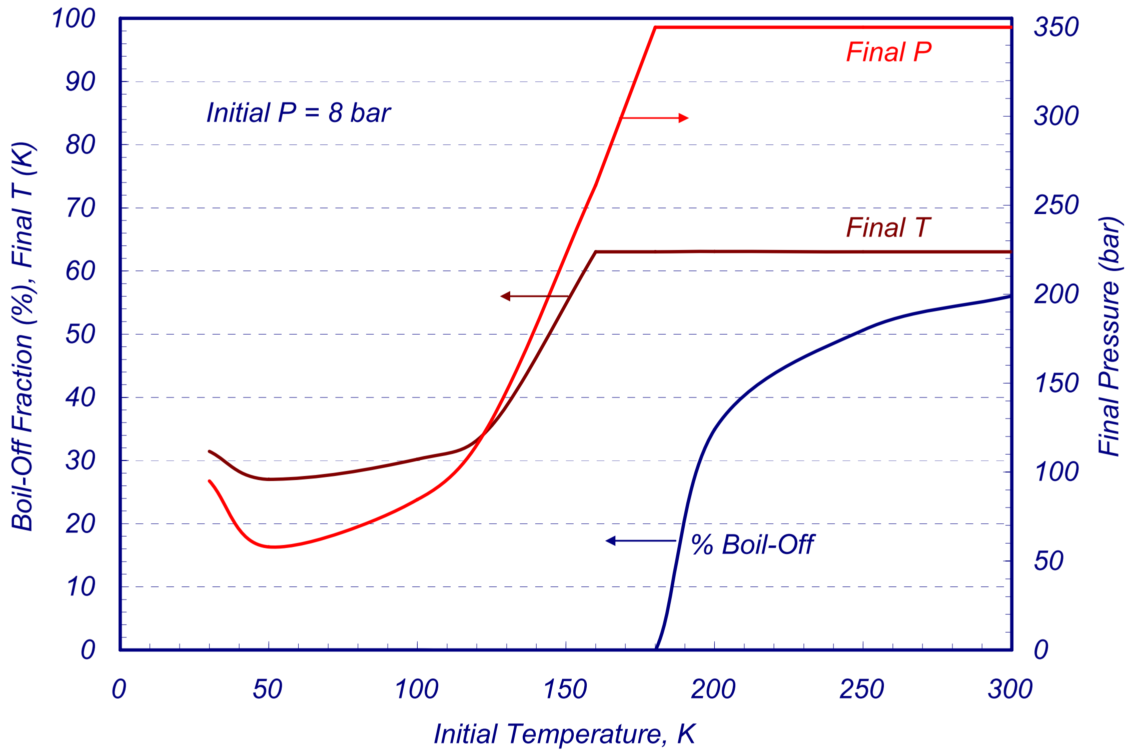
- Review of LLNL Design Data
  - Volumetric capacity
  - Gravimetric capacity
- ANL Analysis
  - Refueling dynamics
  - Discharge dynamics
  - Dormancy and boil-off losses
  - Refueling energy consumption
  - Discharge energy requirement

- Why LH2 in pressurized vessels
  - Flexible refueling: LH2 or cH2
  - Greatly extended dormancy
  - Reduced carbon fiber usage
  - Temperature regulation



High-Pressure LH_2 Refueling
Cryo-Gas or LH2?

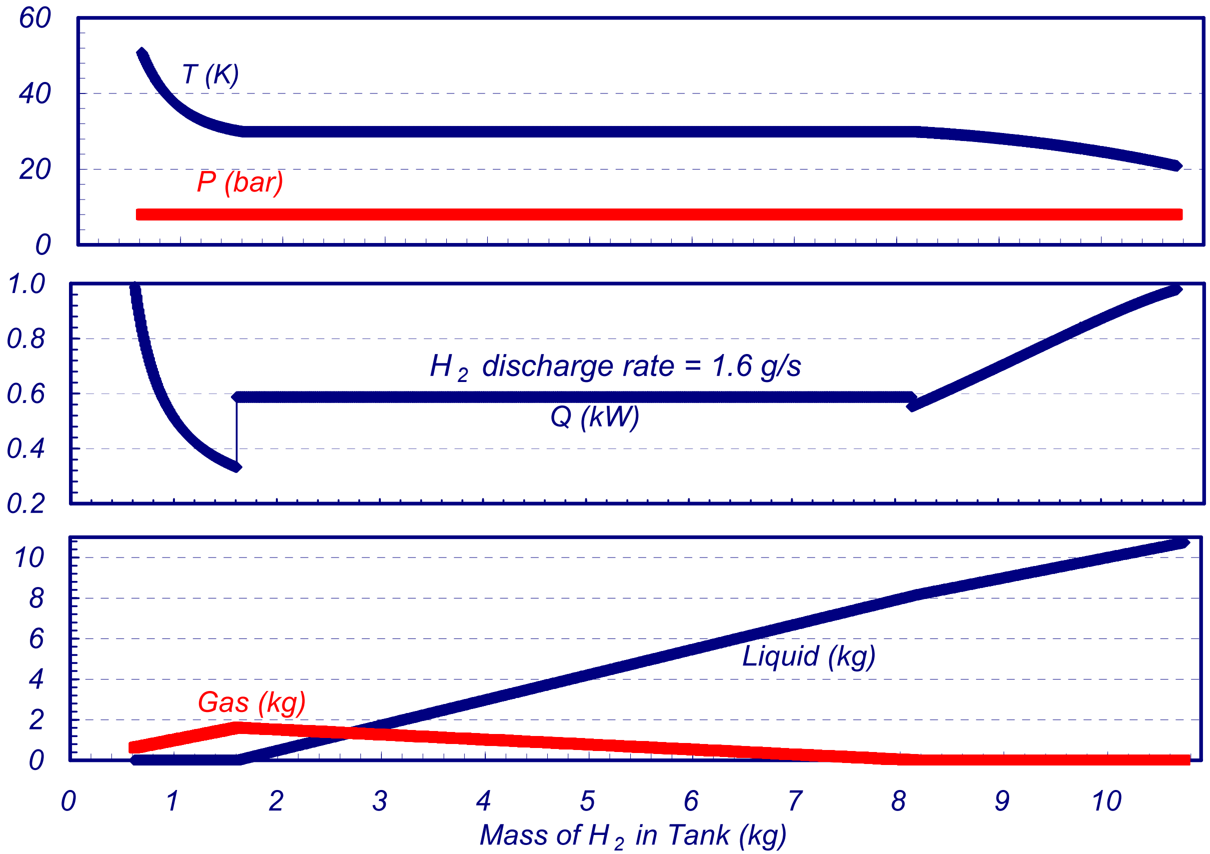
- Cryo-gas if initial T > 120 K, P < 350 bar if initial T < 180 K
- No venting of H_2 if the initial T < 180 K
- Final LH2 P is 58 – 95 bar for initial T between 30 and 100 K



Amount of H_2 that can be stored without venting	
Initial T	Mass H_2
<180 K	10.7 kg
200 K	9.7 kg
250 K	7.9 kg
300 K	6.2 kg

Low-Pressure LH_2 Storage Discharge Dynamics at Full Flow (1.6 g/s)

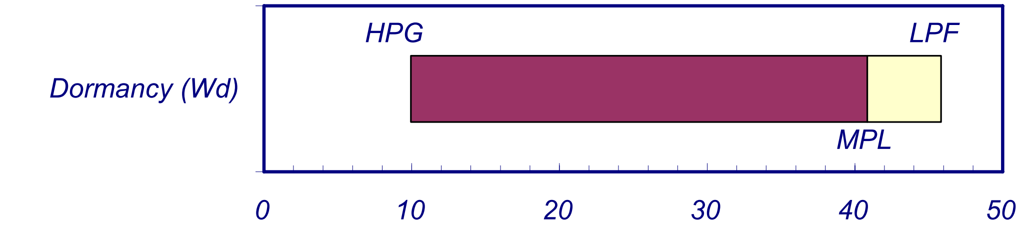
- Subcooled liquid until H_2 decreases to 8.2 kg, saturated liquid-gas mixture if 8.2–1.6 kg, superheated gas for <1.6 kg



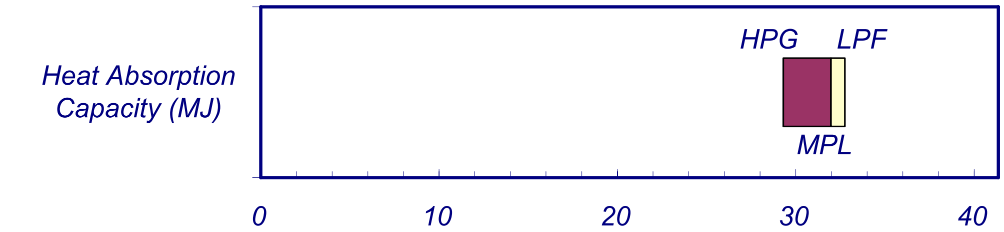
- P kept at 8 bar by heating liquid (>8.2 kg H_2), generating gas (8.2-1.6 kg), or heating gas (<1.6 kg)
- Amount of recoverable H_2 depends on the heater rating

Dormancy and H_2 Loss

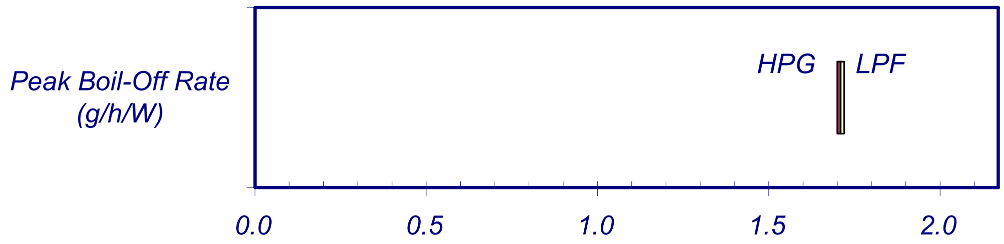
- HPG: Cryo-gas at 350 bar, 63 K
- MPL: Medium pressure liquid at 58 bar, 27 K
- LPF: Low-pressure liquid at 8 bar, 20.9 K
- Heat absorption capacity: Q corresponding to final T = 50°C



Longer dormancy if H_2 stored as liquid



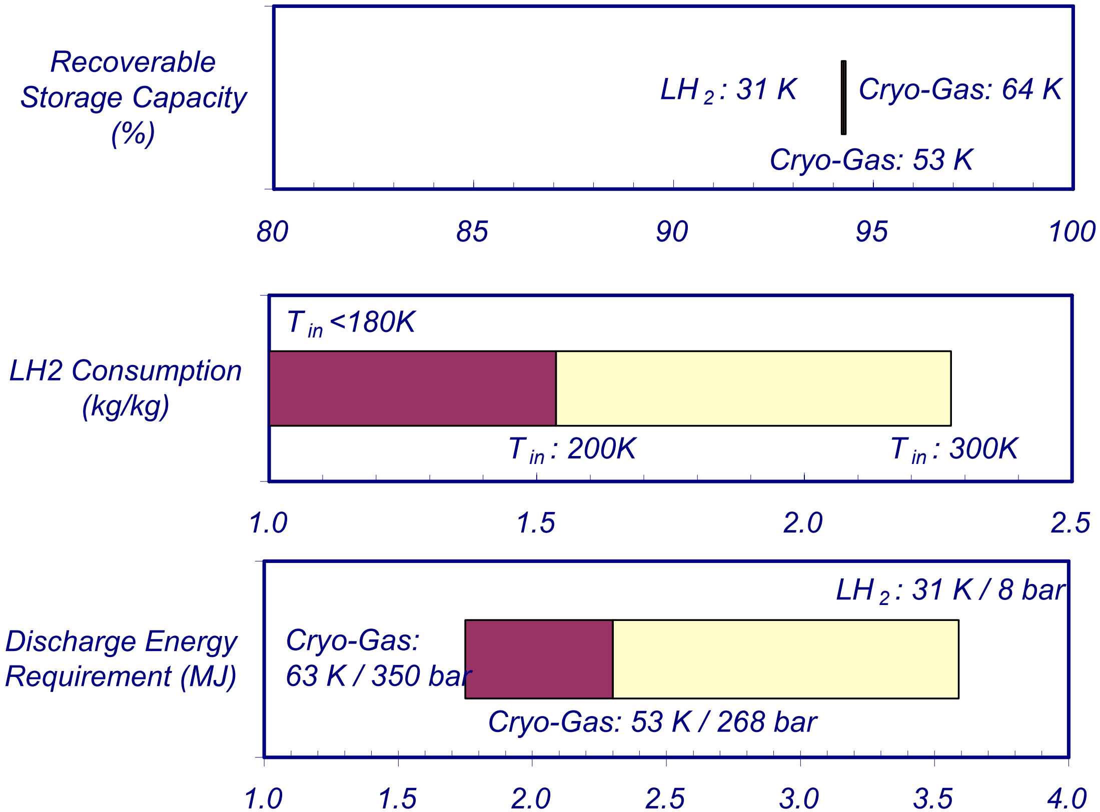
Higher heat absorption capacity if H_2 stored as liquid



Peak boil-off rate independent of H_2 initial state

Summary
High-Pressure LH_2 Refueling Option

- Recoverable gravimetric capacity of system: 4.7 wt%
- Recoverable volumetric capacity of system: 30 kg/m^3



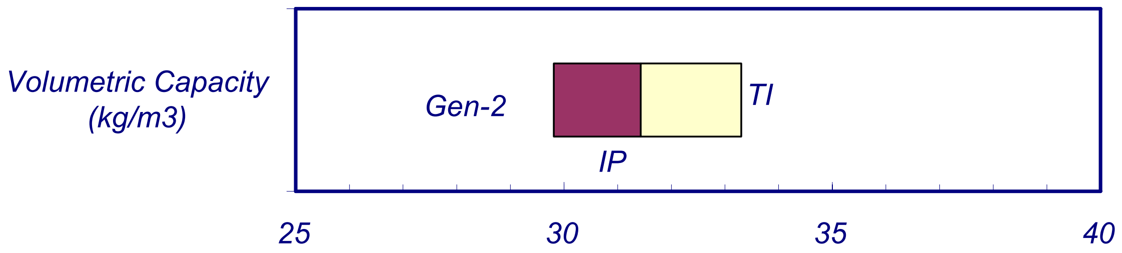
Recoverable storage capacity depends on minimum delivery pressure and heat input

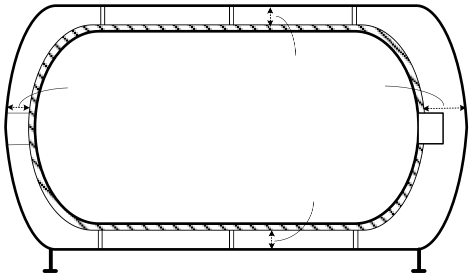
Initial temperature depends on prior refueling and driving events

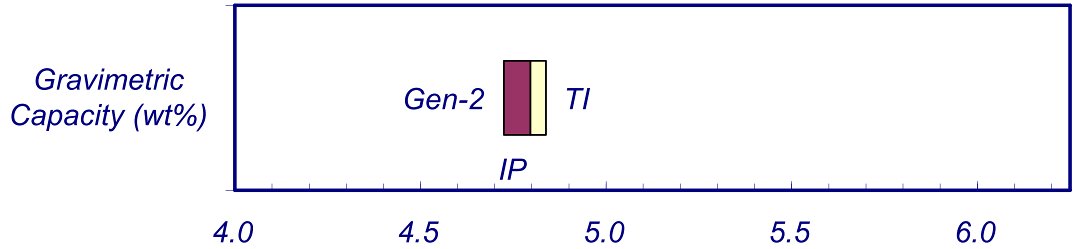
Includes electrical heat input and in-leakage of heat

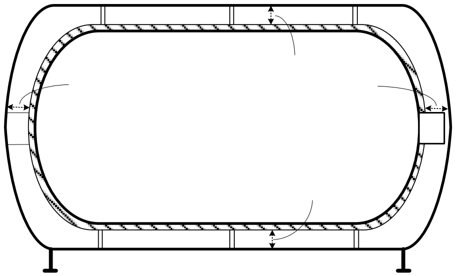
Summary of Sensitivity Analysis: Recoverable System Storage Capacity

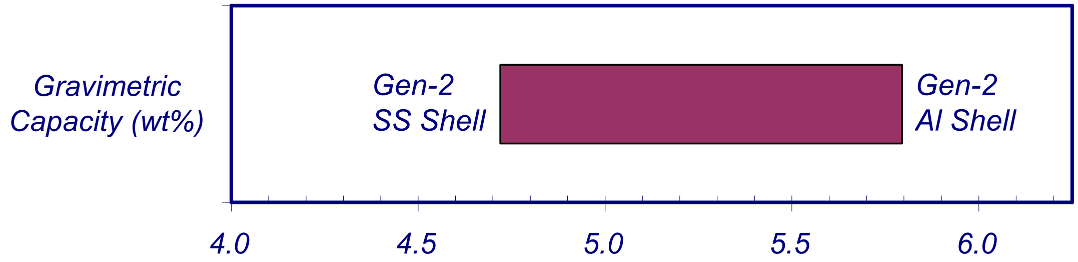
- More significant changes needed to satisfy 2010 volumetric capacity target of 45 kg/m^3

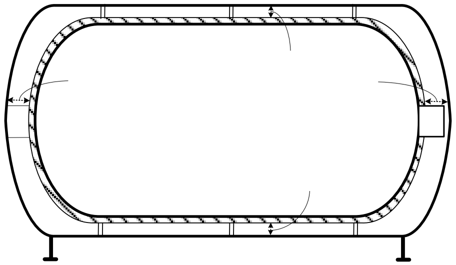












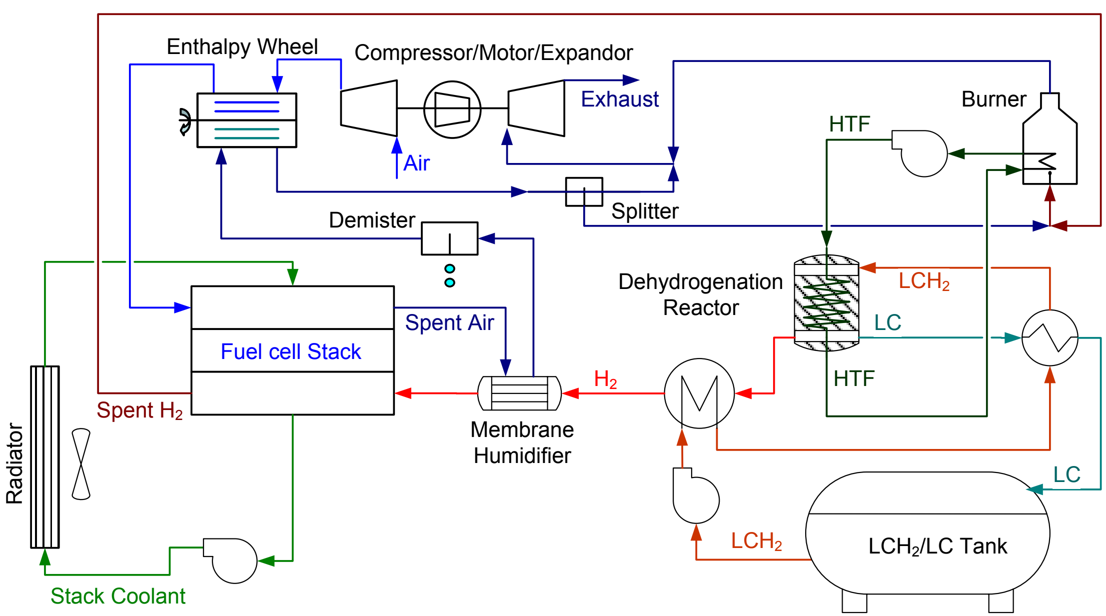
On-Board Hydrogen Storage System with a Liquid Carrier

Objective: To determine the performance of the on-board system relative to the storage targets (capacity, efficiency, etc)

1. On-Board System Configuration
2. Dehydrogenation Reactor
   - Dehydrogenation kinetics
   - Trickle bed hydrodynamics
   - Dehydrogenation reactor model
   - Reactor performance with pelletized and supported catalysts
3. System Performance
   - Storage efficiency
   - Storage capacity

Fuel Cell System with H_2 Stored in a Liquid Carrier

- Once-through anode gas system with controlled H_2 utilization
- Burner uses depleted air split-off from spent cathode stream
- Burner exhaust expanded in gas turbine to recover additional power



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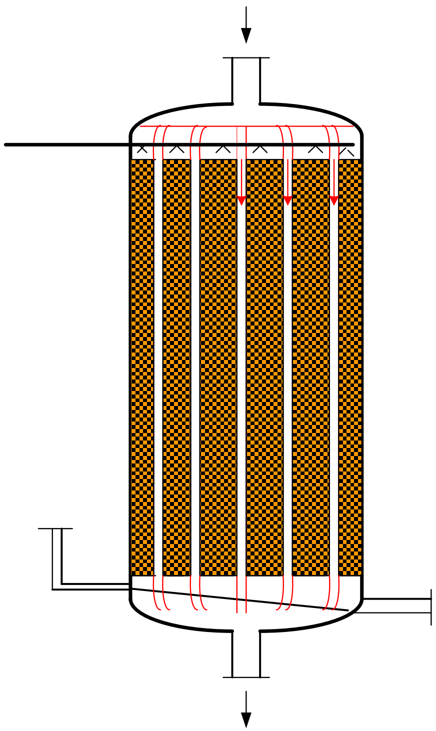
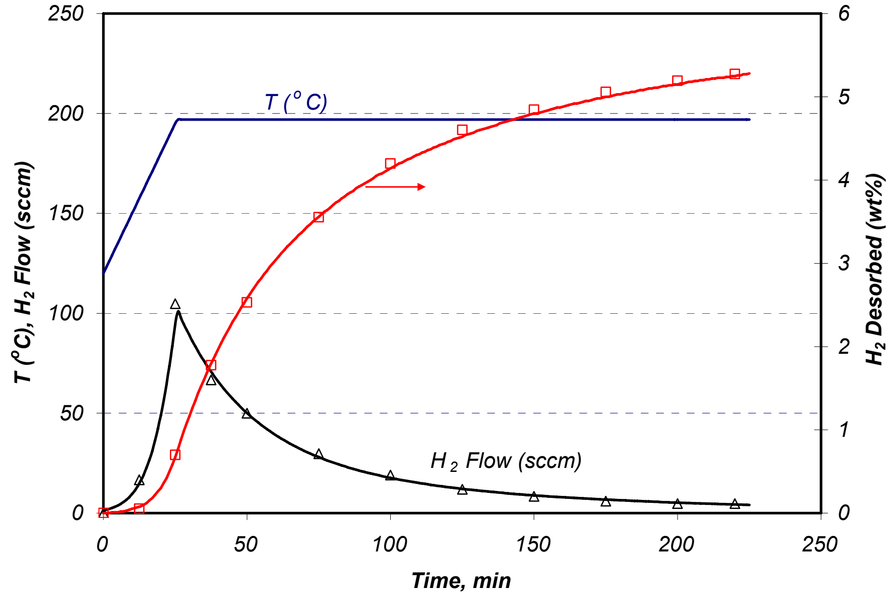
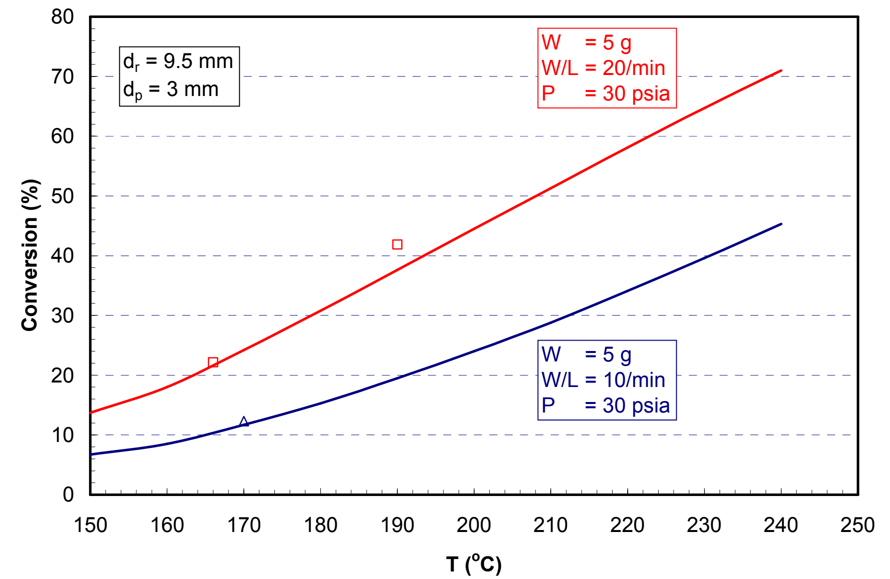


Dehydrogenation Reactor

Developing & Validating Model for DeH2 Reactor

- Dehydrogenation kinetics
  - $R_1 = R_2 + 2H_2$
    $R_2 = R_3 + 2H_2$
    $R_3 = R_4 + 2H_2$
  - Kinetic constants from batch reactor data, APCI Patent
  - 8 g N-ethylcarbazole, 20-cc reactor, 0.2-g 4% Pd on Li aluminate powder catalyst
- Trickle-bed reactor model
  - First-order kinetics with internal & external mass transfer
  - Trickle bed hydrodynamics
  - ODEs for T and species flow
  - TBR data for 5% Pd on alumina catalyst





Conversion with Pelletized Catalysts

- Reactor Parameters
  - Pellet diameter = 3 mm
  - Bulk density = 800 kg/m^3
  - HX tube diameter = 3/8”
  - AL 2219-T81 construction
- Analysis Method

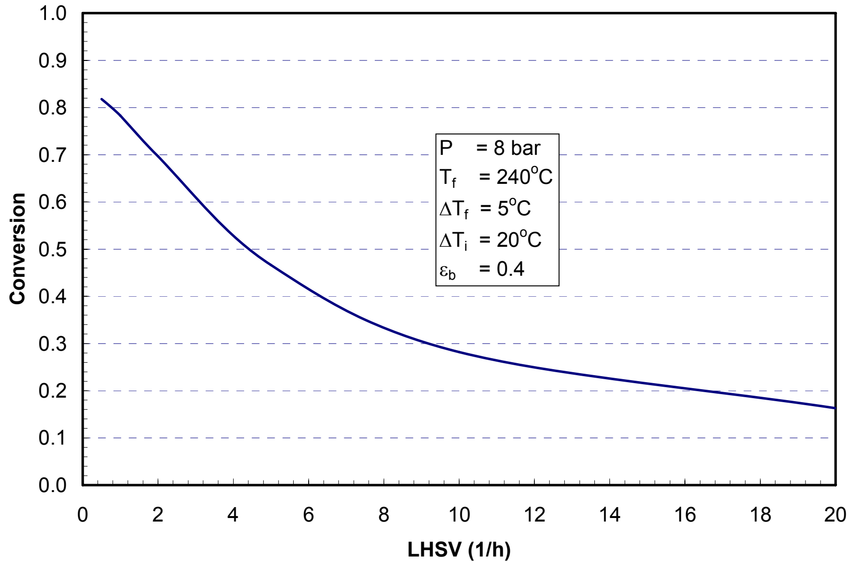
Variable	Constraint
LCH_2 flow rate	2 g/s[a] H_2 to FCS[b]
HTF flow rate	ΔT_f = 5°C
No. of tubes	Q = 83 kW[c]

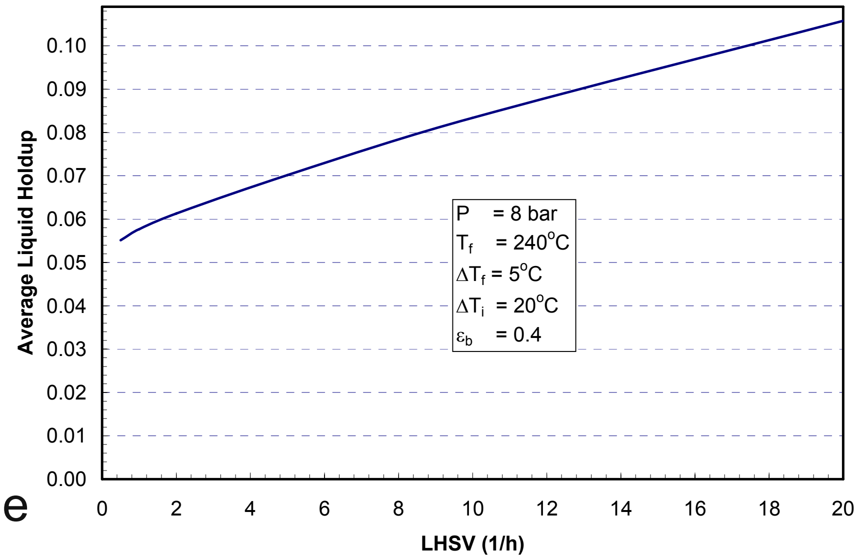
[a]3 g/s total H_2 for N-ethylcarbazole

[b]100-kWe FCS

[c]ΔH = 51 kJ/mol for N-ethylcarbazol

LHSV=volumetric flow rate/reactor volume

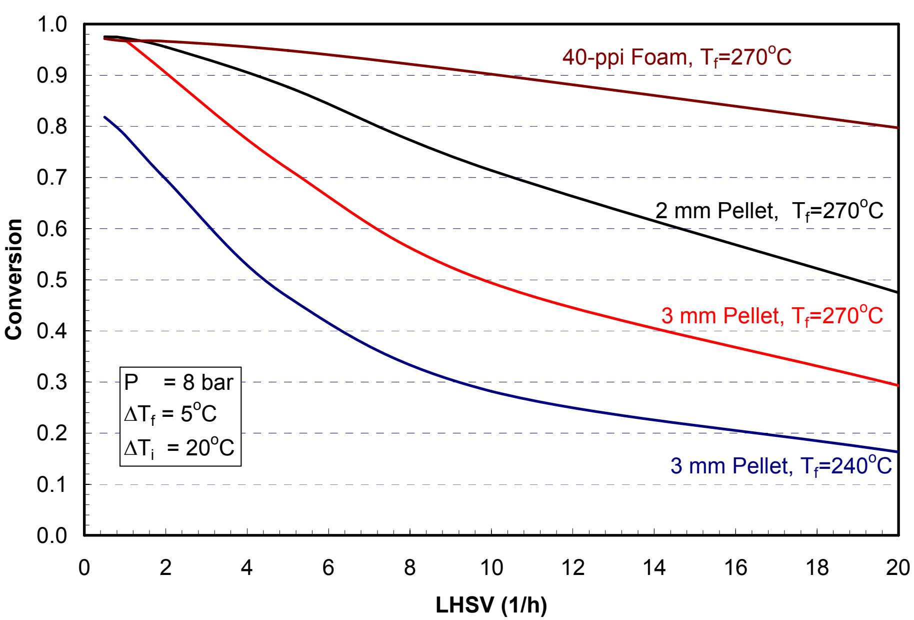


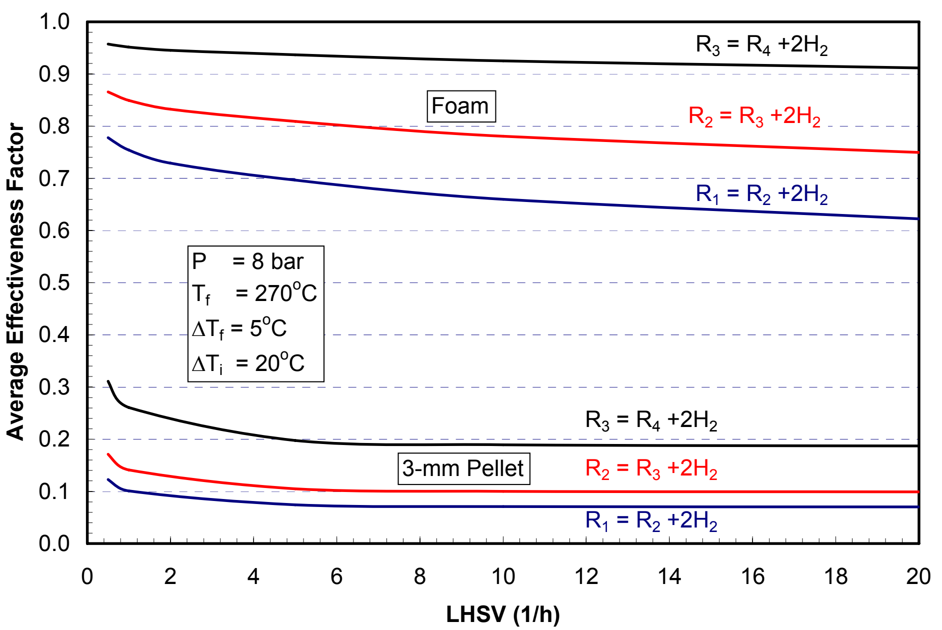


Conversion with Dispersed Catalyst

ANL-IN-07-019

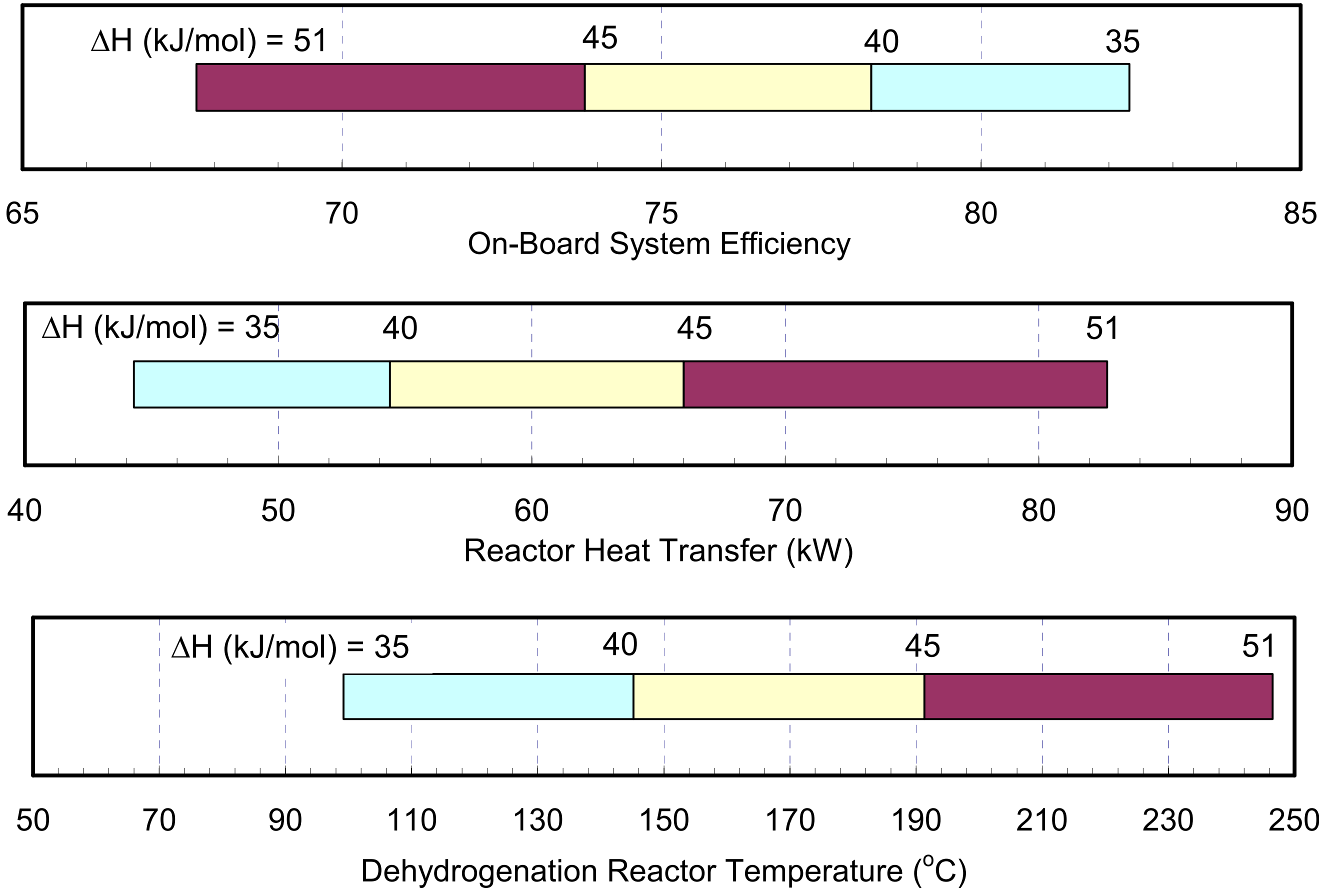
- 40-ppi Al-6101 foam, 92% porosity
  - 50-μm catalyst washcoat, 224 kg/m^3 bulk density
- Marked improvement in catalyst effectiveness if supported on foam although the wetting efficiency decreases
  - Trickle flow on foam has not been demonstrated





On-Board Storage System Efficiency

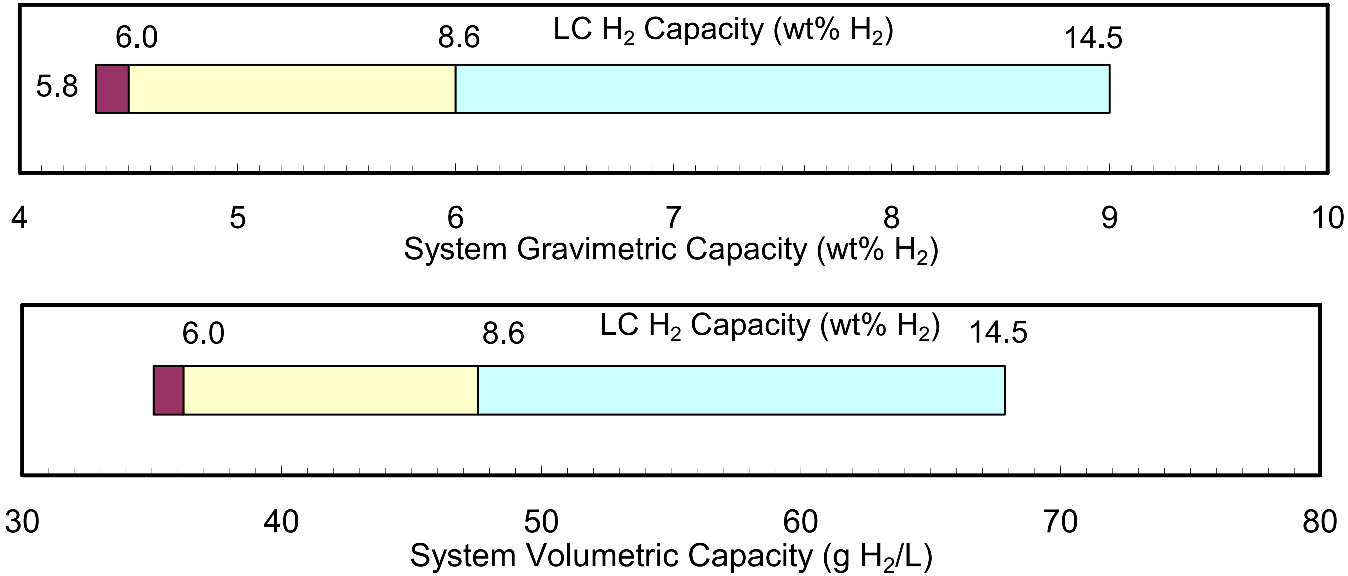
- Storage system efficiency defined as fraction of H_2 librated in dehydrogenation reactor that is available for use in fuel cell stack
- Efficiency could be ~100% if $\Delta H < 40$ kJ/mol <u>and</u> $T_R < T_{FC}$



- LC: 0.95-1.2 g/cc, 5.8 wt% H_2
- 95% conversion
- DeH_2 LHSV: 20 h^{-1}
- ΔT_{eq}: 50°C
- Burner HX: 100°C approach T
- 2 g/s net H_2 output
- $P(H_2)$: 8 bar
- 0.8-1.4 kWe HTF pump
- Start-up energy not included

Reverse Engineering: H_2 Storage Capacity

- System capacity presented in terms of stored H_2
  - Recoverable H_2: 95% intrinsic material capacity (conversion)
  - Usable H_2 = Storage system efficiency x Recoverable H_2
- System capacity with N-ethylcarbazole: 4.4% wt% H_2, 35 g/L H_2 (H_2 stored basis); 2.8% wt% H_2, 23 g/L H_2 including losses
  - 95% conversion, 67.7% storage system efficiency



- LC: 0.95-1.2 g/cc
- LC tank: 10% excess volume
- ΔH_2 LHSV: 20 h^{-1}
- ΔT_{eq}: 50°C
- Burner HX: 100°C approach
- 2 g/s net H_2
- 20-g H_2 buffer
- $P(H_2)$: 8 bar

Preliminary Conclusions

1. Dehydrogenation reactor will need a supported catalyst
   - Desirable to have LHSV > 20 h^{-1} for >95% conversion
   - May need ΔT > 50°C for compact HX ($\Delta T = T_{HTF} - T_R$)
2. Need ΔH < 40 kJ/mol for >90% on-board storage efficiency
3. Material capacities to meet system storage targets

	System Capacity[a]	
Material Capacity	Gravimetric	Volumetric
wt% H_2	wt% H_2	g-H_2/L
5.8	4.4	35
6.0	4.5	36
8.6	6.0	48
14.5	9.0	68[b]

[a] Stored H_2 basis

[b] H_2 buffer has to decrease for 81 g/L volumetric capacity

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Future Work

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

Metal Hydrides
- Analyze system with the most promising candidate
- Reverse engineering to determine material capacities

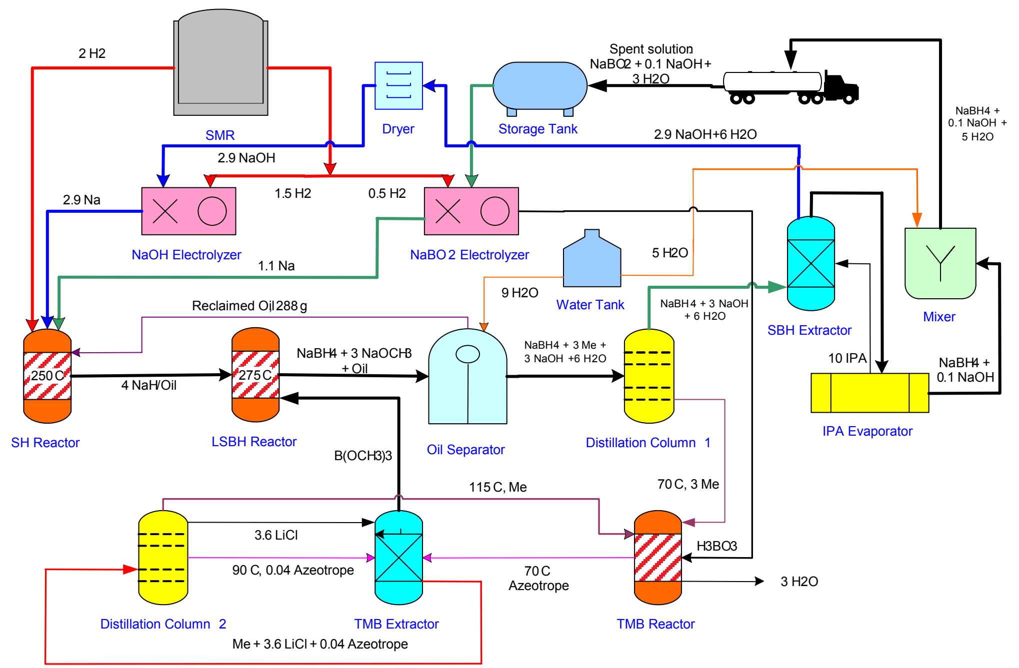
Carbon Storage
- Extend work to carbon and other sorbents

Chemical Hydrogen
- Evaluate regeneration energy consumption and fuel cycle efficiency of candidate materials and processes
- Liquid carrier option
  - Validate model with experimental data for more active catalysts
  - Sensitivity study (P, buffer H_2 storage)
  - Extension to the “best” APCI carrier with the “best” APCI catalyst
  - Fuel cycle analysis
  - Collaboration with TIAX on cost analysis

BACKUP SLIDES

Off-Board Regeneration of NaBH4 from $NaBO_2$

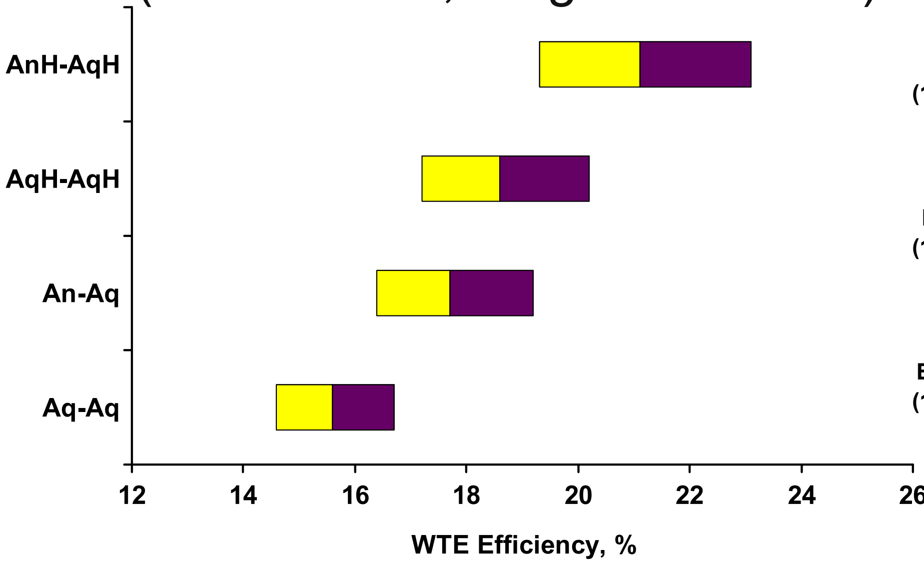
- Brown-Schlesinger process requires 4 moles Na per mole of $NaBH_4$
- Na recovery is the most energy intensive step in SBH regeneration
- MCEL has demonstrated a laboratory method for recycling Na in a closed loop
  - NaOH and $NaBO_2$ electrolysis – with or without H_2 assist
  - No make-up Na needed (assuming 100% recovery efficiency)



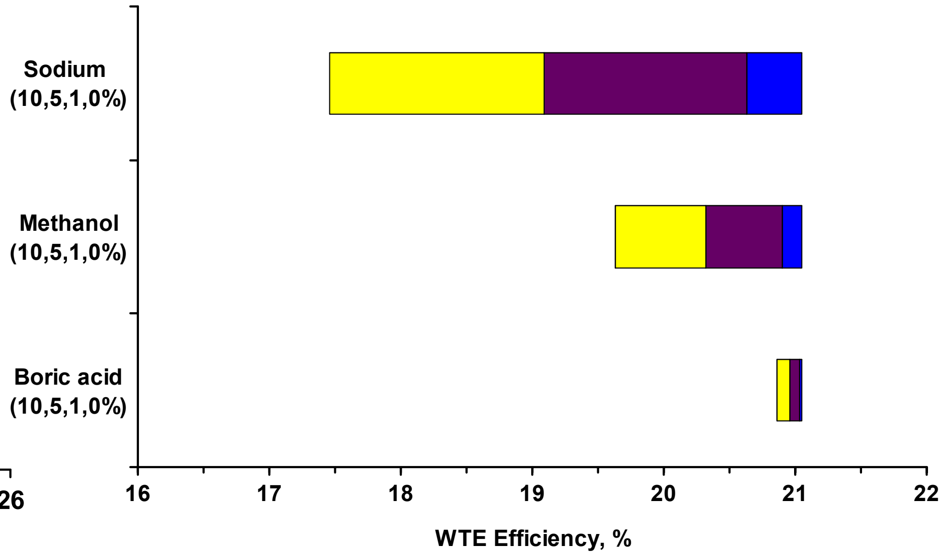
SBH Regeneration Efficiency with Closed Brown-Schlesinger Process

- WTE efficiency is 17-23% for H_2-assisted electrolysis options and 14-19% without H_2 assist.
  - Results based on 2015 U.S. grid 2015 & 80% regen plant thermal efficiency
- Na recovery accounts for 45-80% of total energy consumed in SBH regeneration.
- Loss of material, especially Na, may further reduce the efficiency.

Effect of heat integration
(Base = 50%, range 0 to 100%)



Effect of material losses



Liquid Refueling Interface

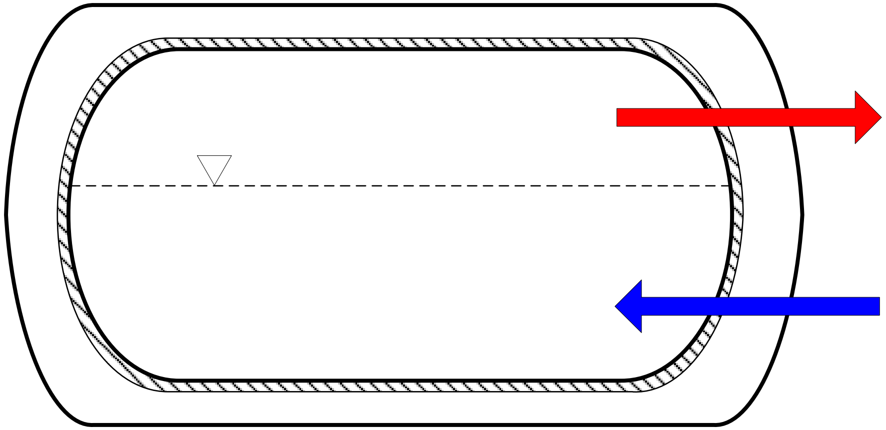
Liquid Feed - Gas Bleed System with Separate Fill and Vent Lines

(A) Low pressure fill (LPF): LH_2 transfer pump

- Gaseous hydrogen vented at low pressure
- After filling tank to 100% capacity, LH_2 heated to minimum delivery pressure (8 bar)

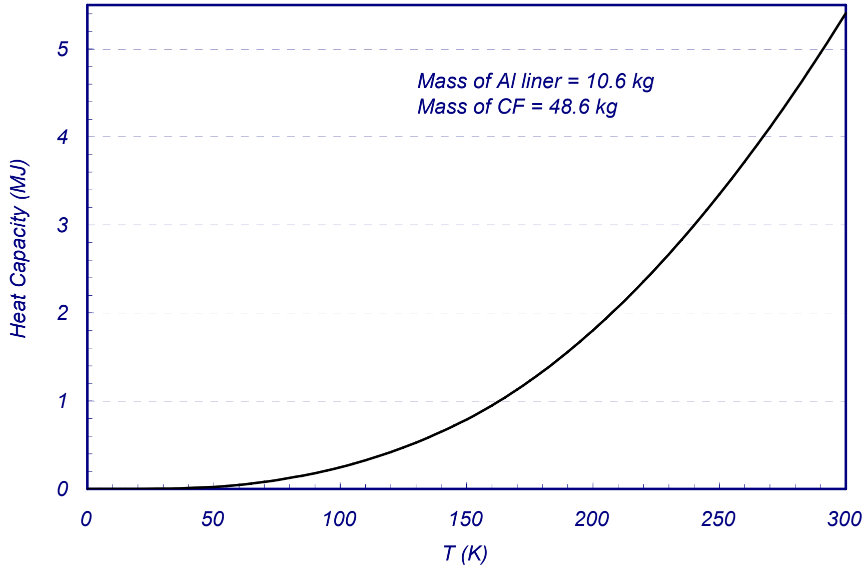
(B) High pressure fill (HPF)

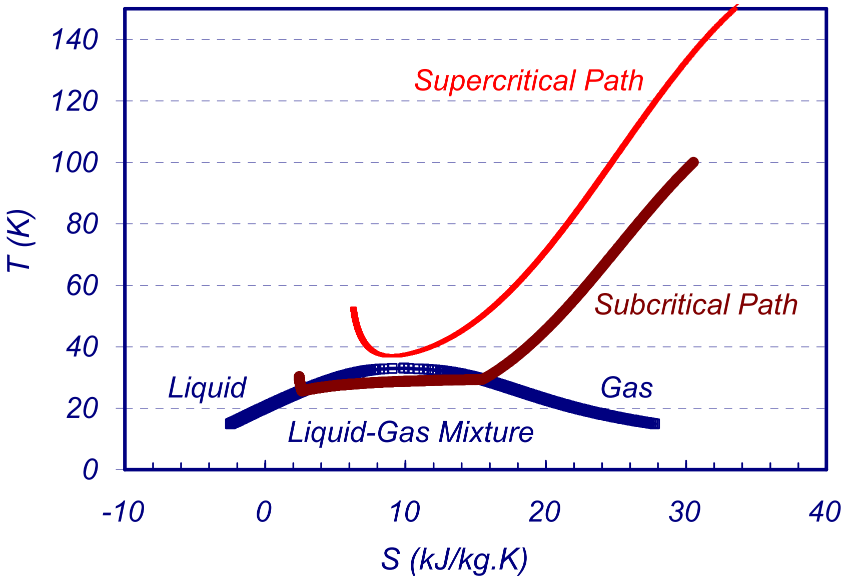
- Gaseous hydrogen vented at 350 bar



Transient Model for Charge, Discharge and Dormancy

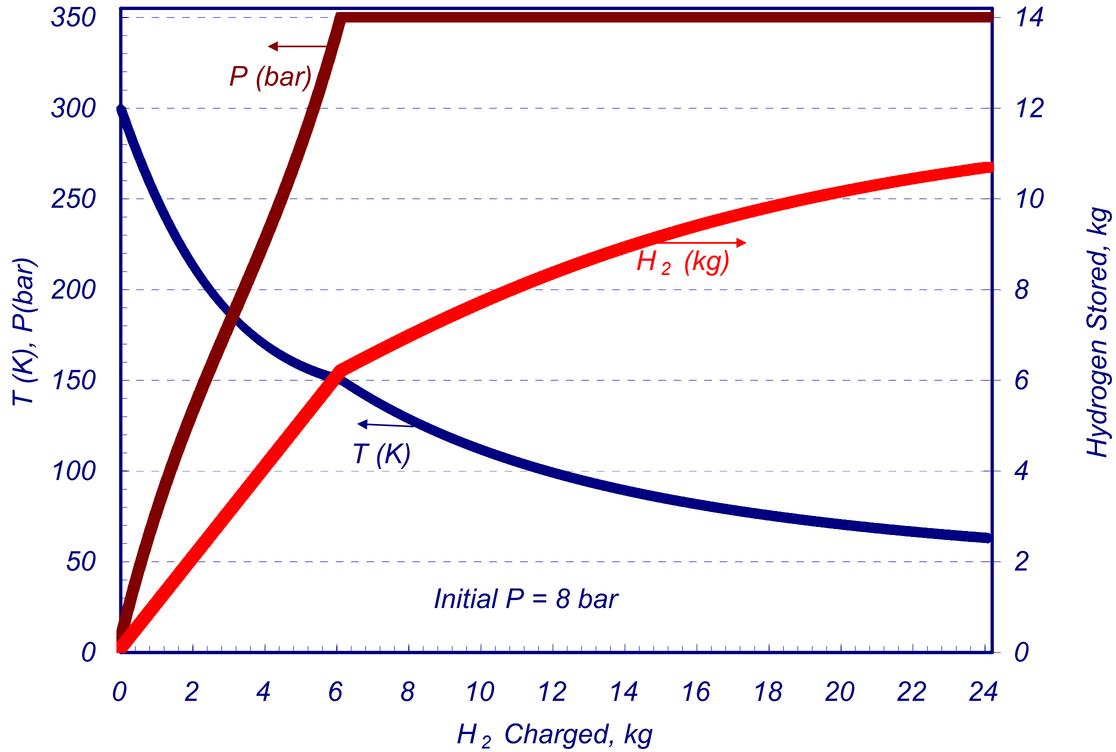
- Variable speed LH2 refueling pump, 75% isentropic efficiency
- In-tank electric heater to maintain H_2 at minimum delivery pressure
- Dormancy based on 425-bar set point pressure for relief valve
- Stored hydrogen, Al liner and CF assumed isothermal
- Debye theory for T-dependent specific heats of Al liner and CF
- BWR EOS for H_2 (REFPROP)





High-Pressure LH_2 Refueling Storage Dynamics: Cryo-Gas

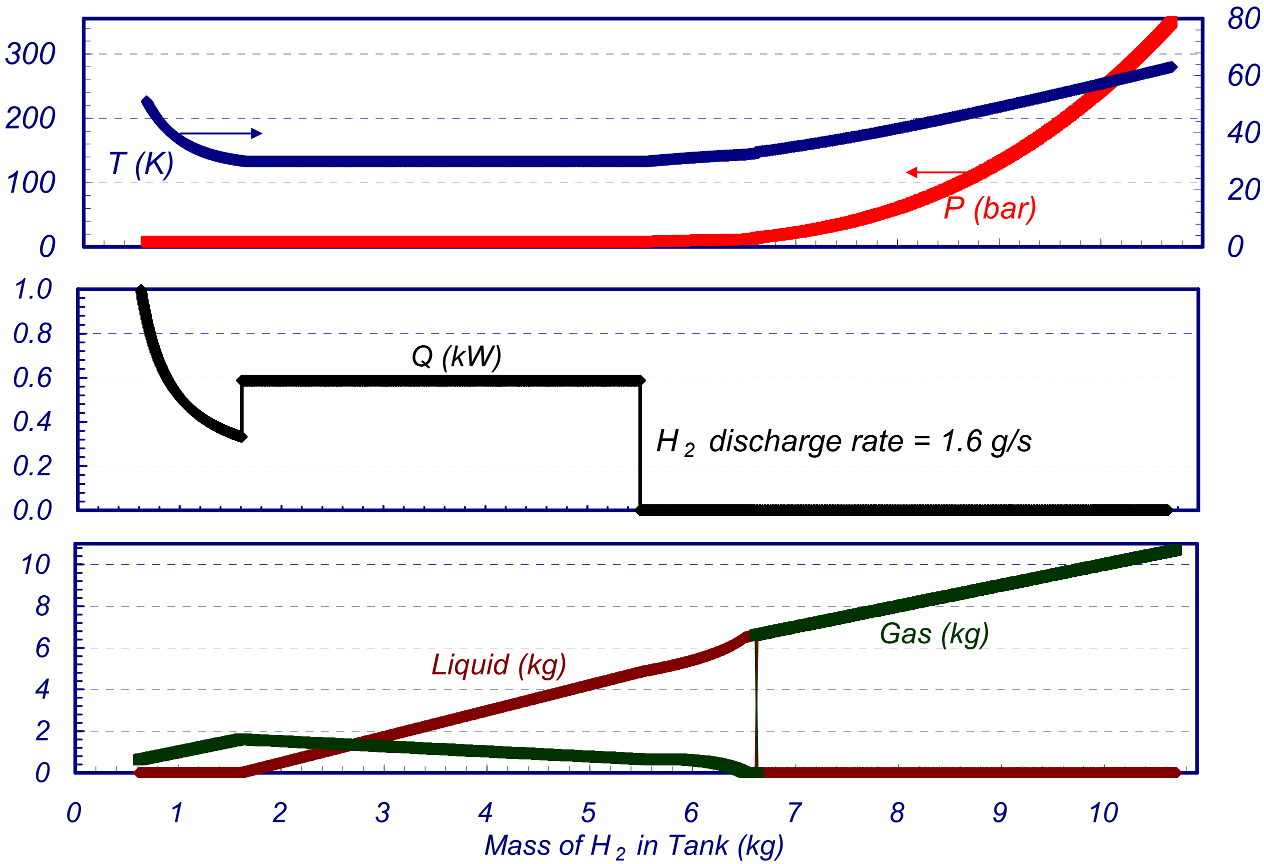
- Initial T = 300 K, P = 8 bar
- Change of slope in H_2 stored signifies onset of venting
- 24.1 kg of LH_2 charged, 10.7 kg stored as cryo-gas at 350 bar, 63 K



- Zero venting if amount of H_2 stored is <6.2 kg

High-Pressure Cryo-Gas Storage Discharge Dynamics

- Initial P = 350 bar, T = 63 K



- Tank initially cools as H_2 is withdrawn. Supercritical gas transforms to liquid as amount of H_2 decreases to 6.6 kg.
- Heat input is needed when P decreases to 8 bar.

Trickle Bed Reactor Hydrodynamics Neural Network Model

Parameter	Re_l	Re_g	Fr_l	Fr_g	We_l	X_l	X_g	St_l	St_g	Sc_l	Sc_g	Ga_l	Ca_l	Ca_g	Bi	Pe_l	Pe_g	$\rho_{g,l}$	α	$d_{p,r}$	Φ	ε
Slip factors: f_s, f_v	√	√	√		√	√		√														
Ergun constants: E_1, E_2																				√	√	√
Liquid-catalyst mass transfer coefficient	√	√						√		√		√							√			
Volumetric liquid-side mass transfer coefficient		√			√			√	√	√			√	√					√	√		
Volumetric gas-side mass transfer coefficient	√	√		√				√			√								√			
Liquid-wall heat transfer coefficient	√			√	√			√								√	√			√		
Bed radial thermal conductivity	√			√	√										√	√	√					
Wetting efficiency	√	√	√		√	√	√	√				√						√	√	√	√	√
Pressure drop	√	√			√	√						√							√			
Liquid holdup	√	√			√		√												√			

Re Reynolds number
Fr Froud number
We Weber number
X Lockhart-Martinelli number
St Stokes number
Sc Schmidt number

Ga Galileo number
Ca Capillary number
Pe Peclet number
Bi Biot number
ρ Density
α Bed correction factor

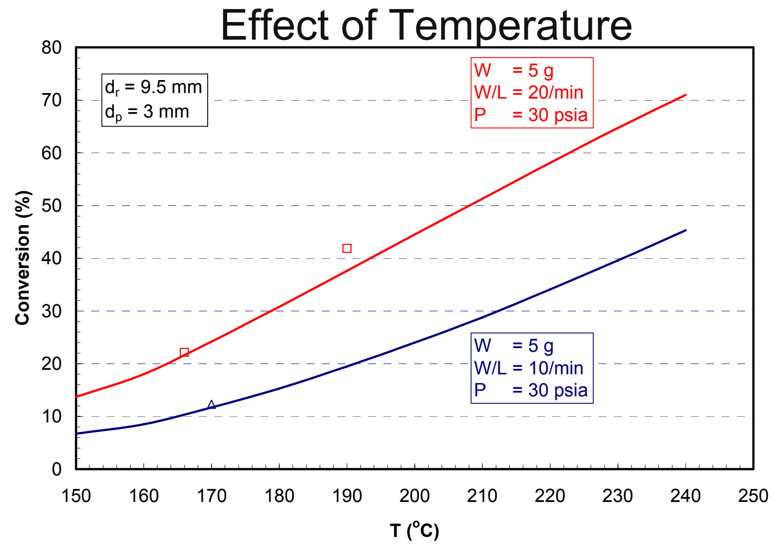
d_p Catalyst diameter
d_r Reactor diameter
Φ Sphericity factor
ε Void fraction

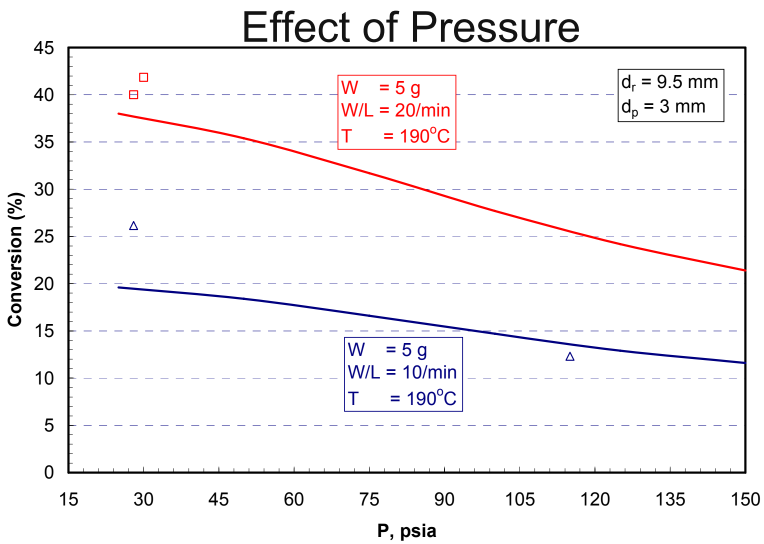
Subscripts:
l Liquid **g** Gas

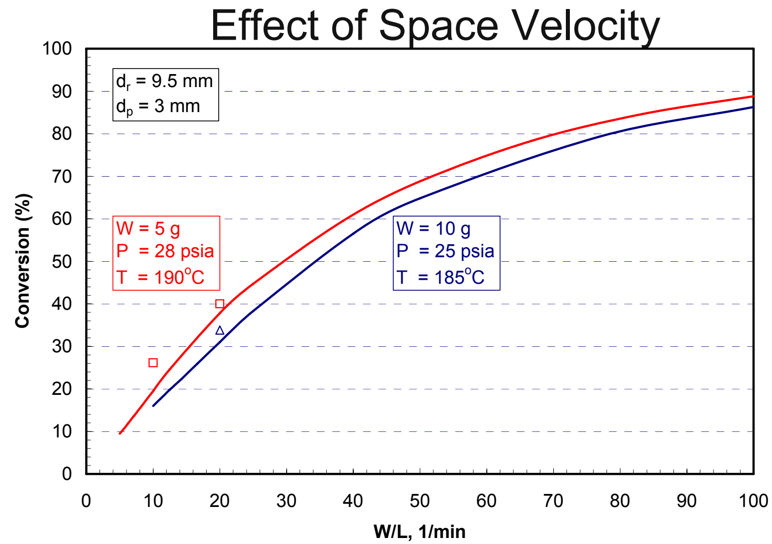
References: Ind. Eng. Chem. Res., 37 (1998), 4542-4550
Ind. Eng. Chem. Res. 42 (2003) 222-242
Chem. Eng. Sci., 54 (1999) 5229-5337

Tubular Trickle Bed Reactor Comparison with APCI Data

- Models written on GCtool platform
  - First-order kinetics with internal & external mass transfer
  - Trickle bed hydrodynamics
  - ODEs for T and species flow
- TBR data for 5% Pd on alumina catalyst, kinetic data for 4% Pd on Li aluminate

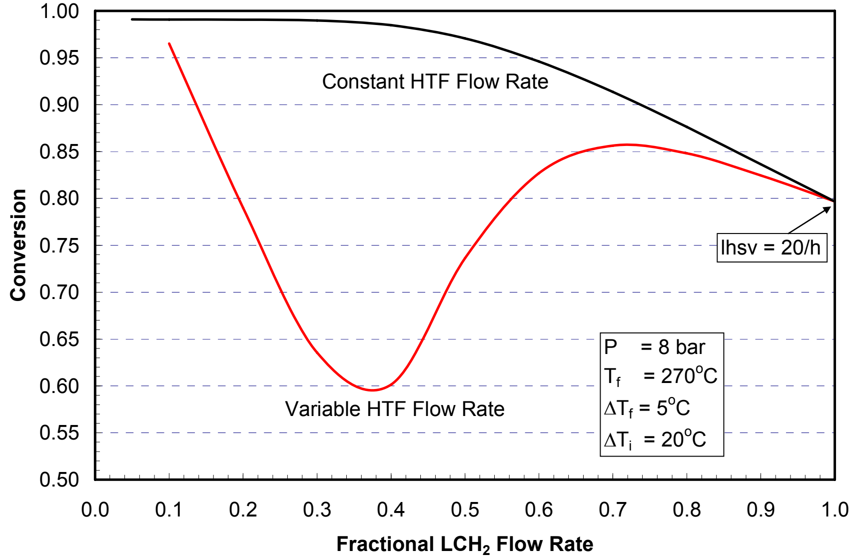


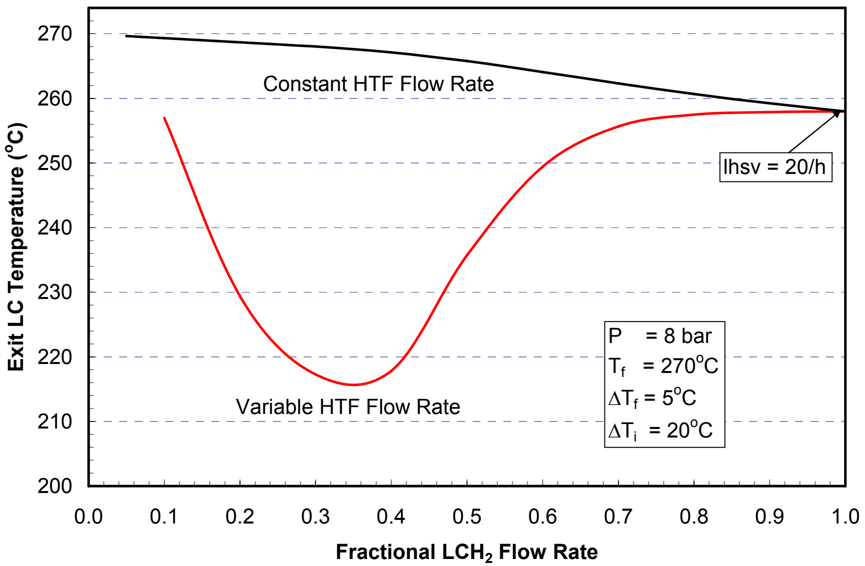




Part-Load Performance

- Higher conversion with constant HTF flow rate especially at low loads
- Transient performance
  - Actual conversion on a drive cycle may be higher or lower than the steady-state value
  - Response time
  - Pressure control?
  - Buffer storage?





Argonne HTCHS: System Analysis

Dehydrogenation Reactor

- T_R function of $P(H_2)$, conversion, ΔH, ΔS, and ΔT_{eq}
- Trickle flow, 20 h^{-1} LHSV
- Catalyst supported on 40-PPI foam
- HX tubes with 90° inserts
- AL-2219-T81 alloy, 2.25 SF
- 2 cm insulation thickness

Heat Transfer Fluid

- XCELTHERM ®
- 5°C ΔT in DeH2-HX, T_{HTF} - T_R = 50°C

HEX Burner

- Non-catalytic, spent H_2 and 5% excess spent air
- Counterflow microchannel, inconel
- 100°C approach temperature

H_2 Cooler

- LCH2 coolant, $T_{outlet} = T_{FC}$
- Counterflow, microchannel, SS

Recuperator

- LC/LCH2 HX, $T_{LCH2} = T_R - 10$°C
- Counterflow, microchannel, SS

LC Radiator

- T_{LC} = 70°C
- Integrated with FCS radiator
- W and V not included in HTCHS

LCH_2/LC Storage Tank

- Single tank design, HPDE construction
- 10% excess volume

Pumps

- HTF pressure head: 1 bar
- LCH2 pressure head: 8 bar

H_2 Separation

- Coagulating filter

H_2 Buffer Storage

- 20 g H_2 at 80°C, $P(H_2)$
- AL-2219-T81 alloy tank, 2.25 SF

Miscellaneous