Hydrogen Storage Materials Requirements to Meet the 2017 On Board Hydrogen Storage Technical Targets

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Materials Requirements Webinar
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Hydrogen Storage Engineering
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Webinar Objective

Give guidance to the

materials development community as to the

important materials characteristic for both

adsorbent and chemical hydrides

required to meet the DoE Technical Targets for

Onboard Hydrogen Storage Systems

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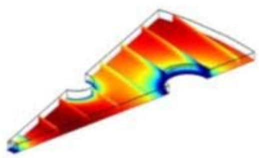
Why Perform Materials Development and System Engineering in Parallel?

continuous feedback with system design
identifying materials requirements



Materials → Thermal Management → H_2 Storage BoP → Fuel Cell → Vehicle → Wheels

Materials	Thermal Management	H_2 Storage BoP	Fuel Cell → Vehicle → Wheels
Engineered Materials Properties	Heat Transfer Designs	BoP Component Requirements	What is Needed of the Hydrogen Storage Media & System

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Technical Targets for Systems

DoE Targets for On-Board Hydrogen Storage Systems for Light Duty Vehicles

Target	Units	2017 DOE Goal (System)	Ultimate DOE Goal (System)
Gravametric Capacity	kg H2/kg system	0.055	0.075
Volumetric Capacity	kg H2/L system	0.04	0.07
System Cost	$/kWh net	TBD	TBD
Fuel Cost	$/gge at pump	2-6	2-3
Min Operating Temp	°C	-40	-40
Max Operating Temp	°C	60	60
Min Delivery Temp	°C	-40	-40
Max Delivery Temp	°C	85	85
Cycle Life	Cycles	1500	1500
Min Delivery Pressure	bar	5	3
Max Delivery Pressure	bar	12	12
Onboard Efficiency	%	90	90
Well to Power Plant Efficiency	%	60	60
System Fill Time	min	3.3	2.5
Min Full Flow Rate	(g/s/kW)	0.02	0.02
Start Time to Full Flow (20°C)	sec	5	5
Start Time to Full Flow (-20°C)	sec	15	15
Transient Response	sec	0.75	0.75
Fuel Purity	%H2	99.97	99.97
Permeation, Toxicity, Safety	Scc/h	Meets or Exceeds Standards	Meets or Exceeds Standards
Loss of Useable Hydrogen	(g/h)/kg H2 store	0.05	0.05

$$v_{media} + v_{components} = V_{system}$$
$$m_{media} + m_{components} = M_{system}$$
$$c_{media} + c_{components} = C_{system}$$

&

How do thermodynamic properties affect mass and volume of system?

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Agenda

- **General Outline**
  - Define System
  - Define Technical Barriers
  - Identify Materials Properties That Will Meet Targets
- **Chemical Systems**
  - Troy Semelsberger, System Architect Chemical Systems
  - Kriston Brooks, Chemical System Designer
- **Adsorbent Systems**
  - Don Siegel, Adsorbent System Architect
  - Bruce Hardy, Transport Phenomenon Technology Lead

Chemical Hydrogen Storage Material Requirements

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DOE Webinar: 25 June 2013

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U.S. Department of Energy
Energy Efficiency and Renewable Energy
Bringing you a prosperous future where energy is clean, abundant, reliable, and affordable

Key Takeaways for Today

Parameter	Units	Range*
Minimum Material capacity (liquids)	$g_{H2} / g_{material}$	~ 0.078 (*0.085*)†
Minimum Material capacity (solutions)	$g_{H2} / g_{material}$	~ 0.098 (*0.106*) †
Minimum Material capacity (slurries)	$g_{H2} / g_{material}$	~ 0.112 (*0.121*) †
Kinetics: Activation Energy	kcal / mol	28–36
Kinetics: Preexponential Factor		$4 \times 10^9 – 1 \times 10^{16}$
Endothermic Heat of Reaction	kJ / mol H_2	≤ +17 (*15*) †
Exothermic Heat of Reaction	kJ / mol H_2	≥ -27
Maximum Reactor Outlet Temperature	°C	250
Impurities Concentration	ppm	No *a priori* estimates can be quantified
Media H_2 Density	kg H_2 / L	≥ 0.07
Regeneration Efficiency	%	≥ 66.6%
Viscosity	cP	≤ 1500

** (a) parameter values are based on a specific system design and component performance with fixed masses and volumes (b) values outside these ranges do not imply that a material is not capable of meeting the system performance targets (c) the material property ranges are subject to change as new or alternate technologies and/or new system designs are developed (d) the minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized*

† values outside of parentheses are the values that correlate to the idealized system design (i.e., 30.6 kg) and the values in parentheses are those that correlate to the base system design (36.3 kg)

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Introduction and Overview

Objective: Provide chemical hydrogen storage material property guidelines that will allow the overall system to meet the DOE 2017 performance targets

Approach:

1. Develop an integrated chemical hydrogen storage system for automotive applications
2. Develop a system model that predicts system performance using various drive cycles (*e.g., US06*)
3. Identify and size components that are material dependent *(e.g., reactor, heat exchanger, etc.,)*
   - Determine material properties for given component size
4. Determine material capacity to meet DOE 2017 performance targets

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Chemical Hydrogen Storage System

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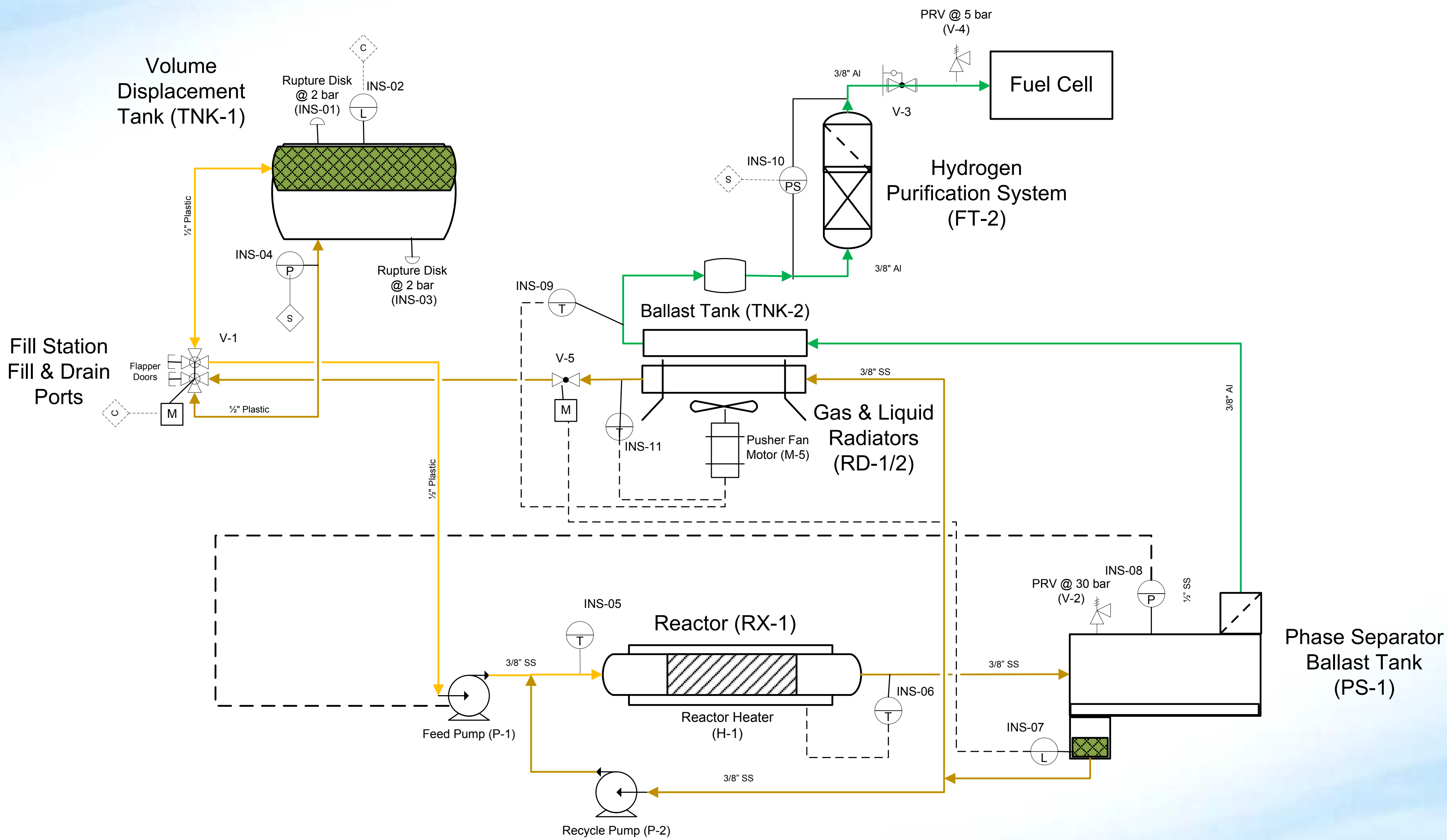
HSECoE Chemical Hydrogen Storage Baseline System



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Itemized Component List of our Baseline System

Item #	Description	Material	Wt (kg)	Vol (L)
Tanks and Tubing				
TNK-1	Volume Displacement Tank	High Density Polyethylene	6.2	65.5
NA	Fill and Drain Lines	10 ft of 1/2" Plastic	0.17	0.38
NA	Low T and P Lines	10 ft 3/8" Aluminum	0.12	0.2
NA	High T and P Lines	10 ft 3/8" Stainless Steel	0.38	0.22
INS-01	Rupture Disk		0.6	0.16
INS-02	Level Sensor for Volume Displacement Tank		0.6	0.16
INS-03	Rupture Disk		0.6	0.16
INS-04	Pressure sensor	316L SS	0.14	0.001
Feed Loop				
V-1	2 Multiport Valves with Actuator	Assured Automation	1.7	0.75
V-1	Flapper Valves		0.5	0.2
P-1	Feed Pump	KNF NF2.35	0.3	0.3
INS-05	Temperature sensor		0.1	0.02
RX-1	Reactor	SS tubing and stirrer	5	4
H-1	Reactor Heater		0.5	
INS-06	Temperature sensor		0.1	0.02
INS-07	Level Sensor for P/S		0.18	0.14
Recycle Loop				
P-2	Recycle Pump	KNF NF2.35	0.3	0.3

Item #	Description	Material	Wt (kg)	Vol (L)
Return Loop				
PS-1	Gas Liquid Separator	347/347L SS	3.2	3.7
INS-08	Pressure sensor	316L SS	0.14	0.001
V-2	Pressure Relief Valve		0.3	0.1
RD-2	Liquid Radiator	304 SS	2.08	2.9
RD-2	Liquid Radiator Header	304 SS	0.16	0.06
M-5	Liquid Radiator Fan Ultra Thin Line 12V Electric Fan (Puller)	Nylon	1	5.9
INS-11	Temperature sensor		0.1	0.02
V-5	Control Valve	Brass	1.7	0.75
Hydrogen Discharge				
FT-1	Coalescing Filter	SS	1.2	0.34
RD-2	Gas Radiator	304 SS	0.3	0.3
RD-2	Gas Radiator Header	304 SS	0.16	0.03
INS-09	Temperature sensor		0.1	0.02
INS-10	Pressure Switch		0.1	0.001
FT-2	H2 Clean-Up System		3.2	4
TNK-2	Additional Ballast Tank	Aluminum, L/D =4 , SF = 1.5	2.6	15
FT-4	Particulate Filter	SS	1.2	0.34
V-3	Pressure Regulator Gas		0.6	0.5
V-4	Pressure Relief Valve		0.6	0.16

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System Components for Projected System Design

Material Independent Components (BOP)

Required system components that are material property independent

e.g., valves, sensors, tubing, filters, regulators, …..

Material Dependent Components

Required system components that are material property dependent

- *Reactor*
- *Hydrogen purification*
- *Volume displacement Tank*
- *Ballast tank*
- *Heat exchangers*

System Independent Material Properties

Required system components that are system independent

- *Media hydrogen storage capacity*
- *Regeneration efficiency*
- *Fuel cost*
- *Shelf-life*

	Baseline		Idealized	
Component	Mass (kg)	Volume (L)	Mass (kg)	Volume (L)
BOP†	21.8	8.9	21.8	8.9
H_2 Purification*	3.2	4	*0*	*0*
Heat Exchangers*	3.7	9.2	3.7	9.2
Reactor*	5	4	*2.5*	*2*
Ballast Tank*	2.6	15	2.6	15
Media + Tank‡	≤ 65.7	≤ 98.9	≤ 71.4	≤ 104.9

† BOP mass and volume were held constant
** Component masses or volumes were sized independent of the material to maintain a material independent system*
‡ volume displacement tank mass was fixed at 6.2 kg

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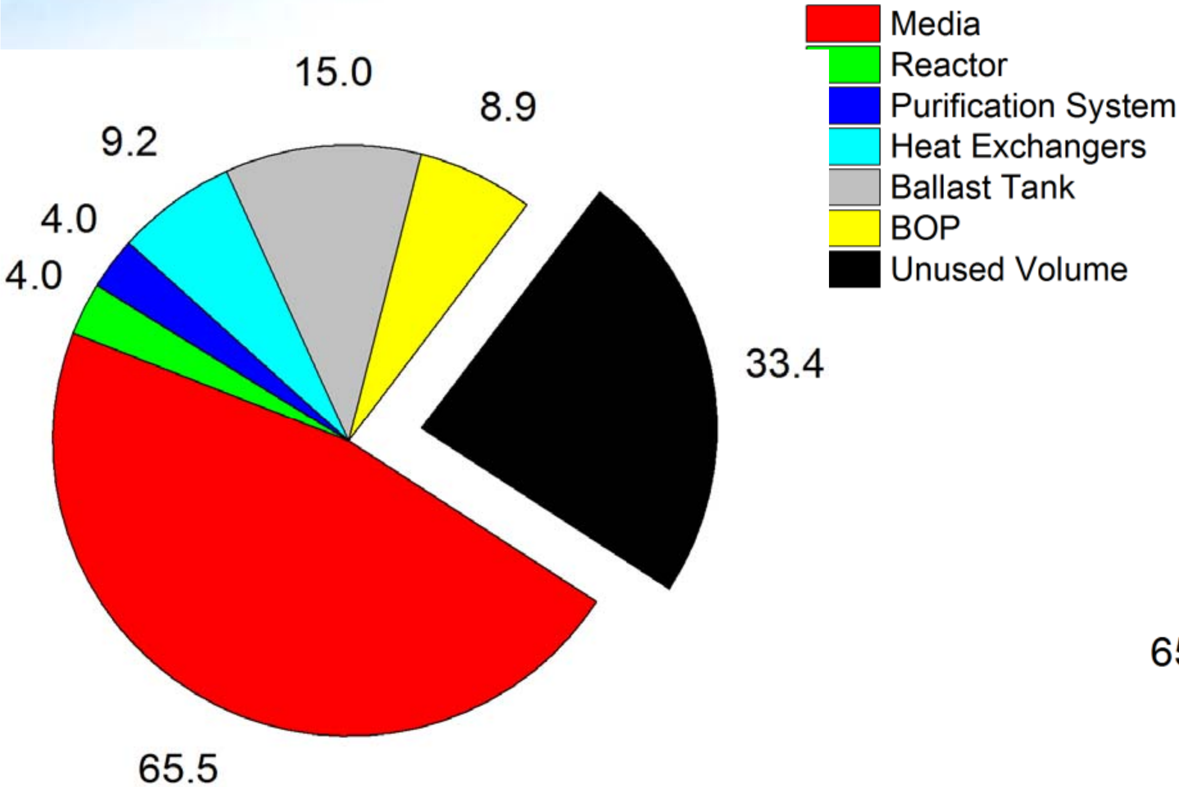
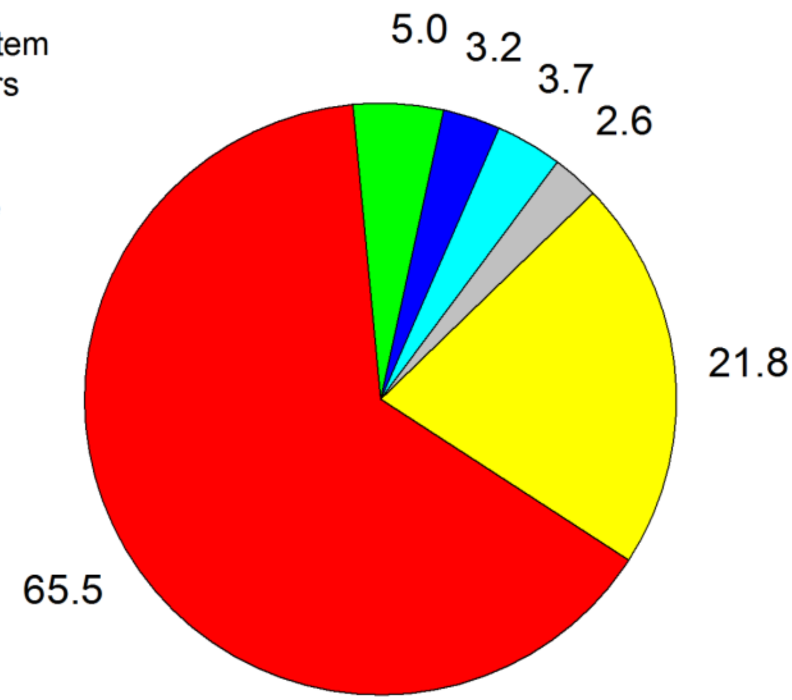
Baseline System Mass and Volume to Meet DOE 2017 Targets

Volume Pie Chart* (L)



Mass Pie Chart* (kg)



Total System Volume = 107 L
DOE Volume Target = 140 L
System Volume (excluding media) = 41.5 L
Unused (available) Volume = 33 L

Total System Mass = 102 kg
DOE Mass Target = 102 kg
System Mass (excluding media) = 36.3 kg
Unused (available) Mass = 0 kg

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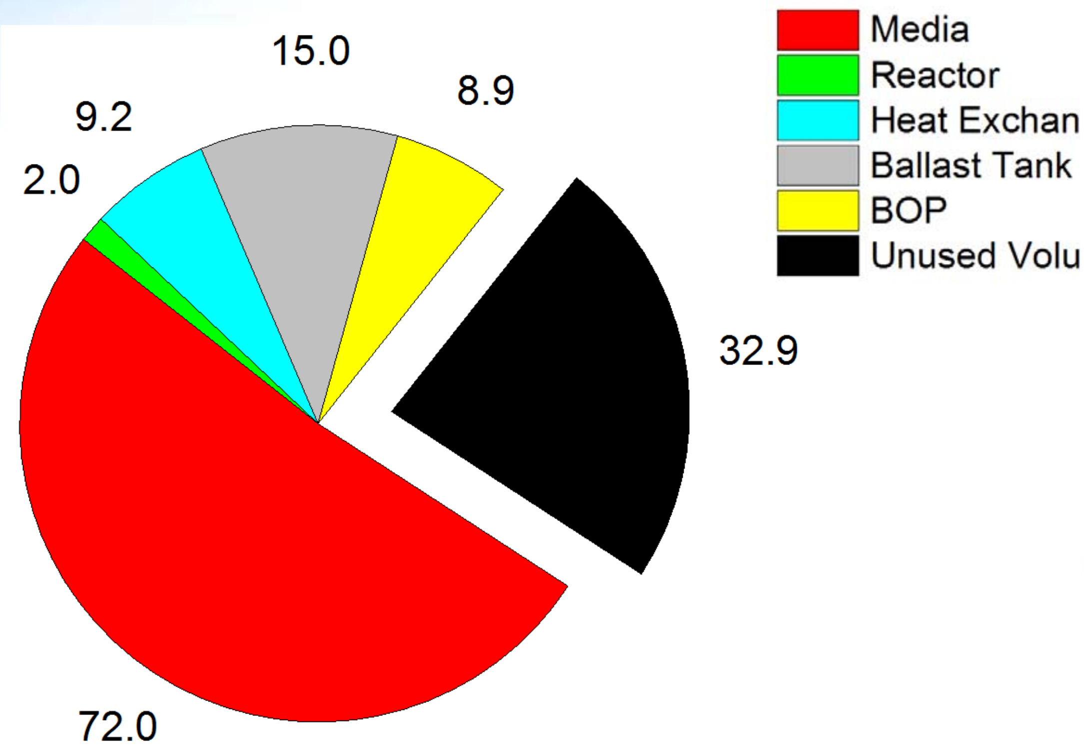
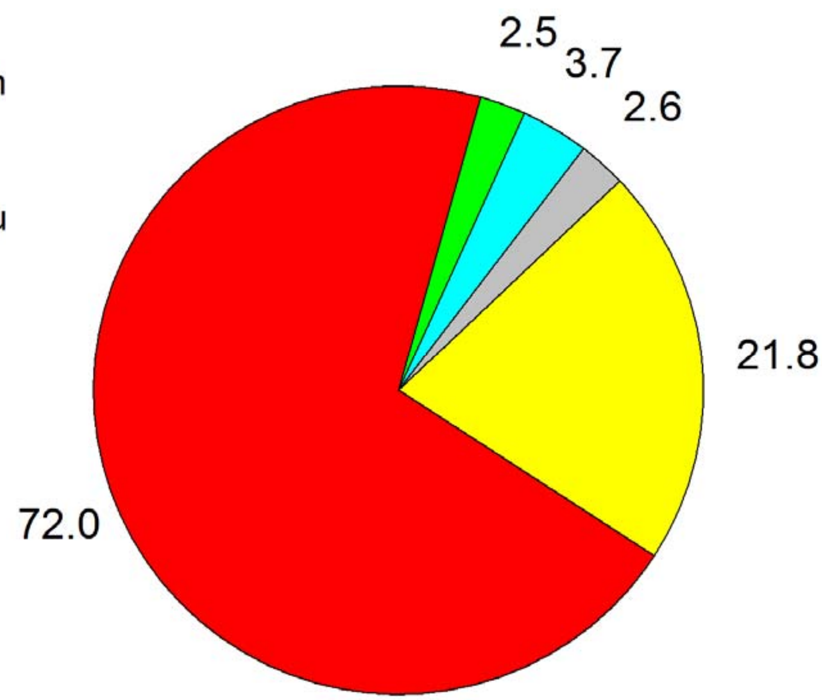
** Values correspond to our baseline system design*

Idealized System Mass and Volume to Meet DOE 2017 Targets

Volume Pie Chart† (L)



Mass Pie Chart † (kg)



Total System Volume = 107 L
DOE Volume Target = 140 L
System Volume (excluding media) = 35 L
Unused (available) Volume = 33 L

Total System Mass = 102 kg
DOE Mass Target = 102 kg
System Mass (excluding media) = 30.6 kg
Unused (available) Mass = 0 kg

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† Values correspond to our idealized system design (30.6 kg), no purification, reactor volume = 2 L, and reactor mass = 2.5 kg

Material Properties

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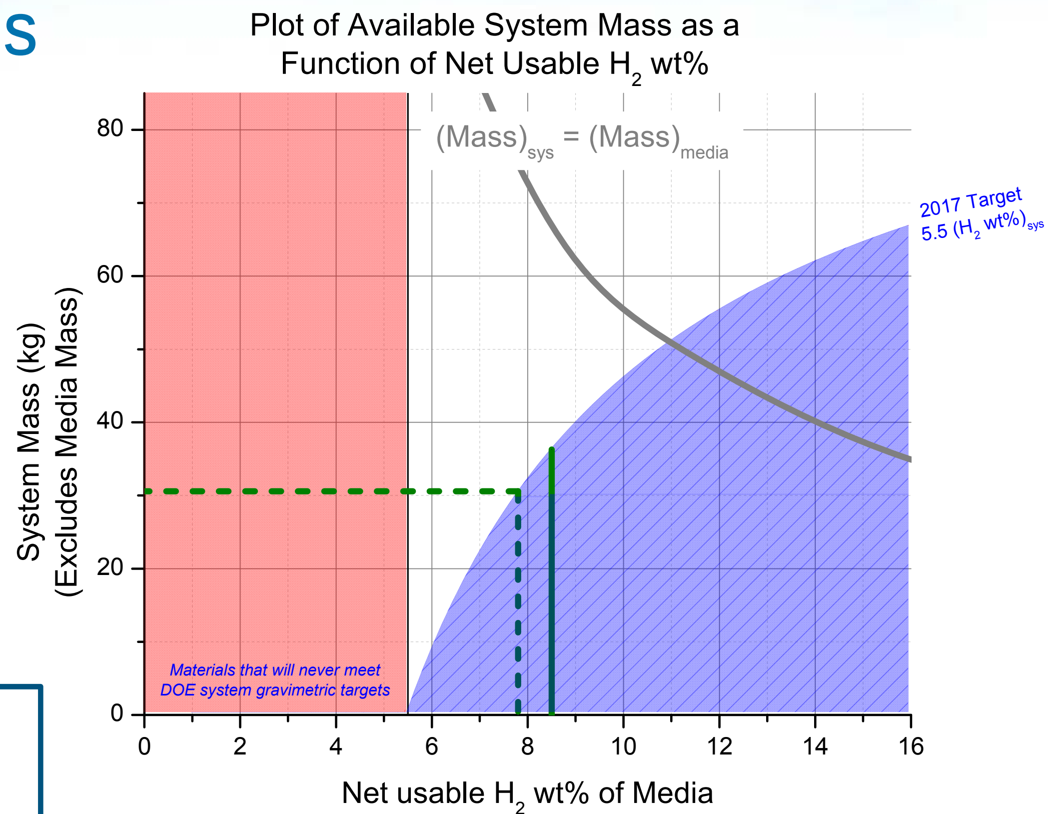
Material Capacity for Liquids

Objective:

Determine net usable H_2 capacity for chemical hydrogen materials to meet 2017 DOE system targets given our idealized system mass (excludes media) of 30.6 kg and our baseline system (excludes media) of 36.3 kg



Assumptions

- $Fixed\ reactor\ mass = 2.5\ kg\ \ (5\ kg)$
- $Fixed\ purification\ mass = 0\ kg\ \ (3.2\ kg)$
- $System\ mass\,(excludes\ media) = 30.6\ kg\ \ (36.3\ kg)$
- *Media is a liquid with no phase change*

Property Range

$$\left(Net\ usable\ wt.\ fraction\ H_2\right)_{liquid} = \gamma_m \approx 0.078\,(0.085)^* \ g_{H_2}/g_{liquid}$$

** value 0.085 represents the minimum capacity for our given baseline system mass (36.3 kg); the minimum capacity can be lowered if reductions in reactor mass, purification mass or system component masses are realized (e.g., if purification is eliminated and reactor mass halved then a liquid material capacity of 0.078 is expected)*

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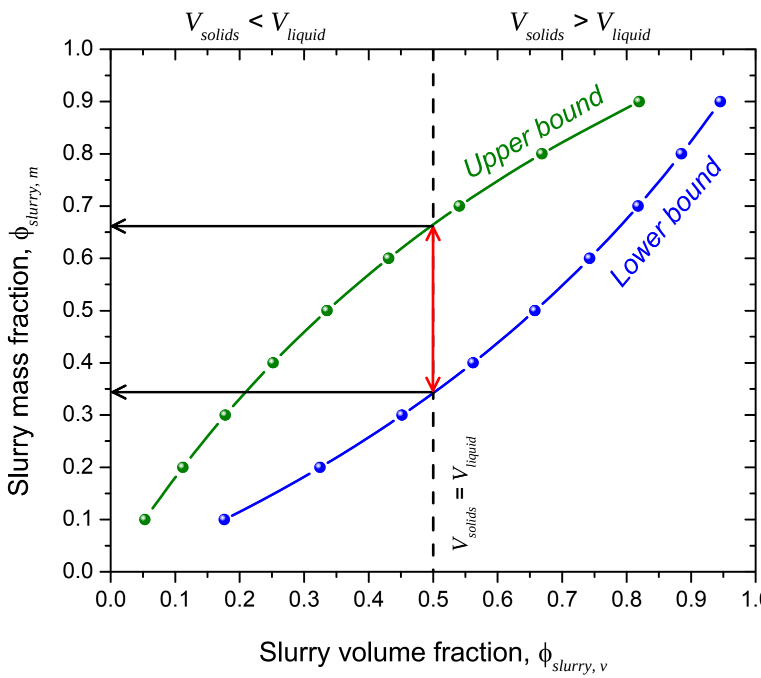
Material Capacity for Slurries

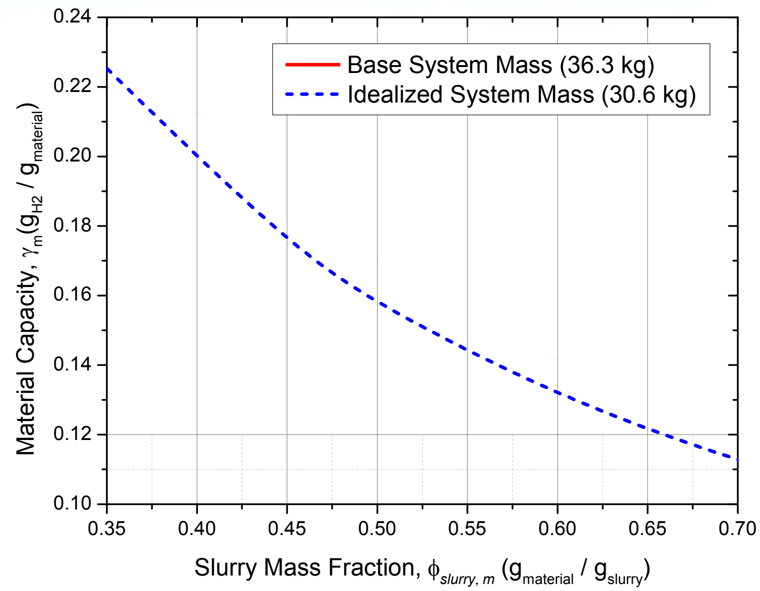
Objective:

Determine required material capacities as a function of slurry mass fraction loadings to meet a 2017 DOE system targets given our idealized system mass (excludes media) of 30.6 kg and our baseline system (excludes media) of 36.3 kg



Upper bound calculated using $\rho_{material}$ = 1.50 g/mL, $\rho_{carrier}$ = 0.75 g/mL, and $\gamma_{material}$ = 0.100 $g_{H2}/g_{material}$
Lower bound calculated using $\rho_{material}$ = 0.80 g/mL, $\rho_{carrier}$ = 1.50 g/mL, and $\gamma_{material}$ = 0.152 $g_{H2}/g_{material}$

Plot of slurry mass fractions and material capacities required for a base system mass of 36.3 kg and an idealized system mass of 30.6 kg



Assumptions

- $System\ mass\,(excludes\ media) = 30.6\ kg\ \ (36.3\ kg)$
- $Slurry\ is\ homogeneous\ and\ non\text{-}settling$

Property Range

$$\left(Max\ slurry\ volume\ fraction\right) = \phi_{slurry,v} = 0.5\ {mL_{solid}}/{mL_{slurry}}$$

$$\left(Slurry\ mass\ fraction\right) = \phi_{slurry,m} \approx\ 0.35 \sim 0.70\ {g_{solid}}/{g_{slurry}}$$

$$\left(Net\ usable\ wt.\ fraction\ H_2\right)_{solid} = \gamma_m\ \approx\ 0.112\ (0.121)\ {g_{H_2}}/{g_{solid}}$$

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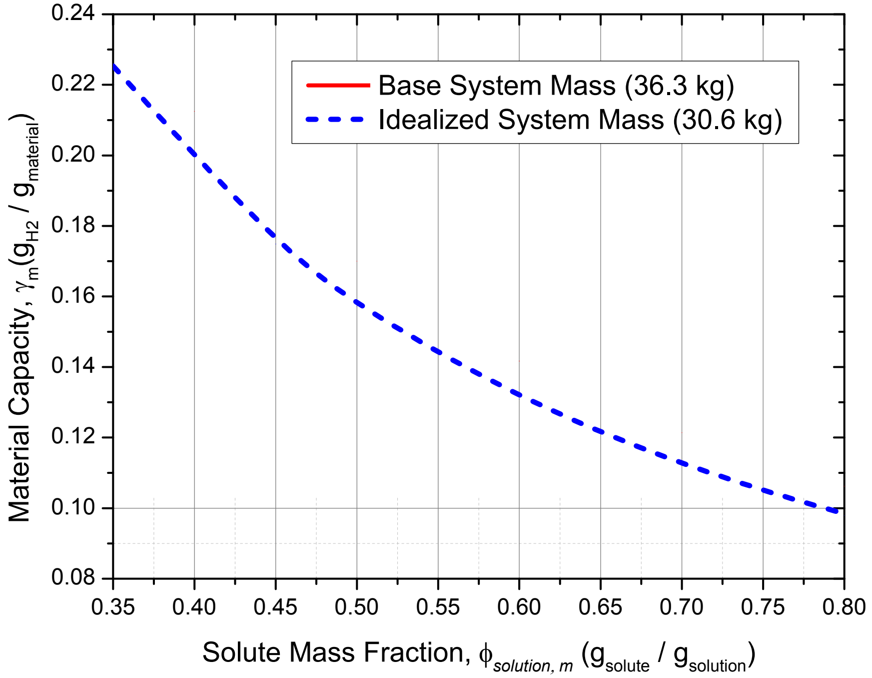
Material Capacity for Solutions

Objective:

Determine required material capacities as a function of solute mass fraction loadings to meet 2017 DOE system targets given our idealized system mass (excludes media) of 30.6 kg and our baseline system (excludes media) of 36.3 kg

Plot of solute mass fractions and material capacities required for a base system mass of 36.3 kg and an idealized system mass of 30.6 kg



Assumptions

- $System\ Mass\,(excludes\ media) = 30.6\ kg\ \ (36.3\ kg)$
- *No phase change*
- *Volume additivity*
- $Maximum\ solute\ mass\ fraction = 0.8\ g_{solute}/g_{solution}$
- *Solvent is non-hydrogen bearing*

Property Range

$$(Solute\ mass\ fraction) = \phi_{solution,m} \approx 0.35 \sim 0.8\ g_{solute}/g_{solution}$$

$$(Net\ usable\ wt.\ fraction\ H_2)_{solute} = \gamma_m \approx 0.098\ (0.106)\ g_{H_2}/g_{solute}$$

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Note: a solution is a two component homogeneous mixture containing a solute and a solvent. Our solution assumes a hydrogen bearing solute dissolved in a non-hydrogen bearing solvent.

Reaction Kinetics

Objective:

Determine viable kinetics parameters to meet volume and shelf-life constraints given our baseline system design and assumptions

Constraints/Assumptions

- $t_{shelf\ life}\Big|_{X=7.2\%}^{T=60^o C} \geq 60\ days$
- $V_{PFR}\Big|_{X\ =\ 99\%}^{T\ =\ 175^o C} \leq 4\ L$
- $F_{H_2}^{max}\Big|_{40kW_e} = 0.4\ \frac{mol\ H_2}{s}\left(0.8\ \frac{g\ H_2}{s}\right)$
- *Reaction is irreversible*

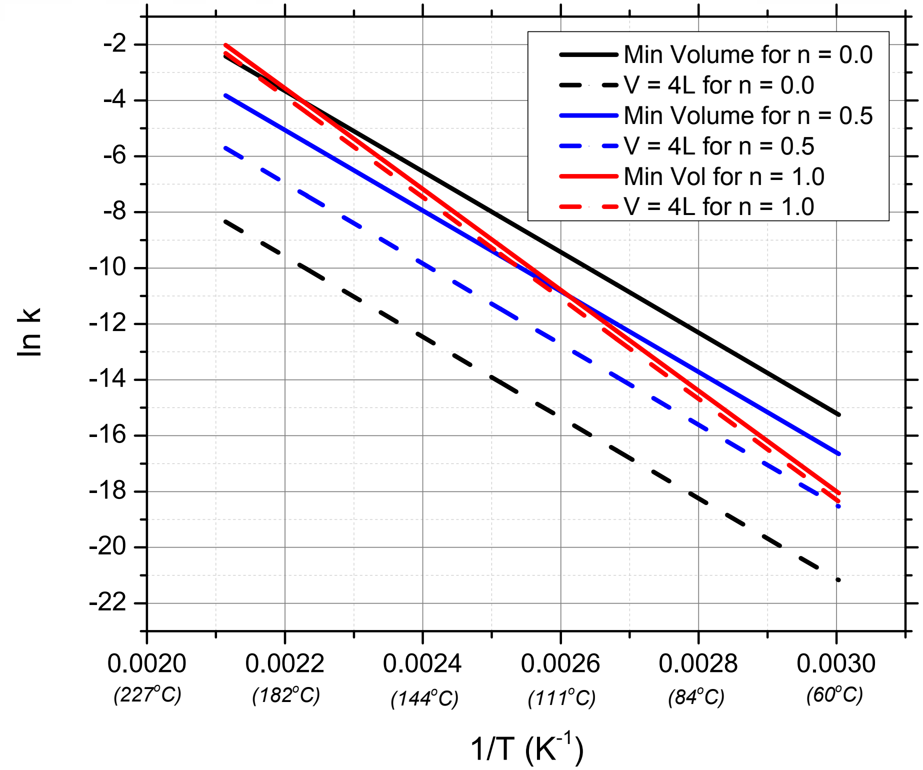
Variables

$$Activation\ Energy\ (E_a) = 24\text{-}37\frac{kcal}{mol}$$

$$Preexponential\ Factor\ (A) = 10^5\text{-}10^{17}$$

$$Reaction\ Order\ (n) = 0\text{-}1.5$$

Arrhenius plots showing the desirable ranges of activation energies (kcal/mol K) and preexponential factors as a function of reaction order



Property Ranges*

$$E_a \approx 28-36\ \frac{kcal}{mol}$$

$$A \approx 4\ x\ 10^9 - 1\ x\ 10^{16}$$

$$Reaction\ order\ n = 0\text{-}1$$

* *these values do not take into account catalytic processes*

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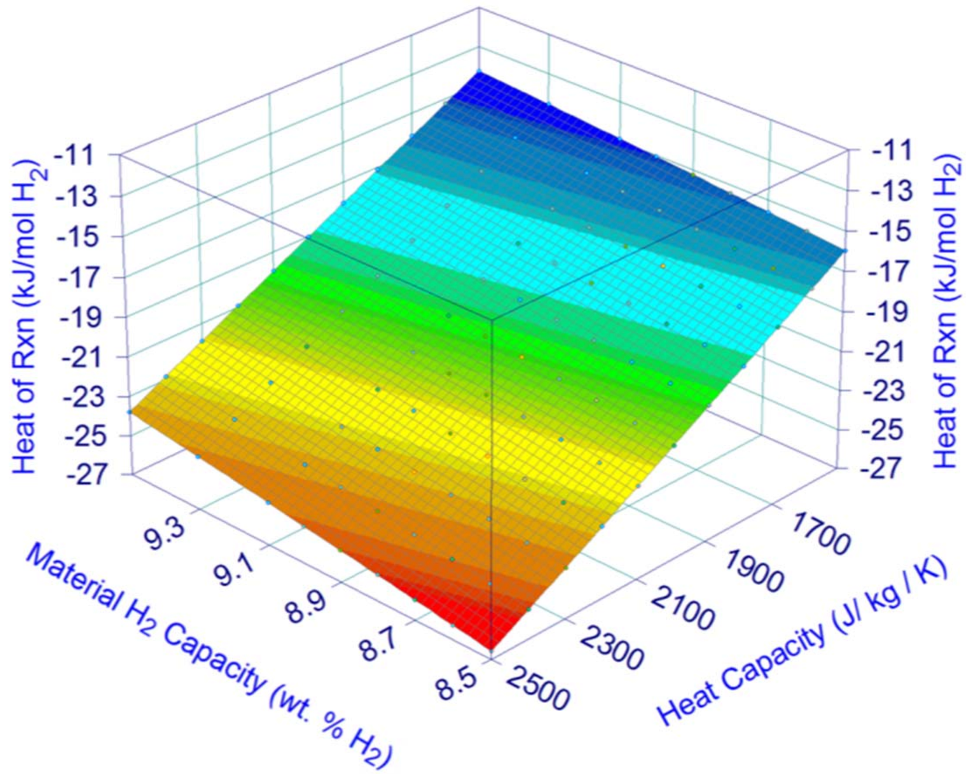
Exothermic Heat of Reaction: System Materials

Objective:

Determine the highest exothermic heat of reaction that will prevent the system materials from being exposed to temperatures greater than 250°C



Constraints/Assumptions

- *System is bounded by the design to accommodate ammonia borane*
- *Material inlet temperature = 24°C*
- *Maximum system temperature = 250°C*
- *Up to 50% recycle ratio*

Variables

$$C_{p,m} = 1500 - 2500 \ J/kg\ K$$

$$(net\ usable\ wt.\ fraction\ H_2)_{material} = \gamma_m \approx 0.085 - 0.092$$

Property Range

$$\Delta H_{rxn} \geq -27 \frac{kJ}{mol\ H_2}$$

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Endothermic Heat of Reaction: On-board Efficiency

Objective:

Determine maximum heat of reaction to meet 90% on-board efficiency given our system designs and assumptions

Assumptions

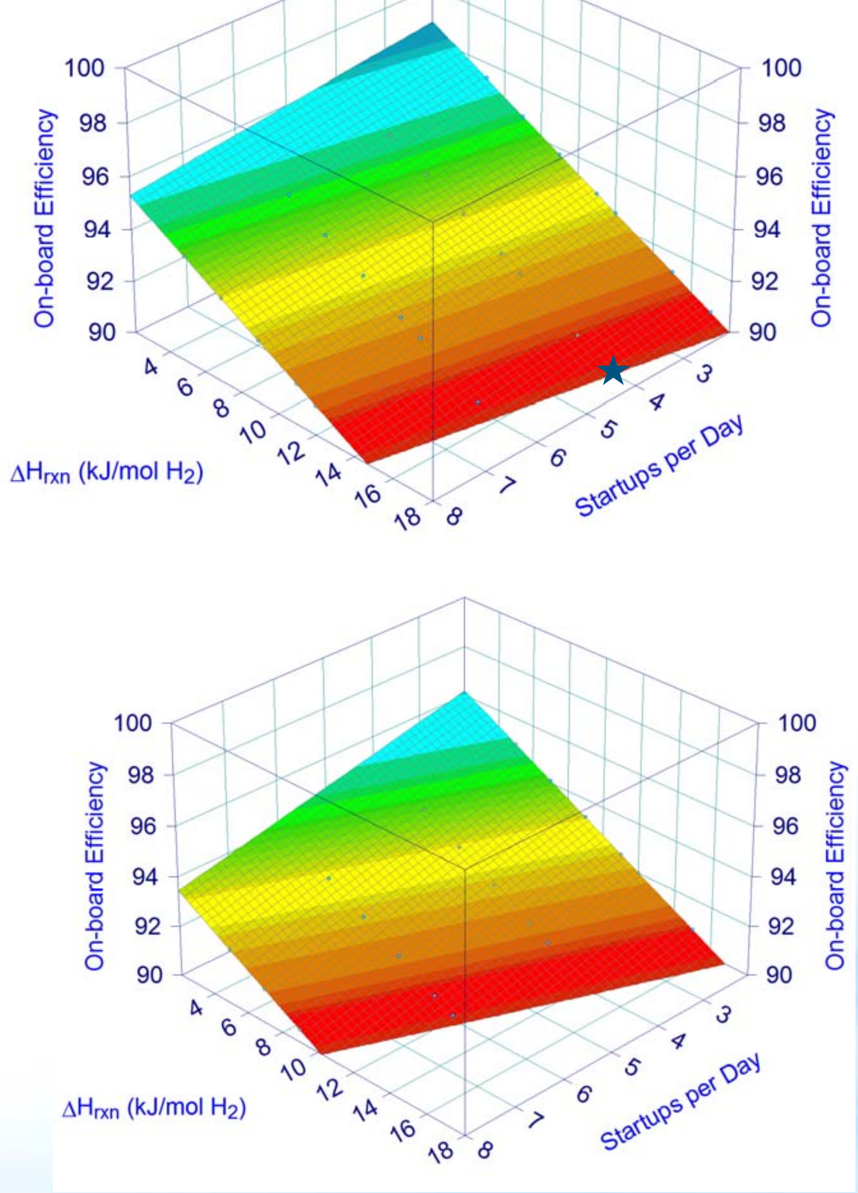
- *No heat recovery*
- *Fixed reactor mass* $= 2.5\ (5.0)\ kg\ SS$
- *Cold Start Up* $\equiv \Delta T = (T_{reactor} - T_{amb}) = 150\ ^{\circ}C$
- *4 Cold Start Ups per day*
- *Average miles driven per day* $= 41$
- *neat liquid with* $\bar{C}_p = 1.6 \frac{J}{g\ K}$

Property Range

$$\Delta H_{rxn} \leq +17\ (15) \frac{kJ}{mol\ H_2}$$

$$for\ \ \eta_{onboard}\Big|_{\Delta T = 150^{\circ} C}^{SU = 4} = 90\%$$

2.5 kg SS Reactor



Media Hydrogen Density: Volume Displacement Tank

Objective:

Determine lower limit on the media hydrogen density subject to a maximum tank mass of 6.2 kg

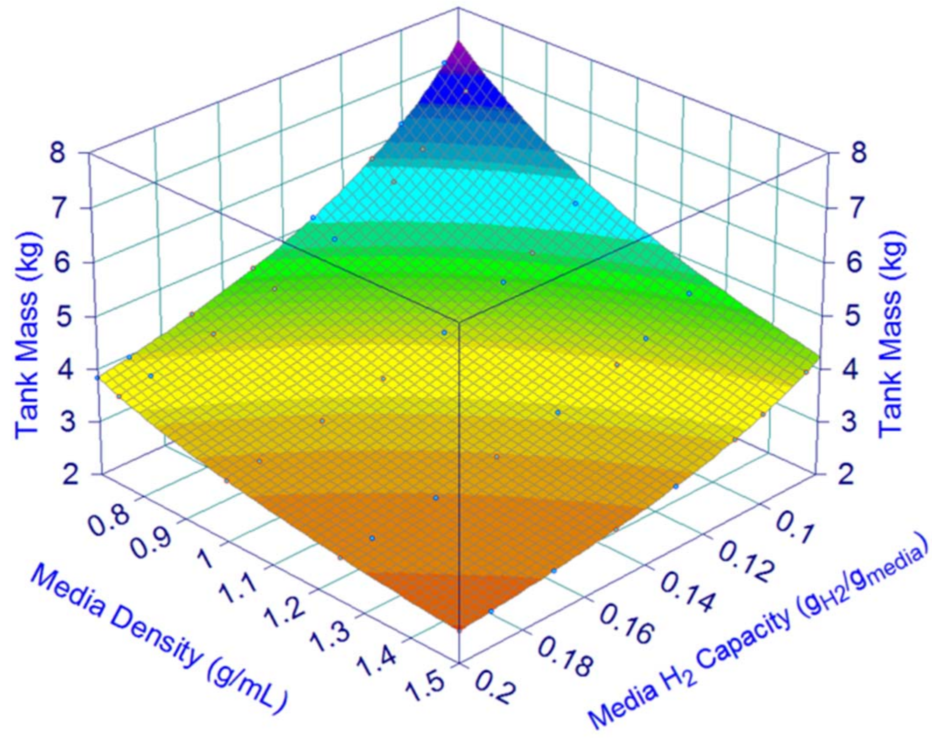
Constraints/Assumptions

- *H_2 Conversion = 99%*
- *On-Board Efficiency = 95%*
- *Rectangular, Conical bottom HD Polyethylene Tank, 15" tall*
- *Tank Mass ≤ 6.2 kg*

Variables

$$media\ H_2\ capacity = 8.0 - 18.5\ wt.\%$$

$$media\ density = 0.7 - 1.5\ \left(\frac{g}{mL}\right)_{media}$$



Property Range

$$\left(H_2\ density\right)_{media} > 0.07\ \frac{kg\ H_2}{L}$$

$$for\ a\ tank\ mass\ \leq\ 6.2\ kg$$

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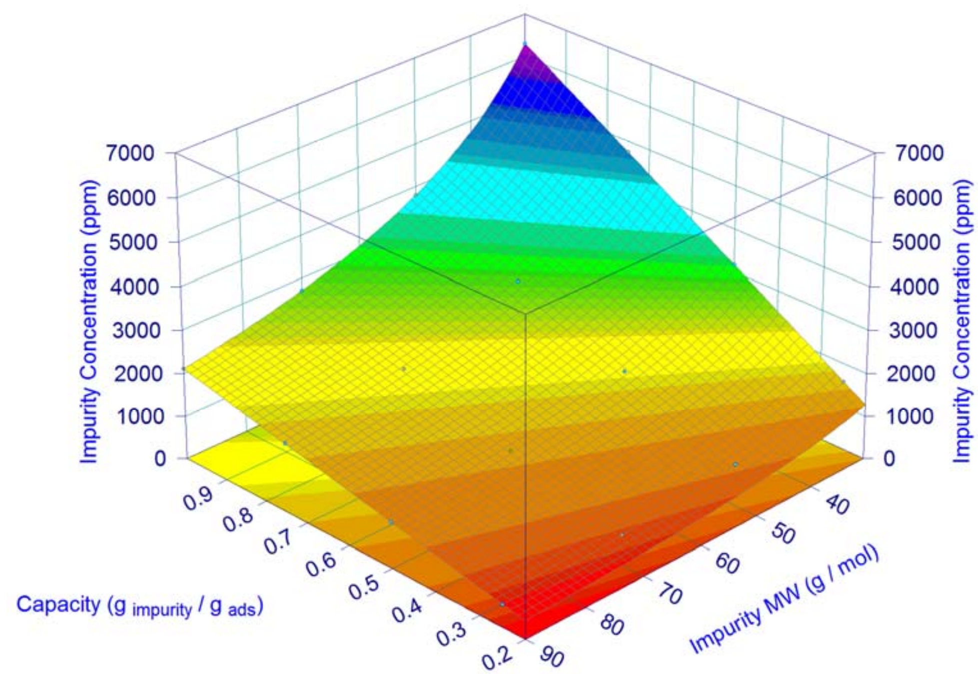
Fuel Cell Impurities

Objective:

Determine the maximum impurity concentration given on our baseline system design and assumptions

Maximum fuel cell impurity (ppm) as a function of scrubbing capacity ($g_{impurity}$ / g_{ads}) and impurity molecular weight (g/mol) for a fixed purification componenet mass of 3.2 kg



Constraints/Assumptions

- *Purification Mass* $\leq$ *3.2 kg*
- *Adsorbent based technology*
- H_2 *Purity = 99.97%*
- *Replacement Frequency = 1800 miles*

The maximum impurity concentration allowed for a fixed purification mass of 3.2 kg will be a function of:

- *Impurity type (e.g., fuel cell or inert diluent)*
- *Chemical and physical properties of the impurity*
- *Hydrogen purification technology*
- *Recycle/Regeneration cost and efficiency*
- *Material cost and availability*

SAE J2719 April 2008 Hydrogen Quality Guideline for FCV	
Impurity	ppm
Helium	300
Inert gases (N_2, Ar)	100
Carbon dioxide	2
Carbon monoxide	0.2
Sulfur compounds	0.004
Formaldehyde	0.01
Formic acid	0.2
Ammonia	0.1
Total halogenates	0.05
Hydrogen Purity	≥ 99.97%

Property Range

The maximum allowed impurity concentration cannot be calculated *a priori*. Therefore, the impact of impurities generated from hydrogen storage materials should be examined on a case-by-case basis

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Summary: Material Property Guidelines

Parameter	Symbol	Units	Range*	Influence	Assumptions
Minimum Material capacity (liquids)	γ_{mat}	g $_{H2}$ / g $_{material}$	~ 0.078 (*0.085*)†	System	• System mass (excludes media) = 30.6 kg (36.3 kg) • 5.6 kg of H_2 stored • Liquid media (neat) • Media density = 1.0 g/mL
Minimum Material capacity (solutions)	γ_{mat}	g $_{H2}$ / g $_{material}$	~ 0.098 (*0.106*) †	System	• System mass (excludes media) = 30.6 kg (36.3 kg) • Solute mass fraction = 0.35 ~ 0.80 • Solution density = 1.0 g/mL
Minimum Material capacity (slurries)	γ_{mat}	g $_{H2}$ / g $_{material}$	~ 0.112 (*0.121*) †	System	• System mass (excludes media) = 30.6 kg (36.3 kg) • Non-settling homogeneous slurry • Slurry mass fraction = 0.35 ~ 0.70 • Slurry volume fraction = 0 ~ 0.5 • Slurry density = 1.0 g/mL
Kinetics: Activation Energy	E_a	kcal / mol	28–36	Reactor and Shelf life	• $V_{reactor} \leq 4$ L • Shelf life ≥ 60 days • Reaction order, n = 0 – 1
Kinetics: Preexponential Factor	A		$4 \times 10^9 – 1 \times 10^{16}$		
Endothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	≤ +17 (*15*) †	On-board efficiency	• On-board Efficiency = 90% • # Cold Startups = 4 • ΔT = 150 °C with no heat recovery • neat liquid (Cp = 1.6 J/g K) • Reactor mass = 2.5 kg SS (5.0 kg SS)
Exothermic Heat of Reaction	ΔH_{rxn}	kJ / mol H_2	≤ -27		• T_{max} = 250°C • Recycle ratio @ 50%
Maximum Reactor Outlet Temperature	T_{outlet}	°C	250	Heat Exchanger	• Liquid Radiator = 2.08 kg • Gas Radiator = 0.3 kg • Ballast Tank = 2.6 kg
Impurities Concentration	y_i	ppm	No *a priori* estimates can be quantified	Purification	• $m_{adsorbent} \leq 3.2$ kg
Media H_2 Density	$(\gamma_{mat})(\phi_m)(\rho_{mat})$	kg H_2 / L	≥ 0.07	Tank size System	• HD polyethylene tank ≤ 6.2 kg
Regen Efficiency	η_{regen}	%	≥ 66.6%	Well-to-Power Plant Efficiency	• On-board Efficiency = 90% • WTPP efficiency = 60%
Viscosity	η	cP	≤ 1500	Fill time Pump size On-board efficiency	None

** (a) parameter values are based on a specific system design and component performance with fixed masses and volumes (b) values outside these ranges do not imply that a material is not capable of meeting the system performance targets (c) the material property ranges are subject to change as new or alternate technologies and/or new system designs are developed (d) the minimum material capacities are subject to change as the density of the composition changes due to reductions in the mass and volume of the storage tank or reductions in system mass are realized*

† values outside of parentheses are the values that correlate to the idealized system design (i.e., 30.6 kg) and the values in parentheses are those that correlate to the baseline system design (36.3 kg)

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Next Steps

- Researchers develop new materials
- Evaluate relative to targets conditions described herein
- As materials show promise, they can be evaluated using the *Chemical Hydrogen Storage System Models* developed by the HSECoE
    - System models offer higher fidelity and provide additional guidance relative to the specific properties of the newly developed materials

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Disclaimer

- The material properties detailed in this presentation were prepared in order to provide general guidance for chemical hydrogen storage researchers and therefore should not be taken as rigid constraints.
- The presented material properties were developed within the constraints of our system design, component sizing, assumptions, and system operating conditions. In addition, the ranges in material properties are not specific to a particular material, and therefore can be applied to the general class of chemical hydrogen storage media.
- Material property values just outside the material ranges presented do not imply that a material is not capable of meeting the system performance targets, but rather that the material will require further examination.
- The material property ranges are subject to change as new technologies and/or new system designs are developed.
- The minimum material capacities are subject to change if the density of the composition changes because of reductions in the mass and volume of the storage tank.
- Material properties that fall within the presented material properties do not establish commercial viability or commercial success.

Acknowledgements

Fuel Cell Technologies Office

Ned Stetson and Jessie Adams

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Adsorption-Based Hydrogen Storage System: An Overview

Don Siegel
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DOE Hydrogen Storage Webinar
June 25, 2013

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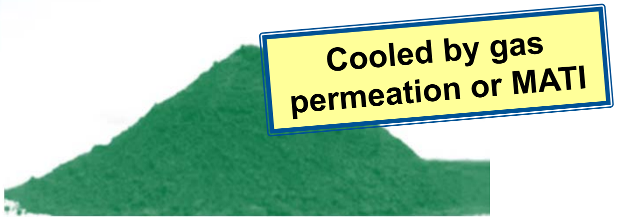
Goals for the Adsorbent System

- Model, design, construct, and evaluate an adsorbent-based hydrogen storage system that has the potential to meet DOE 2017 targets.
- Reveal design tradeoffs, e.g.:
  - → Gravimetric vs. volumetric density
  - → Capacity & cost vs. fill time
- Guide materials development
  - → Identify materials properties that most strongly impact system performance.

Many Design Choices

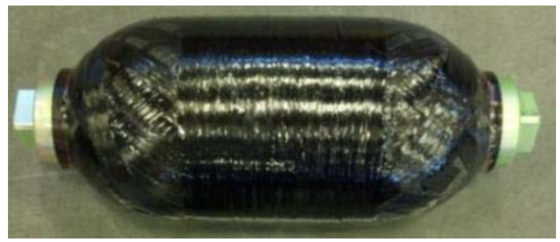
The Center has aimed to identify optimal combinations of adsorbent morphology, tank materials, and tank internals/heat exchanger design

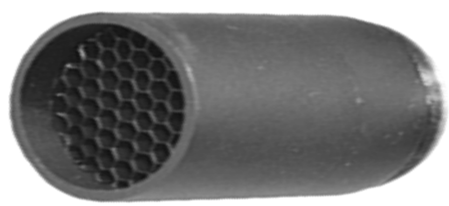


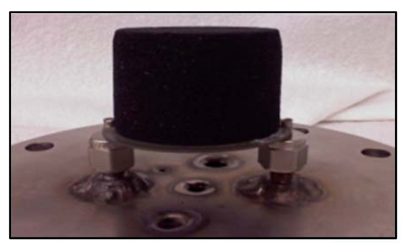
Powder Form

Pellet Form

Large Compressed Form
“Hockey Puck”







Adsorbent Form Selection:

- Powder Form
- Pelletized Form
- Monolithic Forms *(Puck)*
- ENG or other thermal enhancement

Tank Selection:

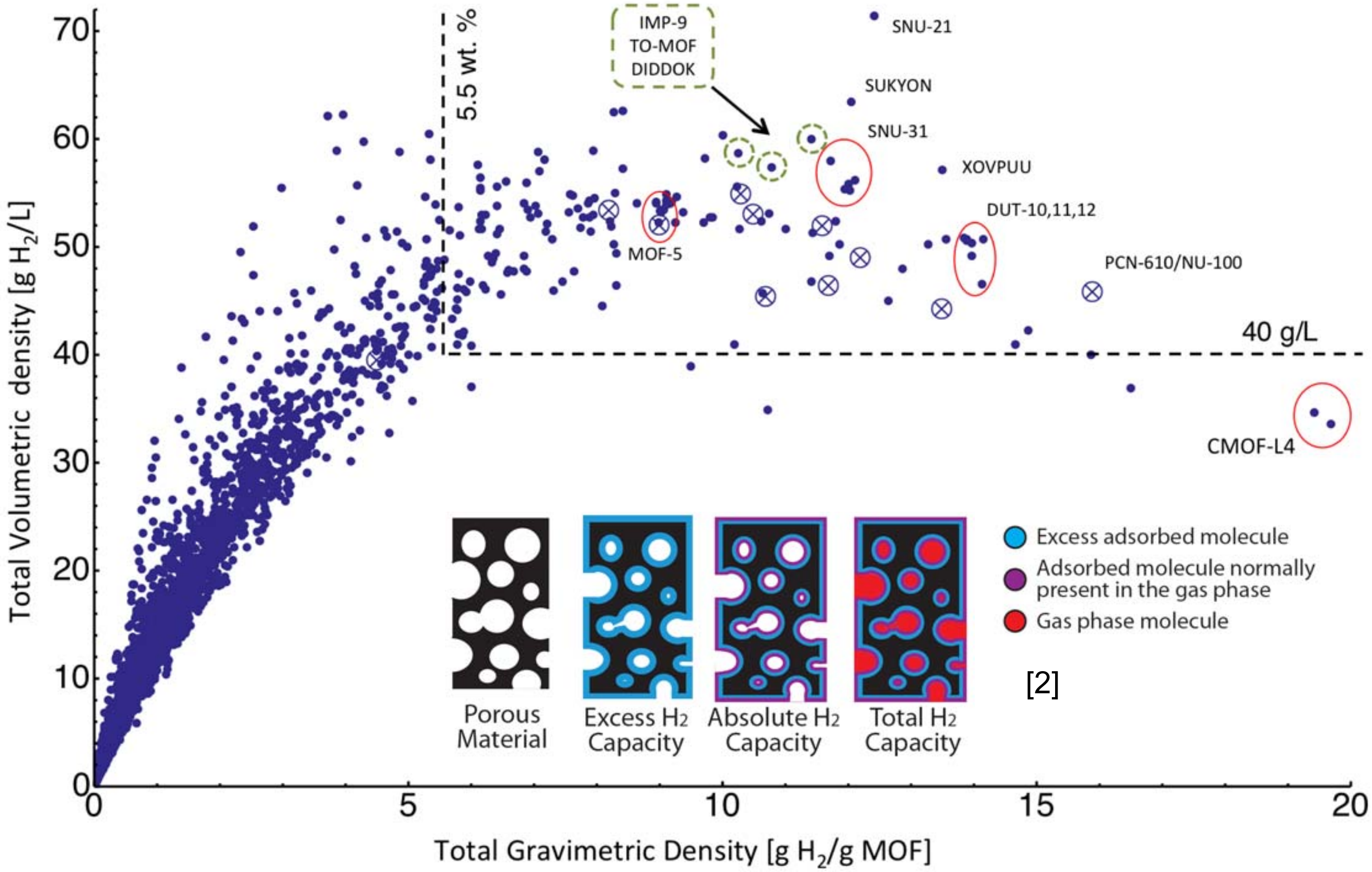
- Aluminum Type I
- Stainless Steel Type I
- Composite Fiber Type III
- Composite Fiber Type IV

Tank Internals/HX Selection:

- Resistance Heater
  - Fin and tube
  - Wire mesh
  - Hex/Honeycomb
- MATI / Isolated-H_2 insert

Materials Selection

The Center has selected MOF-5 as its baseline adsorbent

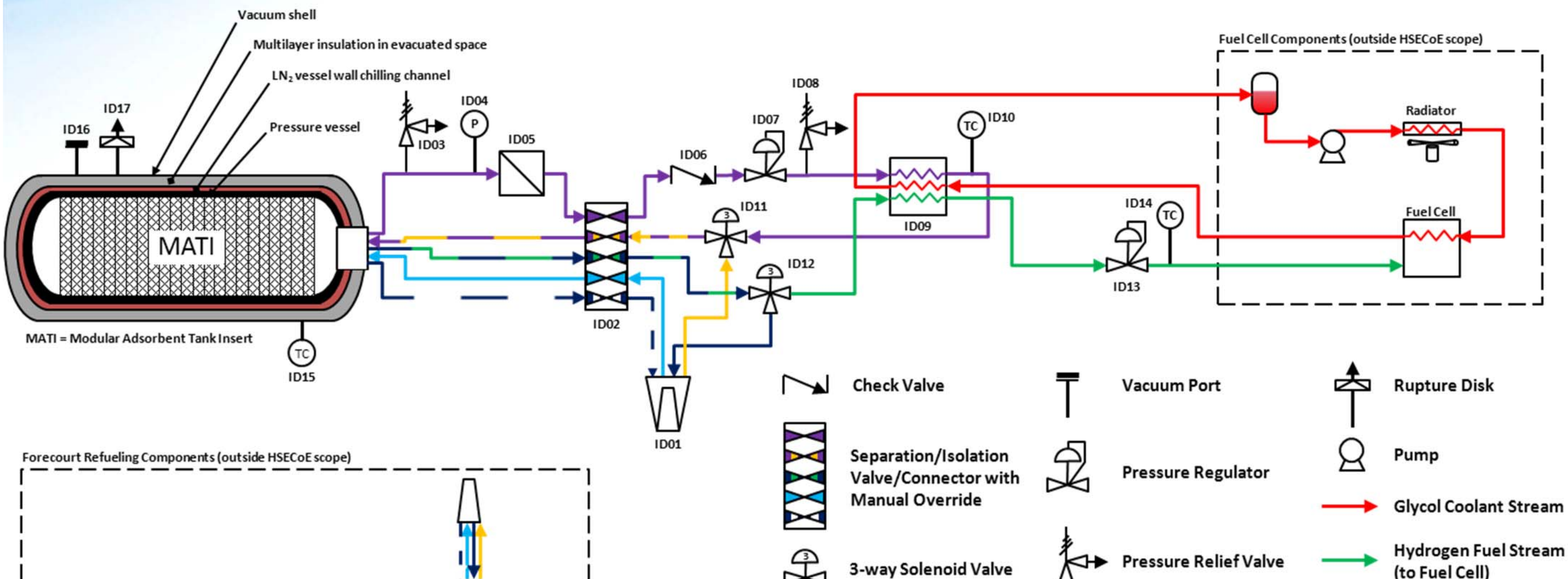


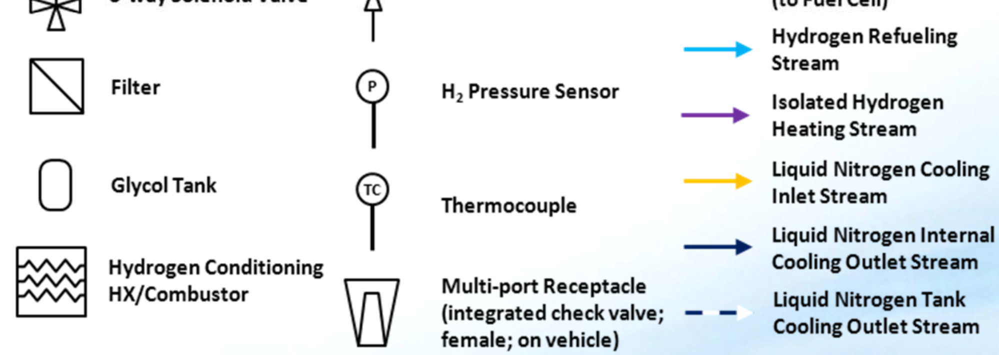
&

[1] *Theoretical Limits of Hydrogen Storage in Metal-Organic Frameworks: Opportunities and Trade-Offs,* Goldsmith, Wong-Foy, Cafarella, and Siegel, *Submitted.*
[2] *Recommended Best Practices for the Characterization of Storage Properties of Hydrogen Storage Materials*, K. J. Gross, *et al.*, V2-81

Example System: Modular Adsorption Tank Insert (MATI)

The MATI concept allows for isolated heating/cooling and densified media

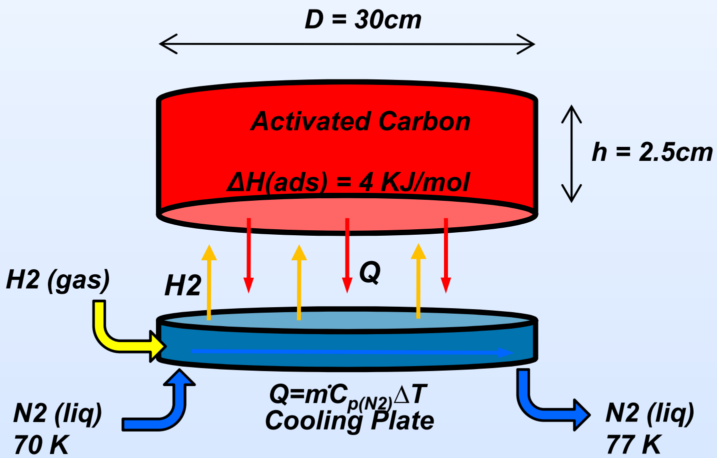




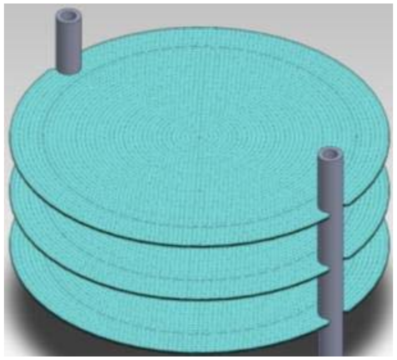
- 0.32 g/cc compacted MOF-5, with 91.6% packing density
- Modular Adsorption Tank Insert (MATI)
  - Internal HX with isolated-LN_2 cooling and isolated-GH_2 heating
- Type 1 Al (6061-T6) Tank
- LN_2 vessel wall chilling channels
- Single tank with oblate endcaps
- Full tank: P = 100 bar, T = 80 K
- Empty tank: P = ~5 bar, T = ~140 K

MATI Internal Heat Exchanger

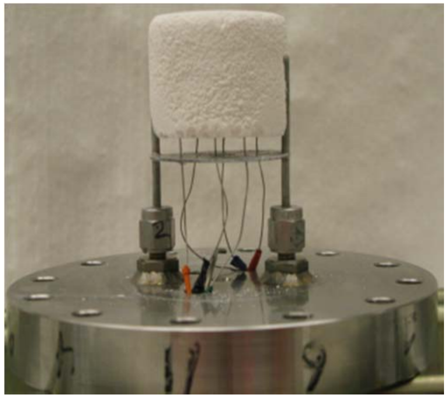
System Concept

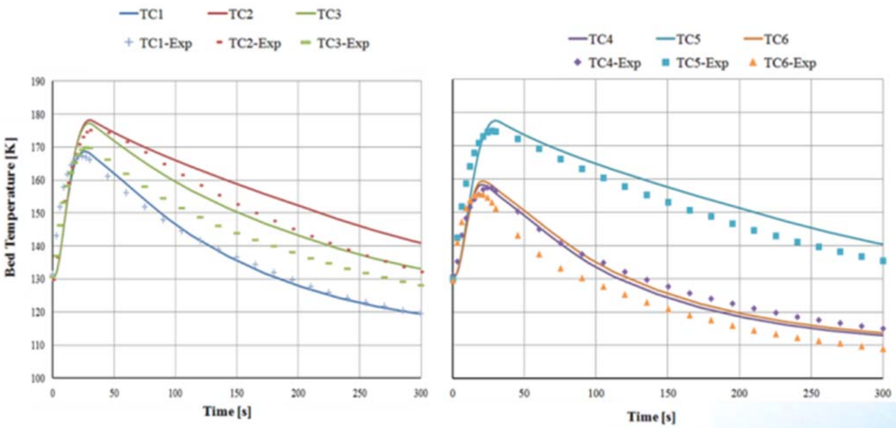


- Cross-flow HX
- Heat of adsorption removed by LN_2
- Radial H2 access to adsorption bed



MATI v1 – Combined LN2 cooling and H2 distribution

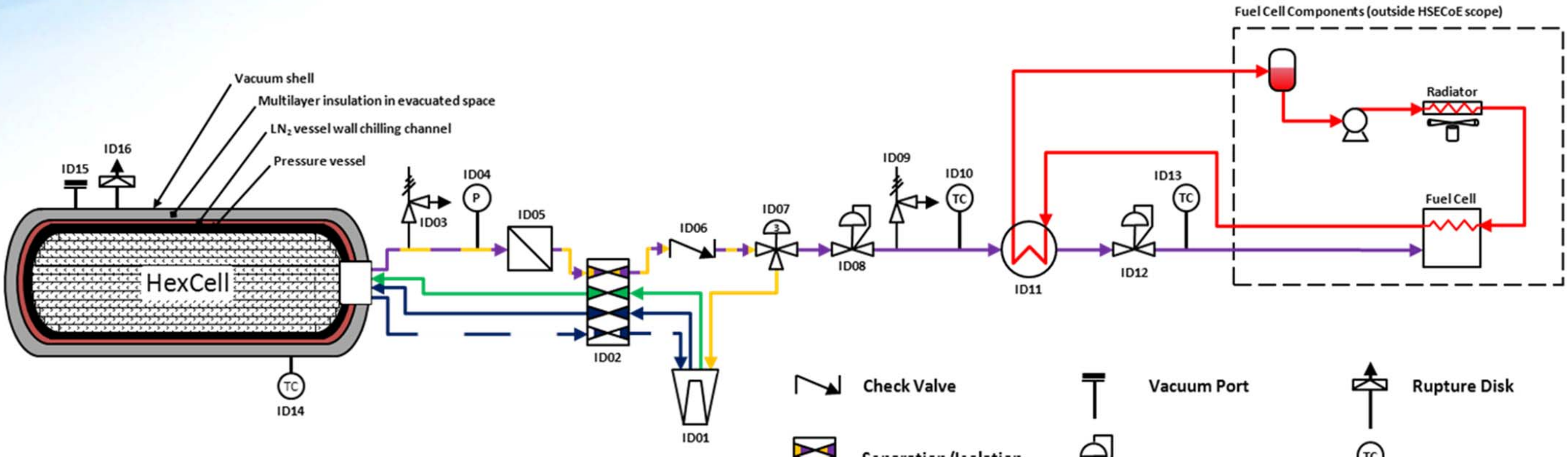


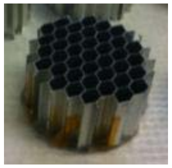


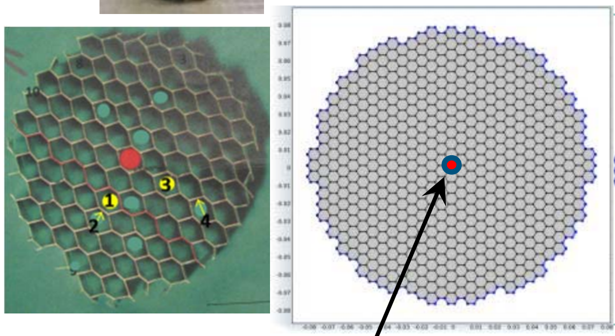
0.38 g/cc densified MOF-5 puck formed around Al pins.
Puck dimensions: 1.3 cm tall, 5 cm diameter, 9.5 g

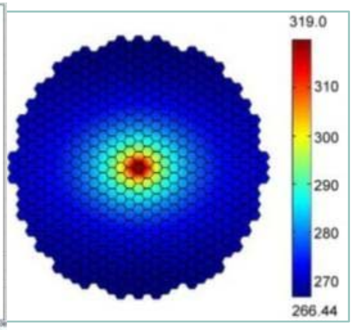
Hex-Cell/Flow-through System Concept

The Hex-Cell system design uses powder MOF-5 with flow-through cooling & resistive heating

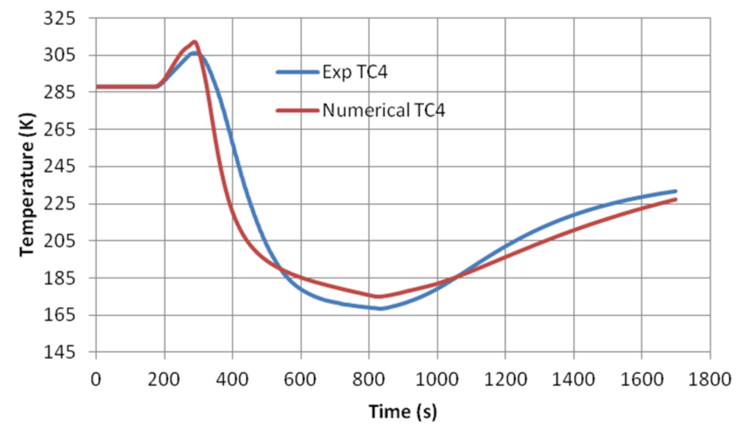






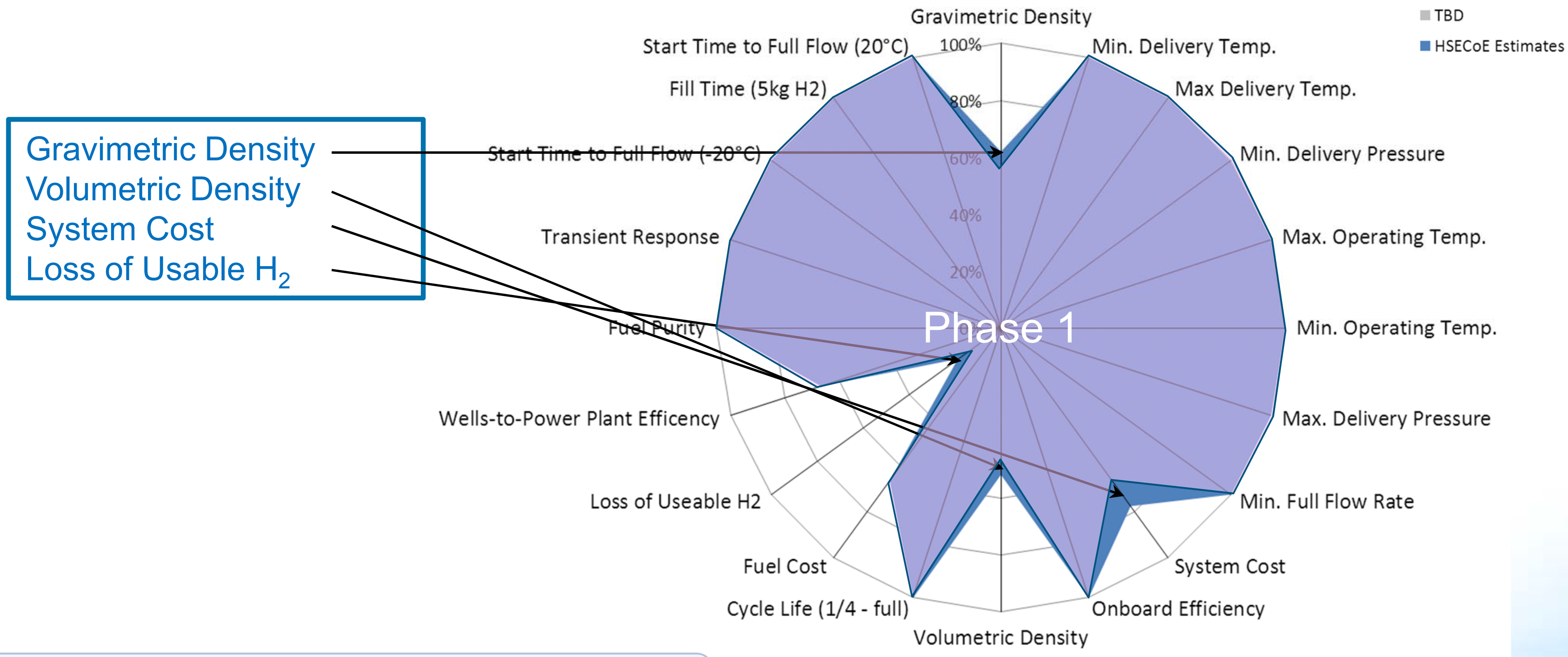


Resistance Heater



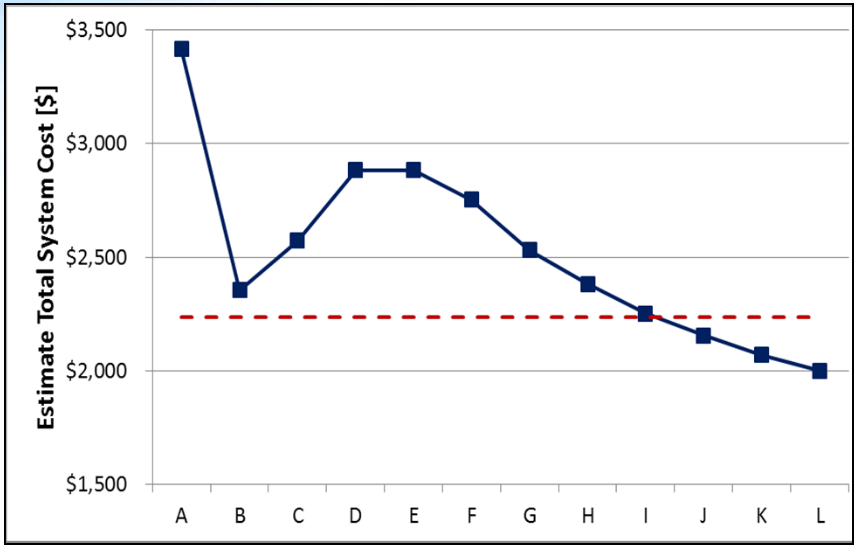
MATI System Performance Projection vs DOE 2017 Targets

Although efficient designs have been identified, system performance remains limited by materials properties

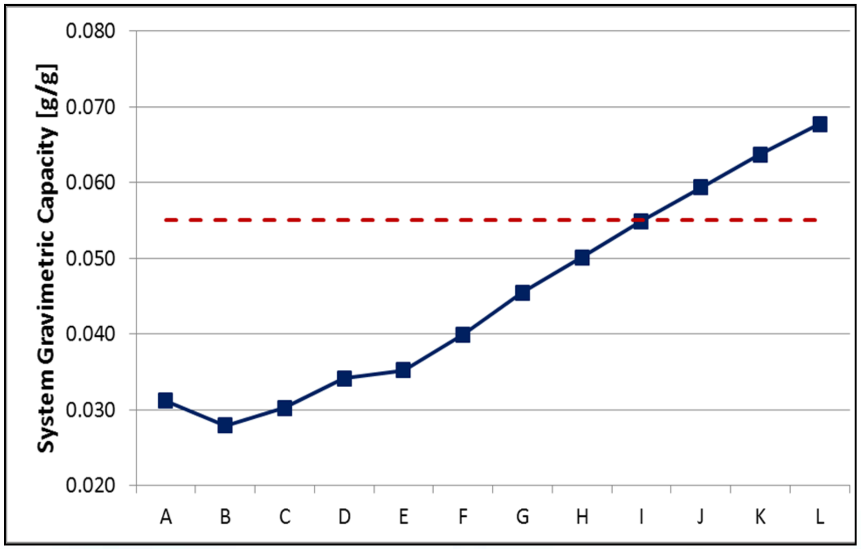


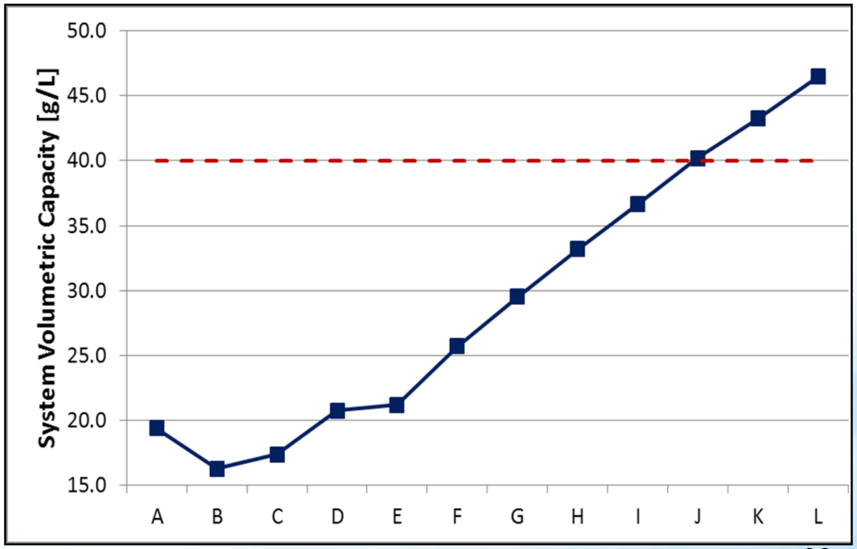
- Compacted MOF-5, no thermal enhancement, 80 K initial fill
- Type 1 Al pressure vessel, 100 bar
- Double-wall 60-layer MLVI jacket design, 5W heat leak @ 80 K
- Adsorption: LN2 chilled plates
- Desorption: BoP heated H2/140K

Improvements needed to reach DOE 2017 targets



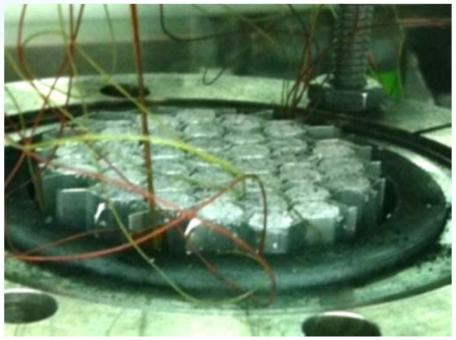
Step	Description
A	Phase 1 Baseline – Activated Carbon; Type 3 tank; Full at 80K, 200 bar; FT Cooling + Generic Resistance Heater
B	Set Operating Conditions to 80 K, 100 bar and Type 1 Al Tank
C	Identify Internal Heat Exchanger Design: MATI
D	Change Material from Activated Carbon to 0.32 g/cc Compacted MOF-5
E	Improve BOP Components (reduce mass and volume by 25%)
F	Maintain Capacity with increased Operating Temperature (reduce MLVI by 50%; remove LN_2)
G	Increase Material Capacity to 120% of Powdered MOF-5
H	Increase Material Capacity to 140% of Powdered MOF-5
I	Increase Material Capacity to 160% of Powdered MOF-5
J	Increase Material Capacity to 180% of Powdered MOF-5
K	Increase Material Capacity to 200% of Powdered MOF-5
L	Increase Material Capacity to 220% of Powdered MOF-5





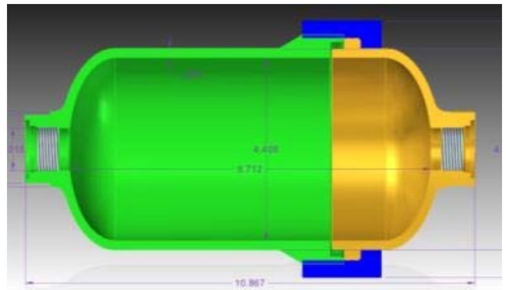
Future Work-Phase 3: Adsorbent System Build/Test

Heat Exchange Systems



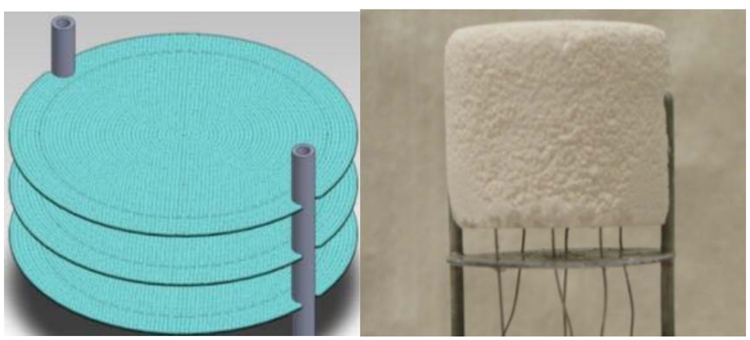
HexCell/MOF-5 Powder
Flow-Through Cooling
Resistance Heating

Containment

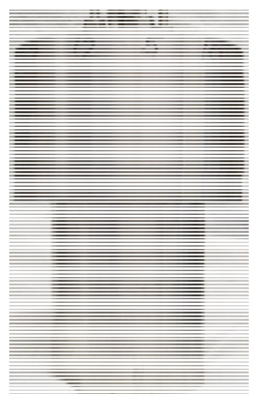


2 Liter Type 1
Segmented Al Tank

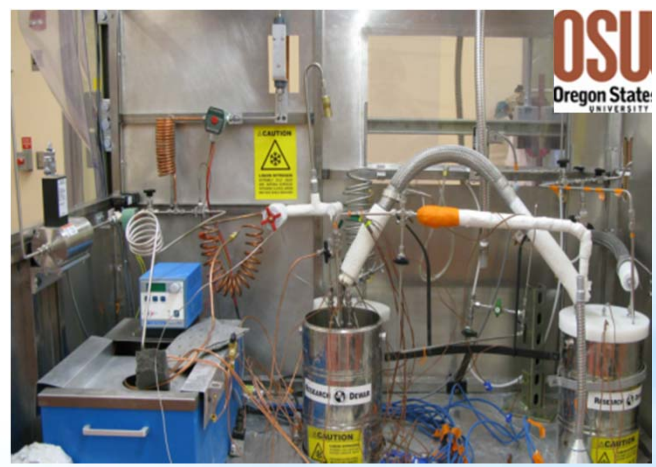
Test Facilities



0.3g/cc MOF-5 Puck
MATI Heating/Cooling



Type 1 SS
Pressure Vessel



Adsorbent Acceptability Envelope

Bruce J. Hardy
Claudio Corgnale
David Tamburello
Savannah River National Laboratory

DOE Webinar
June 25, 2013

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Introduction and Overview

- **Adsorbent Acceptability Envelope (AAE)**
  - Overall objective:
    - Identify coupled adsorbent and storage vessel properties that make it possible to meet performance targets
  - Accomplished in two stages:
    - Stage 1 - Identify isotherms that yield necessary amount of usable (not just total) hydrogen
      - *Depends on final and initial states*
      - *Determined through isotherm parameters*
        - » So far, have considered UNILAN and Dubinin-Astakhov-Radushkevich isotherms
      - *AAE can determine parameters that optimize available hydrogen*
      - *Isotherms determine excess differential enthalpy of adsorption*
    - Stage 2 - Determine coupled adsorbent/storage system parameters required to meet targets
      - *Requires all items in first stage plus design concepts for charging and discharging*

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Stage 1 - Optimal Isotherm Parameters

- **Optimization of Available Hydrogen**
  - Specify initial and final states via temperature and pressure
  - Determine optimal isotherm parameters with respect to usable amount of stored hydrogen
    - For UNILAN, optimize:
      - n_{max}, E_{max}, E_{min}
    - Can also optimize with respect to constrained pore volume and entropy change
    - Can include constrained pressure & temperature in optimization parameters
  - Isosteric heat for optimized parameters is calculated

Material developers will need to fit data to isotherms or attempt to create adsorbents with target isotherm parameters

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Stage 1 - Example Values for Optimal Parameters

UNILAN Isotherm Model

$$n_a = \frac{n_{max} RT}{(E_{max} - E_{min})} ln\left(\frac{e^{-\Delta S_0/R} + \frac{P}{P_0} e^{E_{max}/RT}}{e^{-\Delta S_0/R} + \frac{P}{P_0} e^{E_{min}/RT}}\right)$$

$$n_{Total} = n_a + c(V_v - V_p)$$

$$n_{Usable} = n_{Total}(T_{chg}, P_{chg}) - n_{Total}(T_{disch}, P_{disch})$$

Charged State: T_{chg}=80K, P_{chg}=60 bar

Discharged State: T_{disch}=160K, P_{disch}=5 bar

Constraints: $0 < n_{max} \leq 120$, $E_{min} > 0$, $E_{max} \geq E_{min} + 1$

UNILAN isotherm has singularity in isosteric heat if $E_{max} = E_{min}$

	n_{max}(mol/kg)	E_{max}(J/mol)	E_{min} (J/mol)	ΔS_0(J/mol-K)	Usable Hydrogen (kg_H2/kg_ads)
MOF-5	60.77	4497.9	1997.1	-64.16	0.086
Optimized	120	4655.5	4654.5	-64.16	0.217

Optimized when E_{max}=E_{min} ⇒ No heterogeneity for adsorption sites

Consistent with Bhatia and Myers, "Optimum Conditions for Adsorptive Storage," Langmuir ***2006*** *(2)*

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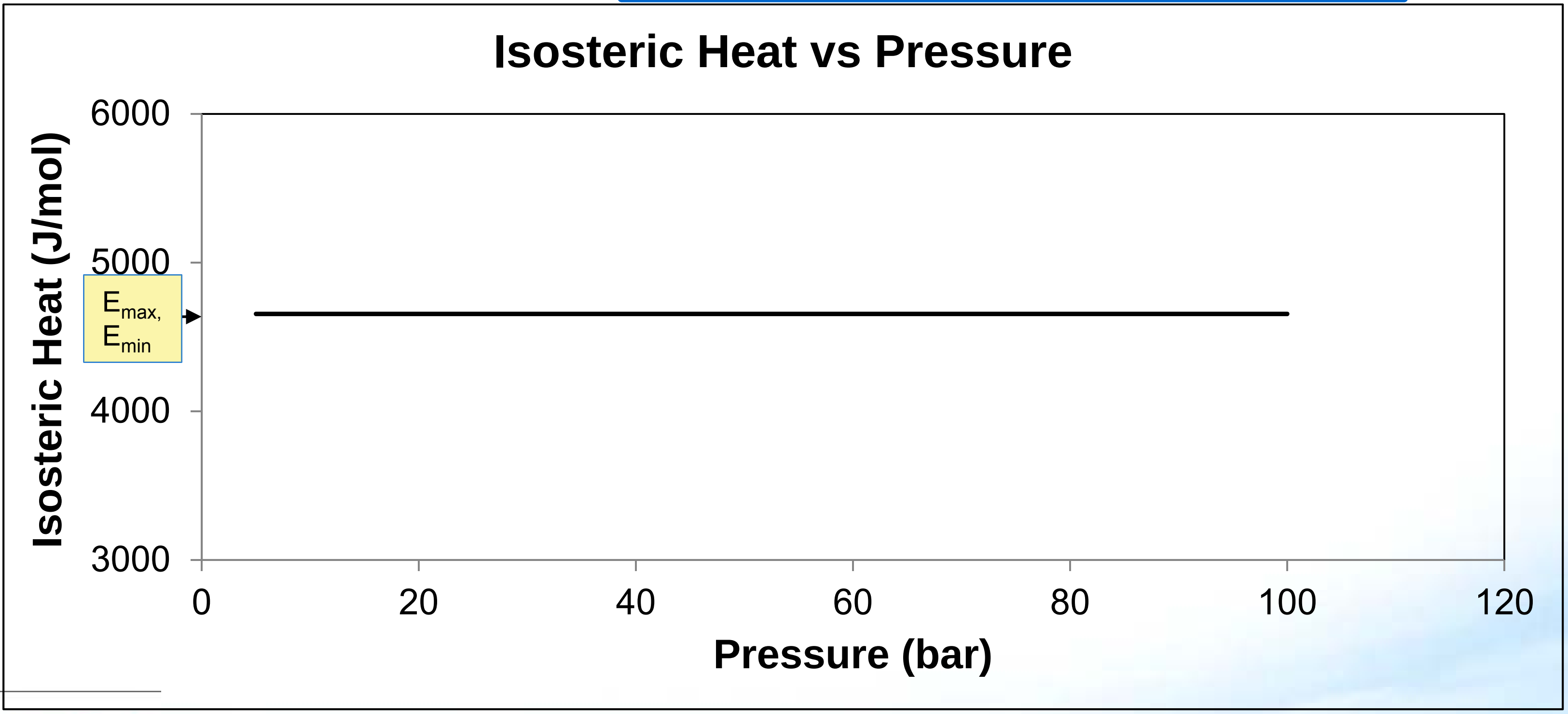
Stage 1 – Isosteric Heat at Optimized UNILAN Parameters

Optimized UNILAN Parameters	
n_{max}	120 mol/kg
E_{max}	4655 J/mol
E_{min}	4654 J/mol
ΔS_0	-64.16 J/mol

Common definition of isosteric heat

$$Isosteric\ Heat \equiv \Delta h = RT^2 \left.\frac{\partial P}{\partial T}\right|_{n_a}$$

At optimized UNILAN parameters the isosteric heat is nearly constant



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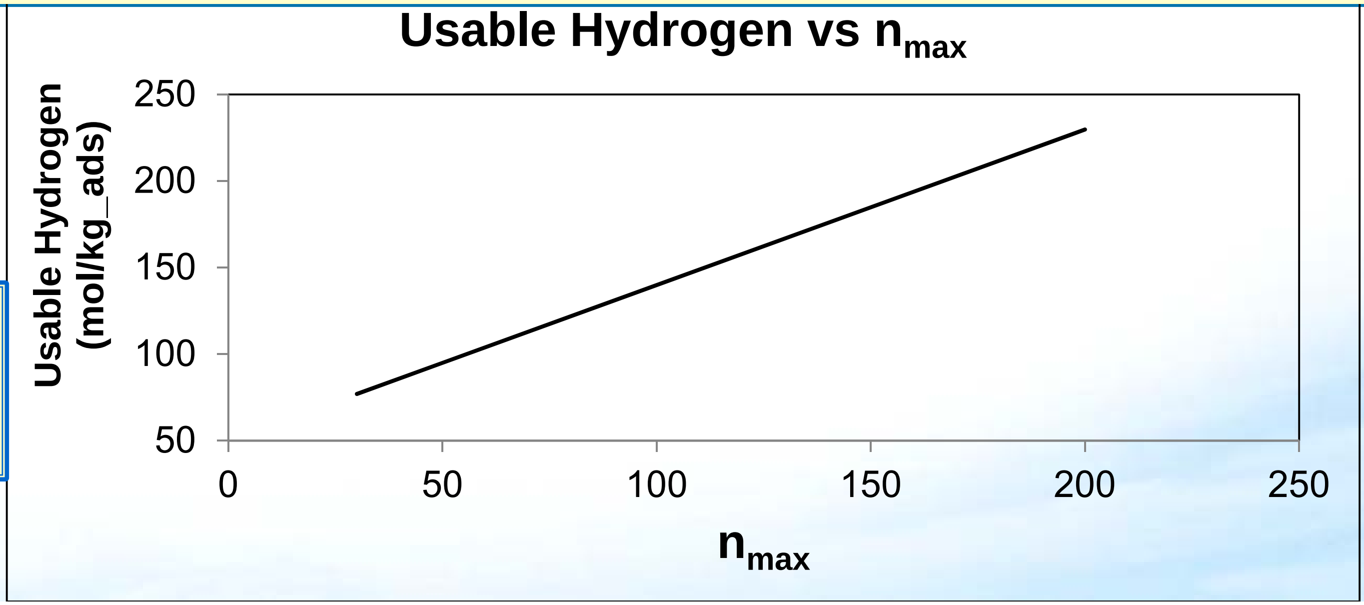
Stage 1 - Relation Between Optimum Parameters for Example Values

At optimum, E_{max} and E_{min} are independent of n_{max}

n_{max}(mol/kg)	E_{max}(J/mol)	E_{min}(J/mol)
30	4655.5	4654.5
50	4655.5	4654.5
70	4655.5	4654.5
100	4655.5	4654.5
120	4655.5	4654.5
150	4655.5	4654.5
200	4655.5	4654.5

At optimum, usable H_2 is linear with respect to n_{max}, as would be expected from the UNILAN model



Volumetric usable H_2 is linear with respect to ρ_{ads}*n_{max}

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Stage 1 - Isotherm Parameter Range

- **Identify (non-optimal) parameter ranges that meet performance targets for hydrogen storage**
  - Based on UNILAN isotherm
  - Employed usable H_2 corresponding to charged and discharged states
- **Targets used as examples in this presentation are the DOE Ultimate Technical Targets for Light Duty Vehicles**
  - Gravimetric capacity 0.075 kg_H_2/kg_system
  - Volumetric capacity 0.070 kg_H_2/L_system

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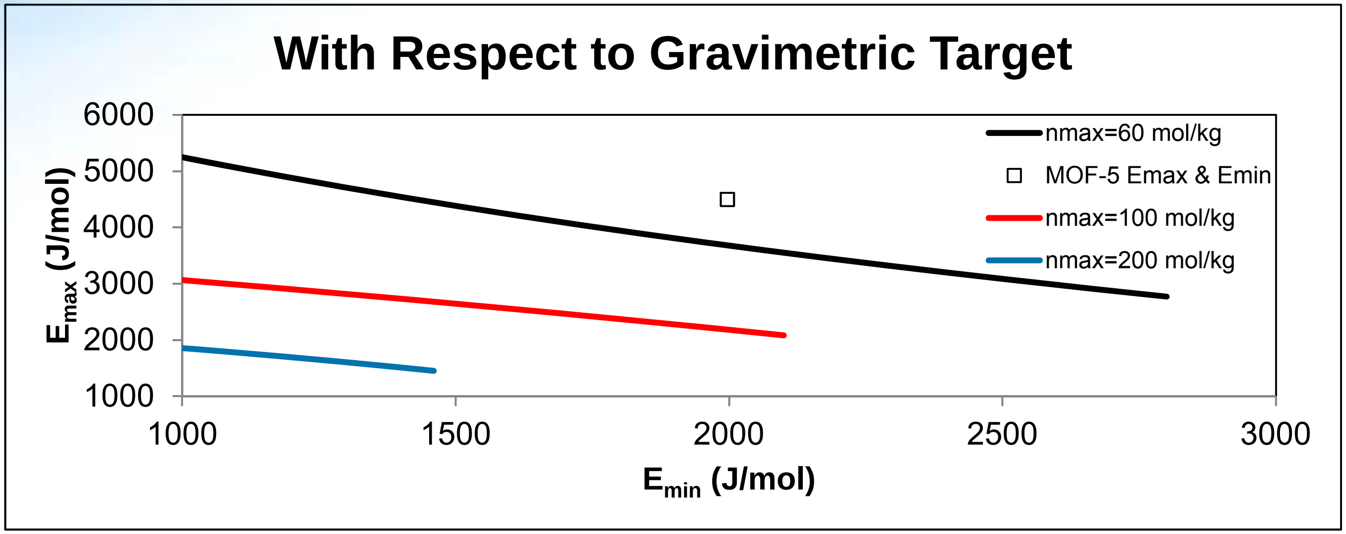
Stage 1 - Relation Between n_{max}, E_{max} & E_{min}

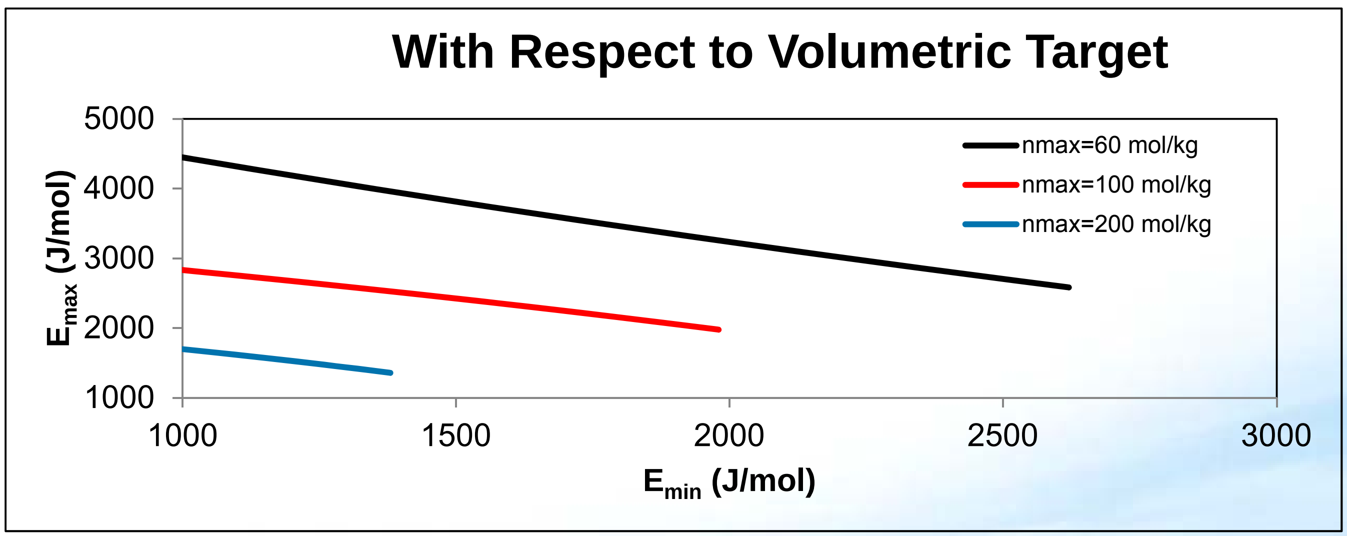


Charged State: T_{chg}=80K
P_{chg}=60 bar

Discharged State: T_{disch}=160K
P_{disch}=5 bar

MOF-5 Density ≈ 130 kg/m³

- For volumetric targets it was assumed that the density was <u>8x130 kg/m³</u>



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Stage 2 – Coupled Adsorbent and Storage System

- **Meeting the technical targets requires more than a definition of gas storage properties (isotherm)**
  - Adsorbent must interface with the storage system
    - Includes heat and mass transfer
- **Stage 1 only addressed part of the adsorbent storage system requirements**
  - Did not consider any kind of transport
- **Upshot is that gas uptake alone does not completely determine if the adsorbent *and storage system* can meet technical targets**

Stage 2 –Storage System Operation

- **During charging:**
  - Heat due to pressure work and enthalpy of adsorption must be removed to maintain target temperature
    - Need sufficiently high thermal diffusivity
      - *or sufficiently high thermal conductivity for steady state*
    - Can modify adsorbent or add amendments to increase thermal conductivity
    - Can closely space heat transfer surfaces
    - Adsorbent permeability must accommodate flow-through cooling, if used
    - Entire mass of adsorbent may not reach target temperature
      - *Can compensate by increasing total mass of adsorbent*
  - Adsorbent must be sufficiently permeable that gas transport to adsorption sites is not impeded
- **However, adsorbent and system modifications affect gravimetric and volumetric capacity**

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Stage 2 – Adsorbent Storage System Coupling

- **The interaction between the adsorbent and storage system is determined through numerical models**
  - Transient calculations
  - Models include:
    - Isotherm parameters
    - Adsorbent thermal conductivity, specific heat, density and porosity
    - Hydrogen flowrate, inlet pressure and characteristic spacing for heat transfer surfaces
  - Differential excess internal energy is calculated from the isotherm
    - Isotherm is used to calculate the enthalpy of adsorption
- **System design**
  - Flow-through cooling
  - Cooling & heating using:
    - Parallel heat transfer surfaces (MATI)
    - Cylindrical surfaces (Hex-cell configuration)

Summary

- **Assessment of adsorbent viability is conducted in 2 stages**
- **In the first stage, the amount of usable hydrogen stored by the adsorbent is evaluated**
  - Determines whether an existing adsorbent can possibly meet the technical targets
  - Determines parameter ranges that an adsorbent must have to meet technical targets
  - Determines optimal adsorbent parameters
- **If the adsorbent meets criteria for Stage 1, then the second stage analysis is applied**
  - Determines whether system meeting technical targets can be designed for an existing adsorbent
  - Determines coupled adsorbent and system parameter ranges required to meet the technical targets

Thanks for Listening!

Questions?